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A New Method for the characterization of Solutes and Solvent Phases Using Solvato-Chromic Parameters

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FINAL REPORT

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SUMMARY

Two general solvation equations for use in LSER and QSAR studies have been developed,

$$\log SP = c + r.R_2 + s.\pi^H_2 + a.\alpha^H_2 + b.\beta^H_2 + v.V_X \qquad [i]$$
$$\log SP = c + r.R_2 + s.\pi^H_2 + a.\alpha^H_2 + b.\beta^H_2 + l.\log L^{16} \qquad [ii]$$

In these equations SP is some solute property for a series of solutes in a given system. Equation (i) is the more useful for processes involving condensed phases, whilst equation (ii) is the more useful for the gas ⇨ condensed phase processes. The explanatory parameters are R_2 - a new excess molar refraction developed during this work, π^H_2 - a new solute dipolarity/polarisability scale also developed in this work, α^H_2 and β^H_2 - the solute hydrogen bond acidity and basicity respectively, V_X - the solute characteristic volume, and L^{16} - the solute gas ⇨ hexadecane partition coefficient.

A rather large number of solute parameters in equations (i) and (ii) have been measured or calculated in this work, so that all parameters are known for several hundred solutes. Equation (i) has been applied to a variety of processes including liquid/liquid partition coefficients and HPLC capacity factors, whilst equation (ii) has been applied to the solubility of gases and vapours in numerous GLC stationary phases, and in common solvents, as well as to the effect of gaseous solutes on respiratory tract irritation in mice.

It is suggested that equations (i) and (ii) represent the best available general solvation equations, and that they can now be applied to a very large number of physicochemical and biochemical processes.

INTRODUCTION

At the start of this work, the Kamlet-Taft solvatochromic comparison method for the characterisation of solvents had been well-established, the solvatochromic parameters being defined as follows:

δ_1 Solvent polarisability correction parameter, $\delta_1 = 1.00$ for aromatic solvents, 0.50 for polyhalogenated, and 0.0 for all others [1].

π^*_1 Solvent dipolarity/polarisability parameter which measures the solvent's ability to stabilise a charge or a dipole [2-6].

α_1 Solvent hydrogen bond acidity parameter, measuring the solvent's ability to donate a hydrogen bond [2,7,8-10].

β_1 Solvent hydrogen bond basicity parameter, measuring the solvent's ability to accept a hydrogen bond [2,11-15].

The solvatochromic principle was first introduced by Kamlet and Taft[11] in 1977 when a paper was published on the determination of the β_1 scale for hydrogen bond basicity using the solvatochromic comparison method. Solvatochromic literally means *solvent colour*, and is derived from the effect the solvent has on the colour of an indicator used in the parameter determination. The principle is based on the fact that the wavelength of maximum absorption of specific indicators in the UV and visible region is measurably shifted when the indicators are dissolved in different solvents. The extent of the wavelength shift is determined by the degree and the type of solvent-solute indicator interactions taking place, especially polar/polarisable and hydrogen bonding interactions. Study of such wavelength shifts enabled initial scales of π^*_1, α_1, and β_1 to be set up.

The solvatochromic comparison principle[2,3,8,11] measures the polarity or dipolarity (π^*_1) of a solvent by its bathochromic shift relative to cyclohexane ($\pi^*_1 = 0.0$) of the π-π^* transition of the greatest wavelength of *non* hydrogen bond donor indicators. Examples of suitable indicators are 4-nitroanisole or 4-(dimethylamino)benzophenone. To measure the solvent hydrogen bond basicity another bathochromic shift is measured using the hydrogen bond acid form (homomorph) of the *non* hydrogen bond donor indicator, eg. if 4-nitroanisole was used to measure solvent polarity, 4-nitrophenol would be used to measure the basicity. To get the sensitivity required in π^*_1 measurement, it was necessary to use indicator solutes which were capable of behaving as hydrogen bond bases. Non hydrogen bond base solutes and hydrogen bond base solutes present no problem, but to measure π_1 values of hydrogen bond acid solvents, indicators were chosen which were least effected by hydrogen bond effects in hydrogen bond acidic solutes

For some classes of solvents, the π^*_1 parameter is not fully capable of accounting for polarity and polarisability effects, so a polarisability correction parameter, δ_1 was introduced by Kamlet *et al*[1]. Both δ_1 and δ_2 (the parameter for solutes) are equal to 0.0 for all non-chlorinated aliphatic compounds, 0.50 for polyhalogenated aliphatics, and 1.0 for aromatics. The δ values are supposed to reflect the difference in solvent or solute polarisability between these classes of compounds (expressed in terms of the refractive index function, $f(\eta^2) = [\eta^2-1]/[2\eta^2+1]$).

The original β_1 scale[2,11-15] was determined by averaging up to 5 β values obtained from 5 different properties. 1) Solvatochromic properties using - a) a nitrogen acid indicator b) an oxygen acid indicator and 2) three properties involving solute basicity towards oxygen acids; ^{19}Fnmr shifts and formation constants which were determined in dilute solutions in carbon tetrachloride solvent. So the average value for β_1 obtained by Kamlet and Taft are a mixture of solvent and solute basicity measurements. There are some shortcomings in this method of measuring solute basicity values. β_1 values of amphiprotic solvents will depend on the extent of self-association, which in a dilute solution of CCl_4 will of course be quite different. So calculating accurate values of β_1 by this method is unsatisfactory for self-associated solvents. Kamlet *et al* also transferred this scale of β_1 values directly to the β_2 scale for solutes[16-19], which might be considered theoretically possible for some solvents, but not for amphiprotic ones.

The Kamlet and Taft method has been criticised by Nicolet and Lawrence[20,21]. They point out that there are too few solvents used to fix a reference homomorphic line to back off hydrogen bonding effects from polar effects with non hydrogen bonding solvents. They also criticise the use of toluene, benzene and CCl_4 as non hydrogen bonding solvents (as they have measurable hydrogen bond properties), and the need for accurate temperature control when making these measurements. Abraham *et al*[22] later re-evaluated the β_1 scale, using only aniline and its derivatives as indicators. This leads to a reasonably general pure solvatochromic scale for hydrogen bond basicity of non-associated solvents. It was noted that β_1 even for non-associated compounds is only an approximation to the solute basicity, β_2.

The solvent hydrogen bond acid scale, α_1[2,8-10], was introduced at the same time as the β_1 scale, measured similarly by the solvatochromic comparison method. Likewise however, there are shortcomings in the α_1 scale. A complication is that the hydrogen bond base homomorphs used for non hydrogen bond solute 4-nitroanisole were completely different in their structure from 4-nitroanisole itself. This may make the separation of hydrogen bond acidity from polarity difficult, and introduce significant additional effects. Kamlet and Taft used two sets of homomorphs with *nitro* group functionality in measuring β_1, which means if that there is any solvent interaction at the *nitro* group, this effect cancels out when the homorphic pairs of indicators are compared. This is not the case when measuring α_1, as the homorphic pairs are quite different in structure. So, if there is any solvent interaction at the *nitro* group of 4-nitroanisole, this will influence the α_1 measurement. In spite of all these drawbacks, there is presently no better way of assessing solvent hydrogen bond acidity.

Some time after Kamlet and Taft's work on solvents, a group of chemists led by Abraham, Doherty, Kamlet and Taft began work on a scheme for the general characterisation of solutes. The aim, as with the solvatochromic parameters, was to use solute parameters in linear free energy relationships (LFERs), to quantify and interpret physicochemical processes. It then became apparent that solute parameters could be used as descriptors in quantitative structure-activity relationships, QSARs, for biochemical or toxicological processes, and this extra dimension afforded considerable impetus for this work. The two LSERs suggested by Abraham, Doherty, Kamlet and Taft (ADKT) were,

$$\log SP = c + d.\delta_2 + s.\pi^*_2 + a.\alpha_2 + b.\beta_2 + v.V_2 \qquad [1]$$

$$\log SP = c + d.\delta_2 + s.\pi^*_2 + a.\alpha_2 + b.\beta_2 + l.\log L^{16} \qquad [2]$$

In equations 1 and 2, SP is some solute property for a series of solutes in a fixed system. For example, in equation 1, SP could be P_{OCT} - the octanol-water partition coefficient for a series of solutes. Or in equation 2, SP could be L - the gas-solvent partition coefficient for a series of solutes in a given solvent. Equation 1 was set up to deal with processes within condensed phases, *e.g.* the water-octanol partition coefficient, whilst equation 2 was preferred for processes involving gas ⇨ condensed phase transfers.

Over a period of time, the solute parameters used as explanatory variables were gradually amended or improved, and when the present work began, the following solute parameters were in use.

δ_2 Solute polarisability correction parameter, $\delta_2 = 1.00$ for aromatic solutes, 0.50 for polyhalogenated solutes, and 0.0 for all others [1].

π^*_2 Solute dipolarity/polarisability parameter which measures the solute's ability to stabilise a charge or dipole [4,16-19,23,24].

α_2 Solute hydrogen bond acidity parameter, measuring the solute's ability to donate a hydrogen bond [16-19].

β_2 Solute hydrogen bond basicity parameter, measuring the solute's ability to accept a hydrogen bond [16-19].

α^H_2 Solute hydrogen bond acidity parameter as developed by Abraham *et al*[25], from log K values for hydrogen bond complexation. Even for amphiprotic solutes, this is the hydrogen-bond acidity of the *monomer* solute.

β^H_2 Solute hydrogen bond basicity parameter as developed by Abraham et al[26], from log K values for hydrogen bond complexation. Even for amphiprotic solutes, this is the hydrogen-bond basicity of the *monomer* solute.

V_I Computer-calculated solute intrinsic volume for specific solute conformations as derived by x-ray structure [27,28].

V_X Characteristic molar volume, trivially calculable by adding atomic volumes for each constituent solute element, and subtracting a constant term for each bond present, (whatever the nature of the bond, - single, double etc.), in the molecule [28,29-31].

Log L_2^{16} (Normally written as Log L^{16}, the subscript 2 referring to solute is assumed as there is no comparable solvent parameter). Log L^{16} is the log of the solute Ostwald solubility coefficient [32], L, on n-hexadecane at 298.15 K[7,33].

This work is mainly concerned with LSER of the type represented by the general equations 1 and 2, specifically studying a series of *solutes* in one fixed system:-

$$\log SP = c + d.\delta_2 + s.\pi^*_2 + a.\alpha_2 + b.\beta_2 + v.V_2 \qquad [1]$$

$$\log SP = c + d.\delta_2 + s.\pi^*_2 + a.\alpha_2 + b.\beta_2 + l.\log L^{16} \qquad [2]$$

Initially π^*_2, α_2, β_2 as a first approximation were taken to be identical to the corresponding solvent parameters, as no solute parameters were available. This may be true for simple non-associating compounds, such as aliphatic ethers, but there is underlying difficulty in that these solute parameters will not be equal to the solvent parameters where the solute is amphiprotic and/or self-associated. Most α_2 and β_2 parameters were in fact estimated using a set of rules (on the basis of some chemical intuition) or calculated from correlation and/or backcalculation techniques.

Kamlet *et al*[2,34] have related the π^*_1 parameter to such fundamental physical properties of solvent as their dipole moment and noted it is a linear function of the Block and Walker[35] reaction field function when the solvent set is limited to *non*-hydrogen bonding, aliphatic liquids, which have only one dominant bond dipole, such as ethers, sulphoxides, and aldehydes. These are known as the so-called "select solvents"[2]. Carr and Brady[36] have also carried out similar correlations. For these compounds π^*_1 can be assumed to be identical to π^*_2, and so correlations such as these can be used to obtain π^*_2 values, (π^*_1 values), for other important classes of compounds, (such as alcohols).

Abraham *et al*[25,26] developed two new empirical solute scales for hydrogen bond acidity (α^H_2), and hydrogen bond basicity (β^H_2) in an attempt to overcome some of the problems previously associated with the Kamlet and Taft scale (α_2 and β_2), especially those problems due to amphiprotic solutes. The two new scales were constructed purely on a *thermodynamic* basis.

The scale of hydrogen bond acidity[25] was formulated using log K equilibrium constants for the 1:1 complexation for a series of monomeric acids with a series of reference bases in tetrachloromethane solvent at 298 K.

$$\text{ACID---H} + \text{BASE} \longleftrightarrow \text{ACID---H} \ldots\ldots\ldots \text{BASE}$$

When log K values for a series of acids (hydrogen bond donors) against a reference base are plotted versus log K values for the acid series against any other reference base, there results a set of lines that intersect at a point where log K = -1.1 (equilibrium constants expressed in molar concentration units). It is then possible to obtain an average hydrogen bond acidity (with some exceptions) for solutes in CCl_4, denoted as log K^H_A. These values are then simply transformed into a solute hydrogen bond acidity scale via equation 3.

$$\alpha^H_2 = (\log K^H_A + 1.1)/4.636 \qquad [3]$$

It can be similarly shown[26] than when log K values for a series of bases against a given reference acid are plotted versus log K values for the base series against any other reference acid, a set of lines is obtained that also intersect at a point where log K = -1.1. Similarly to the case above, it is possible to obtain an average hydrogen bond basicity for solutes in CCl_4, denoted as log K^H_B, and then to transform them into a basicity scale using equation 4, where the factor 4.636 is chosen to initialise the scale so that β^H_2 is equal to 1.0 for the base hexamethylphosphortriamide. The factor has no physical significance other than yielding a convenient working range of α^H_2 and β^H_2 values.

$$\beta^{H}_{2} = (\log K^{H}_{B} + 1.1)/4.636 \qquad [4]$$

The α^{H}_{2} and β^{H}_{2} values so obtained (referring specifically to solute hydrogen bond complexation in CCl_4 at 298 K), can be combined in a general equation that can be used to predict a vast number of Log K values[37]. From the original matrix of 89 primary α^{H}_{2} and 215 primary β^{H}_{2}, (containing 1312 experimental log K values), many more α^{H}_{2} and β^{H}_{2} values can be calculated from:

$$\log K = (7.354 \pm 0.019)\alpha^{H}_{2}.\beta^{H}_{2} - (1.094 \pm 0.007) \qquad [5]$$

$$R = 0.9956 \quad SD = 0.093 \quad N = 1312$$

This equation has been used to considerably extend the database for α^{H}_{2} and β^{H}_{2} parameters. Equations 3-5 are not completely general, in that some particular acid-base combinations are excluded, specifically weak acids such as pyrrole, *etc.* with bases such as pyridine, amines and ethers[38]. These hydrogen bond acids give rise to a different electrostatic:covalent ratio in their complexes, with a Maria-Gal[39] Θ value larger than about 75°. The combination of these acids with other bases is however included.

In the solution of a liquid solute in a liquid solvent, dispersion forces are not considered important[40]. This is because any solute-solvent dispersion interactions will tend to cancel out with the loss of solvent-solvent dispersion interactions in forming the cavity in the solvent. The cavity size can be taken as being proportional to the solute molar volume[40,41], V_2 at 298 K. This is calculated as the bulk molar volume - the ratio of the solute molecular weight divided by the solvent density. The product is then divided by 100 merely to scale the value off into the same sort of range as the polarity and hydrogen bonding parameters. 10 cm^3mol^{-1} was added to V_2 for aromatic and acyclic compounds, leading to V_{2adj}. These two cavity size parameters are not strictly solute parameters as they are measured as bulk solvent properties. For instance, for amphiprotic compounds which are self-associated they will not only reflect the *intrinsic* solute molecular volume of the monomer solute, but also the bulk structure. These two parameters are also inconvenient when considering solid solutes.

The computer-calculated intrinsic volume of Leahy[27] is therefore preferable. It is measured from specific solute conformations as derived from x-ray structures, and can be measured for any solute. It also leads to improved MLRA correlations when used as the cavity term instead of V_2 or V_{2adj}[27,42]. McGowan[29-31] has developed another method of calculating solute intrinsic molar volumes by the addition of characteristic atomic volumes for the constituent elements of the solute molecule, and subtracting 6.56 cm^3mol^{-1} for each bond. The same constant term is subtracted for any bond whether it is single, double or triple etc. There is a very good correlation between V_I and V_X (both in cm^3mol^{-1}):

$$V_I = 0.597 + 0.628V_X$$

$$R = 0.9988 \quad SD = 1.24 \quad N = 209$$

Use of either term as a cavity term in the general LSER used (equation 1), should give completely interchangeable results. However, as V_X is so trivially calculable, this is usually the cavity size parameter employed.

V_X, (or V_I) is the preferred parameter for LSER to quantify the solubility properties of liquid solutes within condensed phases, where the nett dispersion forces will be small, or at least by no means as important a consideration as for the dissolution of a gaseous solute in a solvent[40]. A typical condensed phase process is the partition of solutes between octanol and water, the log P_{OCT} values measured being important for the modeling of biological membranes.

In the gaseous state, there will be no dispersion interaction of solute molecules with each other. Upon dissolution into a solvent, dispersion interactions, (or van der Waals interactions), will be set up between the solute and solvent, and there will be no nett tendency for a canceling out effect, as has been previously described for condensed phases. The log L^{16} parameter was formulated to provide a parameter that was a measure of cavity size and solute-solvent dispersion interactions. Log L^{16} is the log of the Ostwald solubility coefficient[32], L, on n-hexadecane at 298.15 K[7,33]. As it is a parameter directly measured from the dissolution of a gaseous solute into a solvent (n-hexadecane), it will automatically be a measure of cavity size and dispersion interactions. For all LSER not concerned with processes in condensed phases, (ie. gas-liquid partition coefficients), log L^{16} is preferred to V_X or V_I, as it gives consistently better results from MLRA. Coefficients generated for log L^{16} for the process gaseous solute ⇨ solute (in solution) are invariably positive, indicating that energy released from dispersion interactions between the solute and solvent is greater than that required in cavity formation. As a comparison, the log L^{16} coefficient from an MLRA analysis of solutes on n-hexadecane itself would be unity, so other solubility processes can be quantified by reference to this.

The fundamental aim of the present work has been to re-examine the above solute parameters in order to establish a coherent system for the characterisation of solutes. In so doing, there are a number of points that must be addressed.

(i) The δ_2 parameter is a purely empirical correction factor, with no theoretical basis. It would therefore be useful to replace this parameter with one for which some theoretical foundation could be established.

(ii) The π^*_2 has evolved in some *ad-hoc* way. Some π^*_2 values have been taken as identical to π^*_1 values for non-associated solvents, others have been estimated in some way or another, and yet other π^*_2 values have simply been guessed. No track has been kept of the origin of π^*_2 values, and in many cases it has been impossible to find out the actual origin. In addition there is a fundamental theoretical objection to the use of π^*_2 values that are derived from π^*_1 values. The latter are obtained from UV shifts (λ_{max}) and hence cannot be related to any thermodynamic quantity. But SP in equations 1 and 2 is nearly always some form of equilibrium or partition constant, so that log SP is equivalent to a Gibbs-energy change. It would be desirable to replace π^*_2 by a new π_2 parameter based on log K values, and whose origin was well-established.

iii) Use of α^H_2 and β^H_2 in equations 1 and 2 has put the hydrogen bond parameters on a theoretically good footing. However, these parameters can only be obtained directly for monofunctional solutes. It is essential to devise some method, probably of back-calculation using equations 1 and 2, to extend α^H_2 and β^H_2 to multifunctional groups. In addition, the use of the α^H_2 and β^H_2 parameters in LSERs must be carefully examined to see if for monofunctional solutes they do indeed correspond to 'effective' values applicable to a solute surrounded by solute molecules.

(iv) The preferred volume parameter in equation 1, V_X can be simply calculated for any structure. However, the corresponding log L^{16} parameter must be obtained by experiment, and so the database of L^{16} values must be greatly extended.

AIMS OF THE PRESENT WORK

The three major objectives during the course of this work can be summarised as below:-

1) To apply our LSER equations to as many solubility and solubility related processes as possible. This would test the scope of their application, and uniquely characterise in terms of our physicochemical solute parameters as many solvents as is feasible, whether the solvent be a GLC stationary phase, or a more 'typical' solvent,

(such as ethanol *etc*). Solubility related processes would also be quantified in the same manner, such as partitions between immiscible solvents (condensed systems), or the upper respiratory tract irritation by airborne chemicals in mice.

2) To vastly extend our database of solute physicochemical parameters, and 'firm-up' these parameters by their successful application in quantifying numerous varied solubility and solubility related phenomena. Where possible parameters would be directly measured, or if not, back-calculated, or estimated by extrapolation techniques *etc*.

3) To investigate the use of alternative and/or improved physicochemical solute parameters for use in our LSER equations, to backcalculate improved parameters from derived LSER characterisation equations and to use MLRA techniques to calculate solute parameters from sets of numerous LSER equations.

The use of LSERs via the general equation below leads to a remarkably simple model for solubility and solubility related processes.

Log SP = $\boxed{1}$ Log SP_0 **(equation constant) +** $\boxed{2}$ **a correction term for quantitative indication of polarizable n and π electrons +** $\boxed{3}$ **dipolarity or dipolarity/polarisability term +** $\boxed{4}$ **hydrogen-bond acidity term +** $\boxed{5}$ **hydrogen-bond basicity term +** $\boxed{6}$ **solute size & dispersion interaction term**

The two general equations that can be used for the characterisation of solutes and of a wide variety of solvent phases or solvent-like phases are:

$$\log SP = c + d.\delta_2 + s.\pi^*_2 + a.\alpha_2 + b.\beta_2 + m.V_2 \qquad [1]$$

$$\log SP = c + d.\delta_2 + s.\pi^*_2 + a.\alpha_2 + b.\beta_2 + l.\log L^{16} \qquad [2]$$

The equations can be recast to include the hydrogen bonding parameters as derived by Abraham *et al*[25,26].

$$\log SP = c + d.\delta_2 + s.\pi^*_2 + a.\alpha^H{}_2 + b.\beta^H{}_2 + m.V_x \qquad [6]$$

$$\log SP = c + d.\delta_2 + s.\pi^*_2 + a.\alpha^H{}_2 + b.\beta^H{}_2 + l.\log L^{16} \qquad [7]$$

At the start of this work, log L^{16} values were reported for 240 solutes[7]. We had available a large data base on π^*_2, α_2, and β_2 values for monofunctional compounds, and a smaller data base on log L^{16} values for monofunctional, and some other compounds.

The parameters α_2 and β_2 used from our database for MLRA analysis were in fact averaged or 'taken' α^H_2 and β^H_2 values respectively, and **not** the Kamlet and Taft values, although in many cases the two values are identical. The Kamlet and Taft values were not used in this work. Although this was sufficient to be able to use equations 53 and 54 to characterise solvent phases, it was not sufficient to be able to deal with the many important classes of polyfunctional solutes. One of the main aims was therefore to extend the data base to include polyfunctional compounds, and to incorporate further monofunctional compounds. Note that there is no difficulty over V_2; we generally use McGowan's characteristic volumes for solutes, these being calculable for any solute simply from molecular structure [28,29-31].

Primary log L^{16} values can simply be measured from retention information gathered for solutes on n-hexadecane at 298.15K[7], so it was desirable to carry out chromatographic experiments that could be used to extend our list of log L^{16} values. Additional log L^{16} values can rather easily be predicted, for example along homologous series. Secondary values can also be calculated by correlation of primary log L^{16} values with retention data on other apolar stationary phases, such as Apiezon or Squalane. There is a wealth of such data in the literature.

We were already in a position to apply equations 6 and 7 to phenomena involving monofunctional solutes. However, there are two interrelated problems in the general application of these equations to multifunctional solutes. Firstly, the α_2 and β_2 values can be experimentally obtained [25,26] from hydrogen bond complexation constants, only for monofunctional solutes. There seemed no practical possibility of obtaining direct experimental complexation constants for multifunctional solutes, and hence some indirect method of evaluation of α_2 and β_2 was required. Secondly, when equations 53 and 54 are applied to practical solubility situations, a given solute will be surrounded by an excess of solvent molecules, and hence multiple hydrogen bonding involving a number of solvent molecules can take place. This will not only take place with multifunctional solutes, but can also occur with certain solutes that are normally regarded as monofunctional. For example, anisole has $\beta_2 = 0.26$, derived from hydrogen bond complexation constants [26], but when surrounded by an excess of solvent, the solute might act as a base both at the ether linkage and via the benzene ring. Indeed, any "monofunctional" solute that is an activated aromatic compound might have an enhanced effective β_2 value in a bulk solvent. Examples could be aromatic ethers, phenols, and aromatic amines.

At the same time it was desired to obtain effective π_2 and α_2 values for multifunctional compounds. Note that an extra difficulty with polyfunctional acids is that any solute that is a hydrogen bond acid will also be a hydrogen bond base. Apart from the examination and subsequent back-calculation of 'effective' solvation parameters from HPLC data, much GLC data was available for analysis, notably the extensive data of McReynolds[44] and Laffort[45]. Apart from thoroughly characterising the stationary phases of McReynolds, (77 phases, approximately 350 solutes), and Laffort, (5 phases, 240 solutes), using our LSER equations and MLRA analysis, this would also enable back-calculation of 'effective' parameters, for monofunctional and multifunctional solutes alike. Any parameters calculated directly from GLC retention data can indeed be called effective values, as they should quantify accurately the degree and type of solute interaction taking place. It was hoped to take data from many varying sources and for many different phases to calculate values for the solvation parameters which would have the widest and most accurate scope of application.

While α^H_2 and β^H_2 have a sound thermodynamic background, many π^*_2 values and δ_2 as a whole do not, so it would be preferable to investigate the use of other terms, or improved terms. Solute dipolarity was often estimated or obtained from simple correlations with dipole moments. An effective back-calculated solute dipolarity value would be an improvement over π^*_2, and other replacement terms were also investigated. Attempts would also be made to replace the trivial parameter δ_2 with a parameter that could more accurately represent the degree of solute dipolarisability. This parameter should ideally be easily calculated and have some sort of rationale behind it.

PRELIMINARY STUDIES

We first applied the unmodified equations,

$$\log SP = c + d.\delta_2 + s.\pi^*_2 + a.\alpha^H_2 + b.\beta^H_2 + m.V_x \qquad [6]$$

$$\log SP = c + d.\delta_2 + s.\pi^*_2 + a.\alpha^H_2 + b.\beta^H_2 + l.\log L^{16} \qquad [7]$$

to two particular problems. Firstly equation 6 was applied to a very large number of water-hexadecane partition coefficients that we had been able to obtain from our $\log L^{16}$ values, and secondly equation 7 was applied to respiratory tract irritation in mice by airborne gaseous solutes. Results have been fully reported and are summarised in the two papers that follow.

Hydrogen Bonding 12.
A New QSAR for Upper Respiratory Tract Irritation by Airborne Chemicals in Mice.

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Abstract

Upper respiratory tract irritation of male Swiss OF_1 mice by airborne chemicals is well correlated by the following equations for the toxicity of nonreactive compounds,

$$-\log FRD'_{50} = -0.69 + 0.77\delta_2 + 2.81\pi_2^* + 4.93\alpha_2^H + 2.82V_x$$
$$n = 39 \quad r = 0.985 \quad sd = 0.14$$

$$-\log FRD'_{50} = 0.60 + 1.35\pi_2^* + 3.19\alpha_2^H + 0.77\log L^{16}$$
$$n = 39 \quad r = 0.990 \quad sd = 0.10$$

FRD'_{50} is the concentration in mol l^{-1} of the airborne chemical required to elicit a 50% decrease in respiratory rate, and the explanatory variables are δ_2 a polarisability correction term, π_2^* the solute dipolarity, α_2^H the solute hydrogen-bond acidity, V_x the characteristic volume, and L^{16} the gas/hexadecane partition coefficient. These equations considerably resemble corresponding equations for gas/liquid partition coefficients into organic bases such as tricresylphosphate, but do not resemble an equation for gas/water partition coefficients.

1 Introduction

The most common basis for the establishment of threshold limit values (TLVs) for exposure to airborne chemicals is that of sensory irritation of the eyes, nose, and throat. Many years ago, Alarie [1, 2] used an animal bioassay to evaluate sensory irritating properties of airborne chemicals, and later suggested that TLVs for industrial exposure to airborne chemicals could be recommended on the basis of animal bioassay [3]. Alarie [3] and DeCeaurriz *et al.* [4] both stressed this suggestion in subsequent studies. It is therefore of considerable importance to establish quantitative structure-activity relationships (QSARs) for result of animal bioassays in the hope that such QSARs will be applicable to TLVs for industrial exposure to airborne chemicals.

A first attempt was made by Muller and Greff [5] who analysed the sensory irritation of the upper respiratory tract in male Swiss OF_1 mice by 59 airborne chemicals, using results by DeCeaurriz *et al.* [4, 6]. These were given in terms of $\log 1/FRD_{50}$, where FRD_{50} is the concentration in mg/m^3 required to elicit a 50% decrease in respiratory rate. Muller and Greff [5] were able to establish correlations betweeen $\log 1/FRD_{50}$ and such physico-chemical properties as the normal boiling point, but only within families of compound, for example, saturated aliphatic alcohols, or aliphatic ketones. Roberts [7] then re-analysed the results used by Muller and Greff [5] by first of all recalculating FRD_{50} in units of $mmol/m^3$. Using a modified $\log M/FRD_{50}$, Roberts did manage to establish a general QSAR for nonreactive compounds, Eq. (1), where M is the irritant molecular weight

$$\log M/FRD_{50} = 0.0173T'_B - 4.090 \qquad (1)$$
$$n = 42 \quad r = 0.987 \quad s = 0.119$$

In Eq. (1), the explanatory variable T'_B is a modified normal boiling point in which T'_B for alcohols is taken as $(26.5T_B/22) - 8$ and in which T'_B for phenol is taken as $(24T_B/22) - 4$, where T_B is the normal boiling point in °C. As usual, n is the number of data points, r the correlation coefficient, and s the standard deviation. Roberts [7] explicity described Eq. (1) as a QSAR for nonreactive compounds, and excluded all the twelve alkyl acetates studied, as well as methylvinylketone, allyl alcohol, crotyl alcohol, mesityl oxide, and vinyl toluene. Although Eq. (1) is statistically a good correlation, bearing in mind that the expected error in $\log M/FRD_{50}$

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Abbreviations and Symbols: QSAR – quantitative structure-activity relationship, SP – the dependent variable, δ_2 – a polarisability correction term, π_2^* – the solute dipolarity; α_2^H – the solute hydrogen-bond acidity; β_2^H – the solute hydrogen-bond basicity; V_x – characteristic volume, L – a gas/liquid partition coefficient; L^{16} – a gas/hexadecane partition coefficient.

Key words: Upper respiratory tract irritation, toxicity, hydrogen-bond acidity, hydrogen-bond basicity, dipolarity, gas/liquid partition coefficients.

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must be around 0.1 log units, it suffers from two marked deficiencies. First of all, the calculation of T'_B is simply a mathematical transformation that displaces parallel lines to the same position. Secondly, and very importantly, Eq. (1) provides no information at all about the mechanism of toxicity of nonreactive compounds. That is, although Eq. (1) was referred to as a QSAR [7], it actually involves no connection at all between structural features of the irritants and their toxicity.

We have approached this problem in a quite different way. If we deal only with toxicity of nonreactive compounds then the process leading to upper respiratory tract irritation may be regarded as akin to a form of partition of a given compound or solute between air and some condensed phase. We can then use equations that have already been employed to model the partition behaviour of a series of solutes, or the toxicity effects of a series of solutes. Equation (2) has been used to correlate both partition of solutes between water and octanol, and the nonreactive toxicity of aqueous solutes towards a variety of organisms [8], whilst both Eq. (2) and Eq. (3) have been used to analyse the gas/liquid partition of series of solutes [9, 10]. It is worth noting that for compounds that conform to a simple partition model, activity must be proportional to the concentration of the solute in the biophase. All such solutes will bind to the target receptor site with the same intrinsic potency, and the biological effect will be given by the fraction of receptor occupied.

$$SP = c + d.\delta_2 + s.\pi_2^* + a.\alpha_2 + b.\beta_2 + m.V_2 \tag{2}$$

$$SP = c + d.\delta_2 + s.\pi_2^* + a.\alpha_2 + b.\beta_2 + 1.\log L^{16} \tag{3}$$

In these equations, SP is the dependent variable, e.g. log FRD_{50} or a partition coefficient as logP, and the explanatory variables are δ_2 a rather trivial polarisability correction term, π_2^* the solute dipolarity, α_2 the solute hydrogen-bond acidity, β_2 the solute hydrogen-bond basicity, V_2 the solute volume, and $\log L^{16}$ where L^{16} is the solute Ostwald solubility coefficient (or gas-liquid partition coefficient) on n-hexadecane at 298 K. As before, [8], δ_2 is taken as zero except for aromatic solutes ($\delta_2 = 1$), and polyhalogenated aliphatic solutes ($\delta_2 = 0.5$), and the dipolarity parameter π_2^* is also as before [8]. However, we now have to hand the extended results of Abraham and coworkers on a solute hydrogen-bond acidity scale, α_2^H, and a solute hydrogen-bond basicity scale, β_2^H[11 – 14]; we use McGowan's characteristic volume V_x as the solute size [15], and the $\log L^{16}$ values as determined before [16]. We have recalculated the FRD_{50} values of Muller and Greff [5] in units of mol l^{-1} (or mol dm^{-3}) and give values of $\log 10^6 M/FRD_{50}$, denoted as $-\log FRD'_{50}$, in Table 1 together with the parameters used in the calculations that follow. Except for twelve acetate esters, all the compounds studied by Muller and Greff are listed in Table 1, i.e. 47 compounds.

2 Results and Discussion

Applications of Eq. (2) and (3), where $SP = -\log FRD'_{50}$, to all 47 compounds leads to regressions with overall correlation coefficients, r, of only 0.510 on Eq. (2) and 0.568 on Eq. (3). The reason for these poor correlations is obvious – we have included in the data set compounds that cannot be regarded as nonreactive toxicants. These compounds can be identified as "outliers" because their observed sensory irritation is much larger than values calculated through Eq. (2) or Eq. (3). If eight outliers are excluded, then the following regressions are obtained, with V_x in units of $cm^3\ mol^{-1}/100$:

$$\begin{aligned} -\log FRD'_{50} = {} & -(0.685\pm0.236) + (0.768\pm0.055)\delta_2 \\ & + (2.812\pm0.304)\pi_2^* + (4.929\pm0.300)\alpha_2^H \\ & + (2.820\pm0.090)V_x \end{aligned} \tag{4}$$

$$n = 39 \qquad r = 0.9845 \qquad s = 0.136$$

$$\begin{aligned} -\log FRD'_{50} = {} & (0.596\pm0.165) + (1.354\pm0.224)\pi_2^* \\ & + (3.188\pm0.209)\alpha_2^H + (0.775\pm0.019)\log L^{16} \end{aligned}$$

$$n = 39 \qquad r = 0.9902 \qquad s = 0.103 \tag{5}$$

Eq. (5) with three explanatory parameters is clearly superior to Eq. (4), although the two equations lead to closely similar conclusions. However, in some circumstances, Eq. (4) might be preferred simply because it is easy to calculate V_x for any compound. The outliers to Eq. (4) and Eq. (5) are shown in Tables 2 and 3. Methylvinylketone, allyl alcohol, crotyl alcohol, mesityl oxide and 4-vinyltoluene are all much more toxic than calculated, by some $1\frac{1}{2}$ to $3\frac{1}{2}$ log units.

These five compounds were considered by Roberts [7] also to be outliers, to Eq. (1), possibly due to their reactive electrophilic character. In the case of 4-vinyltoluene, Roberts [7] suggested the oxidation of the methyl group to an aldehyde group aided by the electrophilic character of the 4-vinyl group. The present analysis suggests that on Eq. (4) cyclohexanone and 1,4-divinylbenzene are slightly more toxic than calculated and that phenol is much less toxic than calculated. However, on Eq. (5), the compounds 1,4-divinylbenzene and β-chloroethylbenzene are slightly more toxic than calculated and phenol is, again, decidely less toxic than calculated. Since Eq. (5) is theoretically and practically the better equation, we discount cyclohexanone as an outlier, and suggest that possibly the two compounds 1,4-divinylbenzene and β-chloroethylbenzene may be outliers. The position of these two compounds is marginal as can be seen from a plot of Eq. (5), shown in Fig. 1. If 1,4-divinylbenzene and β-chloroethylbenzene are included, then application of Eq. (3) yields the regression,

$$\begin{aligned} -\log FRD'_{50} = {} & (0.597\pm0.199) + (1.287\pm0.267)\pi_2^* \\ & + (3.110\pm0.251)\alpha_2^H + (0.794\pm0.022)\log L^{16} \end{aligned}$$

$$n = 41 \qquad r = 0.9860 \qquad sd = 0.127 \tag{6}$$

There is not a great deal of difference between Eq. (5) and Eq. (6), and it is a moot point whether or not 1,4-divinylbenzene and β-chloroethylbenzene are considered to be slightly reactive toxicants or not.

Phenol, however, is anomalous on all the equations we have used. It is possible that there is a rather large experimental error associated with phenol. On the other hand, phenols can be efficiently removed from the system by diffusion from the receptor compartment to the blood compartment where the concentration is kept low via conjugation with glucoronides or by sulphation.

Table 1. Parameters used in the calculations

Solute	δ_2	π_2^*	α_2^H	β_2^H	log L^{16}	V_x	$-\log FRD'_{50}$
2-propanone	0.00	0.71	0.04	0.50	1.760	0.547	3.01
but-1-ene-3-one	0.00	0.70	0.00	0.48	2.330	0.645	6.67
2-butanone	0.00	0.67	0.00	0.48	2.287	0.688	3.36
2-pentanone	0.00	0.65	0.00	0.48	2.755	0.829	3.61
mesityl oxide	0.00	0.70	0.00	0.55	3.300	0.927	5.60
cyclohexanone	0.00	0.76	0.00	0.52	3.616	0.861	4.51
2-hexanone	0.00	0.65	0.00	0.48	3.262	0.970	3.98
4-methyl-2-pentanone	0.00	0.65	0.00	0.48	3.050	0.970	3.88
3,3-dimethyl-2-butanone	0.00	0.65	0.00	0.48	2.887	0.970	3.64
2-heptanone	0.00	0.65	0.00	0.48	3.760	1.111	4.44
4-heptanone	0.00	0.65	0.00	0.48	3.820	1.111	4.35
5-methyl-2-hexanone	0.00	0.65	0.00	0.48	3.670	1.111	4.30
2-octanone	0.00	0.65	0.00	0.48	4.257	1.252	4.71
5-methyl-3-heptanone	0.00	0.65	0.00	0.48	4.200	1.251	4.51
5-nonanone	0.00	0.65	0.00	0.48	4.640	1.392	4.95
2,6-dimethyl-4-heptanone	0.00	0.65	0.00	0.48	4.180	1.392	4.88
2-undecanone	0.00	0.65	0.00	0.48	5.760	1.674	5.83
methanol	0.00	0.40	0.37	0.41	0.922	0.308	2.99
ethanol	0.00	0.40	0.33	0.44	1.485	0.449	3.21
1-propanol	0.00	0.40	0.33	0.45	2.097	0.590	3.71
2-propanol	0.00	0.40	0.32	0.47	1.821	0.590	3.69
1-butanol	0.00	0.40	0.33	0.45	2.601	0.731	4.29
2-methyl-1-propanol	0.00	0.40	0.33	0.45	2.399	0.731	4.13
1-pentanol	0.00	0.40	0.33	0.45	3.106	0.872	4.60
3-methyl-1-butanol	0.00	0.40	0.33	0.45	3.011	0.872	4.52
1-hexanol	0.00	0.40	0.33	0.45	3.610	1.013	5.01
4-methyl-2-pentanol	0.00	0.40	0.32	0.47	3.400	1.013	4.76
1-heptanol	0.00	0.40	0.33	0.45	4.115	1.154	5.39
1-octanol	0.00	0.40	0.33	0.45	4.619	1.295	5.71
2-ethyl-1-hexanol	0.00	0.40	0.33	0.45	4.500	1.295	5.74
prop-2-en-1-ol, allyl-OH	0.00	0.45	0.33	0.41	1.996	0.547	7.18
but-2-en-1-ol, crotyl-OH	0.00	0.45	0.33	0.41	2.500	0.688	6.44
toluene	1.00	0.55	0.00	0.14	3.344	0.857	3.86
phenol	1.00	0.72	0.60	0.36	3.855	0.775	5.16
chlorobenzene	1.00	0.71	0.00	0.09	3.640	0.839	4.36
bromobenzene	1.00	0.79	0.00	0.09	4.035	0.891	4.78
1,2-dichlorobenzene	1.00	0.80	0.00	0.03	4.405	0.961	5.13
2-chlorotoluene	1.00	0.67	0.00	0.08	4.160	0.980	4.63
acetophenone	1.00	0.90	0.00	0.51	4.483	1.014	5.38
2-xylene	1.00	0.51	0.00	0.17	3.937	0.998	4.23
4-xylene	1.00	0.51	0.00	0.17	3.858	0.998	4.27
β-chloroethylbenzene	1.00	0.70	0.00	0.25	4.600	1.121	5.47
styrene	1.00	0.55	0.00	0.18	3.908	0.955	4.62
ethylbenzene	1.00	0.53	0.00	0.15	3.765	0.998	4.24
α-methylstyrene, $PhMeCCH_2$	1.00	0.55	0.00	0.18	4.322	1.118	4.95
4-vinyltoluene	1.00	0.55	0.00	0.20	4.480	1.096	6.20
4-divinylbenzene	1.00	0.55	0.00	0.20	4.900	1.194	5.49

A class of compounds we have not yet considered is that of the alkyl acetates. Roberts [7] noted that alkyl acetates did not conform to his QSAR, Eq. (1), and suggested that the acetates were at least partially hydrolysed under the test conditions. Our analysis of the sensory irritant properties of the alkyl acetates is given in Table 4 and illustrated in Fig. 2. As the acetates become less susceptible to hydrolysis along the series $MeCO_2R$ where R = Me, Et, Pr^n, Pr^{iso}, Bu^{tert}, for example, so do the observed and calculated $-\log FRD'_{50}$ converge. The hydrolysis products, *viz.* acetic acid and alcohol, will together certainly be more potent than the ester itself. Thus for ethyl acetate, where the observed value is 4.62 and the calculated value on Eq. (5) is 3.18 log units, our calculated value for the hydrolysis product is 4.52, and an observed value is 5.18 [4].

Our suggested QSAR, Eq. (5), thus seems to provide the basis for a reasonable analysis of the sensory irritation of the upper respiratory tract in male Swiss OF_1 mice by nonreactive compounds. If our model of such nonreactive toxicity as taking place via a process akin to partitioning is in any way realistic, we can go further and attempt to interpret the process using Eq. (5). The partition we refer to is simply that of airborne

Table 2. Outliers using the equation in V_x

	$-\log FRD'_{50}$		
Outlier	Obs	Calc	Δ
methylvinylketone	6.67	3.10	3.57
mesityl oxide	5.60	3.90	1.70
cyclohexanone	4.51	3.88	0.63
allyl alcohol	7.18	3.75	3.43
crotyl alcohol	6.44	4.15	2.29
phenol	5.16	7.25	−2.09
4-vinyltoluene	6.20	4.72	1.48
1,4-divinylbenzene	5.49	5.00	0.49
Included			
β-chloroethylbenzene	5.47	5.21	0.36
styrene	4.62	4.32	0.30
α-methylstyrene	4.95	4.78	0.17

$$-\log FRD'_{50} = -0.658 + 0.768\delta_2 + 2.812\pi_2^* + 4.929\alpha_2^H + 2.820\,V_x$$

$r = 0.984$ $s = 0.136$ $n = 39$

Table 3. Outliers using the equation in $\log L^{16}$

	$-\log FRD'_{50}$		
Outlier	Obs	Calc	Δ
methylvinylketone	6.67	3.35	3.32
mesityl oxide	5.60	4.10	1.50
allyl alcohol	7.18	3.80	3.38
crotyl alcohol	6.44	4.19	2.25
phenol	5.16	6.47	−1.31
4-vinyltoluene	6.20	4.81	1.39
1,4-divinylbenzene	5.49	5.14	0.35
β-chloroethylbenzene	5.47	5.11	0.36
Included			
cyclohexanone	4.51	4.43	0.08
styrene	4.62	4.37	0.25
α-methylstyrene	4.95	4.69	0.26

$$-\log FRD'_{50} = -0.596 + 1.354\pi_2^* + 3.188\alpha_2^H + 0.775\log L^{16}$$

$r = 0.990$ $s = 0.103$ $n = 39$

Table 4. Calculations on alkyl acetates.

	$-\log FRD'_{50}$		
R in CH_3CO_2R	Obs	Calc[a]	Δ
Me	4.47	2.93	1.54
Et	4.62	3.18	1.44
n-Pr	4.49	3.57	0.92
iso-Pr	3.76	3.38	0.38
n-Bu	4.52	3.96	0.56
iso-Bu	4.47	3.81	0.66
t-Bu	3.18	3.51	−0.33
n-Pe	4.19	4.29	−0.10
iso-Pe	4.36	4.24	0.12
n-Hexyl	4.52	4.65	−0.13
2-Methoxyethyl	4.63	–	–
2-Ethoxyethyl	4.53	–	–

[a] Using equation (5).

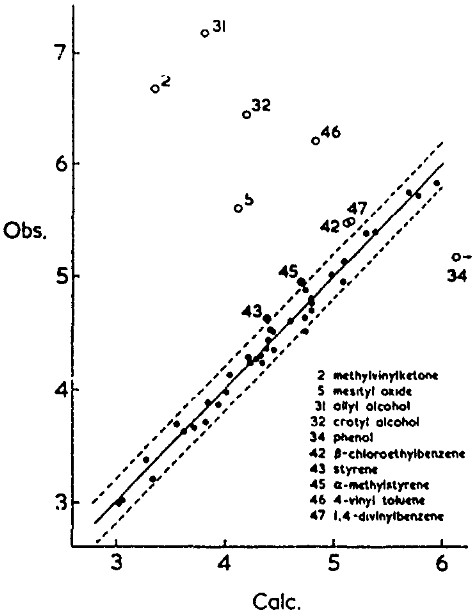

Figure 1. Observed and calculated $-\log FRD'_{50}$ according to Eq. (5): • included points, ○ outliers. The dashed lines show ± two standard deviations

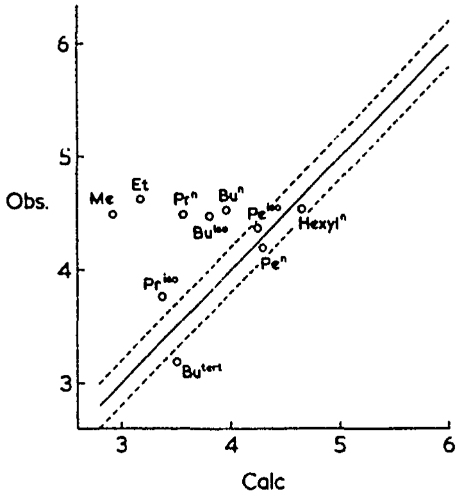

Figure 2. Deviations of alkyl acetates, CH_3CO_2R, from Eq. (5). The dashed lines show ± two standard deviations

chemicals between the vapour phase and some condensed phase. Now since the hydrogen-bond basicity of the solutes is not significant on Eq. (5), we can infer that the condensed phase, whatever its nature, does not act as a hydrogen-bond acid. On the other hand, the coefficient of α_2^H in Eq. (5) is quite large, and hence we infer that the condensed phase behaves as a hydrogen-bond base.

We can place the coefficients of Eq. (5) in context, by comparison with those obtained for the partition of vapors between the gas phase and some particular solvent phase. Abraham *et al.* [10] have shown how the general equation (3; SP = logL) can be applied to gas-liquid partitions. They gave as an example the solvent tricresylphosphate (TCPH), taking logL (TCPH) values at 298 K from Alessi *et al.* [17].

$$\log L(\mathrm{TCPH}) = -0.35 - 0.25\delta_2 + 1.71\pi_2^* + 2.98\alpha_2^H + 0.911 \log L^{16} \quad (7)$$

$$n = 22 \qquad r = 0.991 \qquad s = 0.09$$

Abraham and Whiting [18] have recently analysed logL values for the gas/N-methylpyrrolidinone (NMP) partition using results of Weidlich *et al.* [19] extrapolated to 298 K, Eq. (8).

$$\log L(\mathrm{NMP}) = -0.11 + 2.10\pi_2^* + 5.05\alpha_2^H + 0.779 \log L^{16} \quad (8)$$

$$n = 31 \qquad r = 0.988 \qquad s = 0.11$$

Comparison with Eq. (5) suggests that the general receptor site acts as a resonably polar area (s = 1.354) and has hydrogen-bond basicity about the same as TCPH but less than NMP, with a = 3.188 in Eq. (5). The receptor site is still reasonably hydrophobic with l = 0.775 (note that for the gas/hexadecane partition l = 1, by definition). Abraham *et al.* [10] also listed a provisional equation for gas/water partition, Eq. (9). It is very clear, by inspection, that Eq. (5) resembles equations for gas/organic solvent partitions, as in Eqs (7) and (8), but bears little resemblance to Eq. (9). The main differences are the minor dependence on $\log L^{16}$ and the dependence on β_2^H in Eq. (9), the latter dependence due to the strong hydrogen-bond acidity of water.

$$\log L(\mathrm{water}) = -1.46 + 3.99\pi_2^* + 6.10\alpha_2^H + 3.22\beta_2^H - 0.060 \log L^{16} \quad (9)$$

$$n = 59 \qquad r = 0.989 \qquad s = 0.33$$

In conclusion, we have been able to construct a QSAR for nonreactive upper respiratory tract irritation in male Swiss OF_1 mice by airborne chemicals, Eq. (5), that will allow predictions of $-\log FRD'_{50}$ to be made. It must be noted, however, that predictions may be hazardous if the explanatory variables for the solutes concerned fall outside the range of those studied. Thus Franks and Lieb [20] have shown that in the inhibition of firefly luciferase activity by aqueous solutes, there is a definite "cut-off" effect in terms of solute size. Such an effect could not have been predicted by the analysis of a series of solutes all below the critical size. Our QSAR is additionally valuable in that it leads to some understanding of the partition mechanism of toxicity of nonreactive compounds. In future we hope to analyse results on Swiss-Webster male mice for which, at the moment, we are gathering relevant data.

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Thermodynamics of Solute Transfer from Water to Hexadecane

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New measurements of enthalpies of solution in hexadecane and in water (ΔH_s°), and gas–hexadecane Ostwald solubility coefficients (L_H) of neutral monomeric organic solutes are reported. These values, together with literature values of ΔH_s°, L_H, and gas–water Ostwald solubility coefficients (L_W), have been used to derive the Gibbs energies, enthalpies, and entropies of solute transfer from water to hexadecane (ΔG_{tr}°, ΔH_{tr}°, and ΔS_{tr}°), as well as water–hexadecane partition coefficients (as log P_H). Results have been examined by the method of multiple linear regression analysis, using the equation,

$$SP = c + d\delta_2 + s\pi_2^* + a\alpha_2 + b\beta_2 + vV_2$$

The $s\pi_2^*$ term is difficult to interpret, but the $a\alpha_2$ and $b\beta_2$ terms can be shown to arise through hydrogen bonding of solute molecules to the bulk water that is exothermic but rather disfavoured entropically. It is shown also that the vV_2 term arises due to a combination of cavity effects and general dispersion interactions in bulk water and bulk hexadecane.

The use of water–octanol partition coefficients is widespread in medicinal and pharmaceutical chemistry, and, indeed, forms part of the general rationale governing most quantitative structure–activity relationships (QSARs).[1] Although water-saturated octanol, according to this rationale, is a suitable model for biological membranes, other solvents, and hence other water–solvent partition coefficients, have also been used in QSARs. For example, Finkelstein[2] and, later, Franks and Lieb[3] used water–hexadecane partition coefficients, the latter workers specifically to test for hydrophobic binding sites in the luciferase enzyme. In these studies the required water–hexadecane partition coefficients were obtained by the traditional 'shake-flask' method. Unlike the water–octanol system, in which the mutual miscibility of the two solvents is quite high, the water–hexadecane system can be regarded as a system containing the two pure solvents (the solubility of water in hexadecane is 2×10^{-3} mol dm^{-3} and that of hexadecane in water is 4×10^{-4} mol dm^{-3})[4] Hence water–hexadecane partition coefficients can be determined indirectly using equation (1), where L_W and L_H are the respective gas–solvent

$$P_H = L_H/L_W \qquad (1)$$

Ostwald solubility coefficients.† We,[4] and Shantz and Martire,[5] have shown almost simultaneously that values of P_H obtained indirectly *via* equation (1) are, indeed, identical with values determined by the direct 'shake-flask' method Since the values of L_H can be measured very accurately by a gas-chromatographic method using hexadecane as the stationary phase,[4,5] it is possible from known aqueous solubilities of gases[6–10] to obtain P_H values relatively simply for a wide range of not-too-involatile solutes.

One of the aims of the present work is to set out values of P_H for the water–hexadecane partition of neutral, monomeric solutes, either as log P_H or as transfer Gibbs energies, ΔG_{tr}°, for as wide a range of solutes as possible The second aim is to present values for the enthalpy, and hence, the entropy, of transfer of examples of these solutes. To date, there have been very few sets of ΔG_{tr}°, ΔH_{tr}°, and ΔS_{tr}° values for partition from water to a given solvent. The most substantial set of data is that of Riebesehl and Tomlinson,[11] who used a direct flow-microcalorimeter method to obtain ΔH_{tr}° values for transfer of 29 solutes from water to 2,2,4-trimethylpentane. We later analysed the thermodynamic results of Tomlinson and co-workers,[11,12] but found[13] that the data were not extensive enough to examine aliphatic and aromatic solutes separately. We have therefore obtained ΔH_{tr}° values through a combination of enthalpies of solution in water and in hexadecane separately, and set out ΔG_{tr}°, ΔH_{tr}°, and ΔS_{tr}° values for as many solutes as possible. We have, as well as our own calorimetrically determined ΔH_s° values, used literature data on ΔH_s° values in water and hexadecane, where possible, selecting calorimetrically determined values. Of course, for solutes that are gaseous at room temperature and pressure, ΔH_s° values have nearly always been obtained through the temperature variation of solubility—the so called van't Hoff method—but the method of direct calorimetry is to be preferred.

Experimental

Values of L_H for solutes on hexadecane at 298.15 K were obtained as described before.[4] The instruments used were either a Pye–Unicam 104 chromatograph fitted with a katharometer detector, for the determination of absolute L_H values, or a Perkin-Elmer F-11 chromatograph fitted with a flame detector, for the determination of relative L_H values to be converted into absolute values.

Enthalpies of solution in hexadecane and in water were measured as described previously,[14] with liquid solute samples of 10, 20, or 50 mm^3 injected through Teflon-faced silicone septa into vapour-tight, vacuum-jacketed solution calorimeters containing 80–110 cm^3 of solvent. For solutes which dissolve slowly the normal stirring speed of 300 rpm was increased to 600 rpm. Solutes and solvents, all of >99% purity, were dried with 4A molecular sieve, with the ex-

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† Note that L_H is the same as L,[16] the symbol we previously used[4]

Table 1. Thermodynamics of transfer of solutes from water to hexadecane, and calculation of ΔG°_{tr} (mole fraction scale) and log P_H (molar scale) for water to hexadecane at 298 K

Solute	Water[a]		Hexadecane[b]		Water ⟶ Hexadecane					
	ΔG°_s	ΔH°_s	ΔG°_s	ΔH°_s	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}	log L_W	log L_H	log P_H
Helium	7.03	−0.16	4.99	1.97[c]	−2.04	2.13	14.0	−2.023	−1.741	0.28
Neon	6.94	−0.92	4.77	1.62[c]	−2.17	2.54	15.8	−1.958	−1.575	0.38
Argon	6.27	−2.93	3.56	−0.19[c]	−2.71	2.74	18.3	−1.467	−0.688	0.78
Krypton	5.93	−3.74	2.91	−1.20[c]	−3.02	2.54	18.6	−1.213	−0.211	1.00
Xenon	5.60	−4.63	2.10	−2.41[c]	−3.50	2.22	19.2	−0.972	0.378	1.35
Radon	5.15	−5.74	1.42	−3.39[c]	−3.73	2.35	20.4	−0.646	0.877	1.52
Methane	6.27	−3.15	3.06	−0.95[c]	−3.21	2.20	18.1	−1.452	−0.323	1.14
Ethane	6.09	−4.66	1.95	−2.75[c]	−4.14	1.91	20.3	−1.336	0.492	1.83
Propane	6.23	−5.56	1.19	−3.81[c]	−5.04	1.75	22.8	−1.436	1.050	2.49
Butane	6.34	−6.20	0.42	−4.97[c]	−5.92	1.23	24.0	−1.518	1.615	3.13
2-Methylpropane	6.59	−5.78[d]	0.70	−4.48[c]	−5.89	1.30	24.1	−1.70	1.409	3.11
Pentane	6.60	−6.76	−0.33	−6.20	−6.93	0.56	25.1	−1.704	2.162	3.87
Hexane	6.76	−7.65	−1.02	−7.42	−7.78	0.23	26.9	−1.821	2.668	4.49
Heptane	6.95	−8.13	−1.71	−8.64	−8.66	−0.51	27.3	−1.962	3.173	5.14
Octane	7.15	−8.60	−2.40	−9.83	−9.55	−1.23	27.9	−2.109	3.677	5.79
Cyclopropane	5.02	−5.56[d]	0.83		−4.19			−0.55	1.314	1.86
Cyclopentane	5.48	−7.25	−0.72	−6.61[e]	−6.20	0.64	22.9	−0.88	2.447	3.33
Cyclohexane	5.50	−7.84[d]	−1.35	−7.53[e]	−6.85	0.31	24.0	−0.90	2.913	3.81
2,2-Dimethylpropane[f]	6.78		0.14		−6.64			−1.84	1.82	3.66
3,3-Diethylpentane[f]	6.50		−2.59		−9.09			−1.63	3.82	5.45
Tetramethylsilane[f]	7.32		−0.30		−7.62			−2.23	2.14	4.37
Tetraethylsilane[f]	7.04		−3.24		−10.33			−2.03	4.33	6.36
Tetramethyltin[f]	6.48		−1.36		−7.84			−1.62	2.92	4.54
Tetraethyltin[f]	6.75		−4.31		−11.06			−1.82	5.08	6.90
Ethene	5.55	−3.93[d]	2.23	−2.67[g]	−3.32	1.26	15.4	−0.94	0.289	1.23
Propene	5.59	−5.17[d]	1.33	−3.19[h]	−4.26	1.98	20.9	−0.97	0.946	1.92
But-1-ene	5.65	−5.77[d]	0.59		−5.06			−1.01	1.491	2.50
Pent-1-ene	5.94		−0.13		−6.07			−1.23	2.013	3.24
Hex-1-ene	5.85		−0.86		−6.71			−1.16	2.547	3.71
Hept-1-ene	5.93		−1.56		−7.49			−1.22	3.063	4.28
Oct-1-ene	6.19		−2.28		−8.47			−1.41	3.591	5.00
Non-1-ene	6.33		−2.84		−9.17			−1.51	4.00	5.51
Ethyne	4.26	−3.49[d]	2.41	1.67[i]	−1.85	5.16	23.5	0.01	0.150	0.14
Propyne	3.79	−3.73[j]	1.22		−2.57			0.35	1.025	0.68
But-1-yne	4.11	−3.71[j]	0.55		−3.56			0.12	1.52	1.40
Pent-1-yne	4.29		−0.12		−4.41			−0.01	2.01	2.02
Hex-1-yne	4.56		−0.80		−5.36			−0.21	2.51	2.72
Hept-1-yne	4.87		−1.47		−6.34			−0.44	3.00	3.44
Oct-1-yne	4.98		−2.13		−7.11			−0.52	3.48	4.00
Non-1-yne	5.32		−2.78		−8.10			−0.77	3.96	4.73
Benzene	3.39	−7.59	−1.20	−7.26	−4.59	0.33	16.5	0.65	2.803	2.15
Toluene	3.48	−8.67	−1.94	−8.58	−5.42	0.09	18.3	0.58	3.344	2.76
Ethylbenzene	3.61	−9.62	−2.52	−9.59	−5.13	0.03	20.7	0.48	3.765	3.28
Propylbenzene	3.75	−10.50	−3.14	−10.55	−6.89	−0.05	22.9	0.38	4.221	3.84
Butylbenzene	3.91	−10.55[m]	−3.17		−7.68			0.27	4.686	4.42
Pentylbenzene	4.04	−11.82[m]	−4.41		−8.45			0.17	5.152	4.98
Hexylbenzene	4.23	−12.60[m]	−5.04		−9.27			0.03	5.617	5.59
o-Xylene	3.36[k]	−9.01[n]	−2.75		−6.11			0.67	3.937	3.27
m-Xylene	3.56[l]	−9.37[n]	−2.65	−9.89	−6.21	−0.52	19.2	0.52	3.864	3.34
p-Xylene	3.54[k,l]	−9.49[n]	−2.64	−9.92	−6.18	−0.43	19.3	0.54	3.858	3.32
1,2,3-Trimethylbenzene	3.30[k,l]	−8.96[n]						0.71		
1,2,4-Trimethylbenzene	3.47[k,l]	−9.54[n]						0.59		
1,3,5-Trimethylbenzene	3.59[k]	−9.36[n]	−3.38	−11.13	−6.97	−1.77	17.4	0.50	4.399	3.90
Isopropylbenzene	3.81[k,l]	−9.46[n]	−2.98		−6.79			0.34	4.105	3.77
Naphthalene	1.87[k,o]	−11.20[o]	−4.67		−6.54			1.76	5.34	3.58
Fluorene	0.92[k]							2.46		
Phenanthrene	0.41							2.83		
Pyrene	−0.30							3.35		
Propanone	0.46	−9.90[p]	0.22	−5.14	−0.24	4.76	16.8	2.79	1.760	−1.03
Butanone	0.56	−10.91[p]	−0.50	−6.33	−1.06	4.58	18.9	2.72	2.287	−0.43
Pentan-2-one	0.75	−11.63[p]	−1.14	−7.42	−1.89	4.21	20.5	2.58	2.755	0.18
Hexan-2-one	0.98	−12.57[p]	−1.83	−8.55[q]	−2.81	4.02	22.9	2.41	3.262	0.85
Heptan-2-one	1.23	−13.43[p]	−2.51	−9.67	−3.74	3.76	25.1	2.23	3.760	1.53
Octan-2-one	1.39	−14.15[q]	−3.19	−10.73[q]	−4.58	3.42[q]	26.8	2.11	4.257	2.15
Nonan-2-one	1.78	−14.90[j]	−3.87	−11.80[q]	−5.65	3.10[q]	29.3	1.83	4.755	2.92
Decan-2-one	1.92		−4.56		−6.48			1.72	5.260	3.54
Undecan-2-one	2.11		−5.24		−7.35			1.58	5.760	4.18
Pentan-3-one	0.86[j]	−11.82[j]	−1.22		−2.08			2.50	2.811	0.31

Table 1 (*continued*)

Solute	Water[a] ΔG°_s	Water[a] ΔH°_s	Hexadecane[b] ΔG°_s	Hexadecane[b] ΔH°_s	Water → Hexadecane ΔG°_{tr}	Water → Hexadecane ΔH°_{tr}	Water → Hexadecane ΔS°_{tr}	log L_W	log L_H	log P_H
Heptan-4-one	1.35[j]	−14.40[j]	−2.59		−3.94			2.14	3.820	1.68
Nonan-5-one	1.63[j]	−16.04	−3.71		−5.34			1.94	4.64	2.70
3-Methylbutan-2-one	1.03[j]		−1.01		−2.04			2.38	2.66	0.28
4-Methylpentan-2-one	1.21[j]		−1.54		−2.75			2.24	3.05	0.81
Cyclopentanone	−0.43[r]	−12.36	−1.64		−1.21			3.45	3.120	−0.33
Cyclohexanone	−0.64[s]	−12.90[t]	−2.31	−8.72	−1.67	4.18	19.6	3.60	3.616	0.02
Acetophenone	−0.31[j]	−12.64[t]	−3.50	−11.32	−3.19	1.32	15.1	3.36	4.483	1.12
Formaldehyde	1.52[u]		1.62		0.10			2.02	0.73	−1.29
Acetaldehyde	0.77[t]		0.94		0.17			2.57	1.230	−1.34
Propanal	0.83[t]		0.14		−0.69			2.52	1.815	−0.70
Butanal	1.09[t]		−0.48		−1.57			2.33	2.270	−0.06
Pentanal	1.24[v]		−1.16		−2.40			2.22	2.770	0.55
Hexanal	1.46[t]		−1.98		−3.44			2.06	3.370	1.31
Heptanal	1.60[v]		−2.65		−4.25			1.96	3.86	1.90
Octanal	1.98[r]		−3.35		−5.33			1.68	4.38	2.70
Nonanal	2.20[t]		−4.07		−6.27			1.52	4.90	3.38
2-Methylpropanal	1.41[u]		−0.19		−1.60			2.10	2.06	−0.04
Benzaldehyde	0.25[j]	−10.79[t]	−2.82	−9.84	−3.07	0.95	13.5	2.95	3.985	1.03
(*E*)-But-2-enal	0.05[j]		−0.89		−0.94			3.10	2.57	−0.53
Dimethyl ether	2.38[j]		1.33					1.39	1.09	−0.30
Diethyl ether	2.68[j]	−11.20[t]	−0.19	−6.02	−2.87	5.18	27.0	1.17	2.061	0.89
Dipropyl ether	3.11[j]		−1.46		−4.57			0.85	2.989	2.14
Di-isopropyl ether	3.74[x]		−0.87		−4.61			0.39	2.559	2.17
Dibutyl ether	3.44[x]		−2.84		−6.28			0.61	4.001	3.39
Tetrahydrofuran	0.80[t]	−11.31[t]	−0.84	−6.82	−1.64	4.49	20.6	2.55	2.534	−0.02
Tetrahydropyran	1.15[j]	−11.68[j]	−1.46					2.29	2.99	0.70
Anisole	1.82[y]	−9.90[t]	−2.74	−9.90	−4.56	0.00	15.3	1.80	3.926	2.13
Phenetole	2.05[y]		−3.03		−5.08			1.63	4.14	2.51
Methyl formate	1.49		0.63		−0.86			2.04	1.459	−0.58
Methyl acetate	1.13	−9.44[t]	−0.05		−1.18			2.30	1.960	−0.34
Methyl propanoate	1.34	−10.16[j]	−0.74		−2.08			2.15	2.459	0.31
Methyl butanoate	1.44	−11.50[j]	−1.40		−2.84			2.08	2.943	0.86
Methyl pentanoate	1.70	−12.33[j]	−2.08		−3.78			1.88	3.442	1.56
Methyl hexanoate	1.78		−2.81		−4.59			1.83	3.984	2.15
Ethyl formate	1.70		0.03		−1.67			1.88	1.901	0.02
Ethyl acetate	1.33	−10.78[t]	−0.62	−6.69	−1.95	4.09	20.3	2.16	2.376	0.22
Ethyl propanoate	1.59		−1.31		−2.90			1.97	2.881	0.91
Ethyl butanoate	1.77		−1.99		−3.76			1.83	3.379	1.55
Ethyl pentanoate	1.77							1.83		
Ethyl hexanoate	2.03							1.64		
Ethyl heptanoate	1.95							1.70		
Propyl formate	1.79[x]		−0.67		−2.46			1.82	2.413	0.59
Propyl acetate	1.48		−1.31		−2.79			2.05	2.878	0.83
Propyl propanoate	1.83		−1.98		−3.81			1.79	3.370	1.58
Propyl butanoate	1.99[x]		−2.58		−4.57			1.67	3.81	2.14
Butyl acetate	1.63	−12.36[t]	−1.99	−9.20	−3.62	3.16	22.7	1.94	3.379	1.44
Pentyl acetate	1.76		−2.58		−4.34			1.84	3.81	1.97
Pentyl propanoate	2.16		−3.32		−5.60			1.55	4.350	2.80
Hexyl acetate	2.01[x]		−3.21		−5.22			1.66	4.27	2.61
Isopropyl formate	2.25[x]		−0.42		−2.67			1.48	2.23	0.75
Isopropyl acetate	1.63[x]		−0.97		−2.60			1.94	2.633	0.69
Isopropyl propanoate	2.05[x]		−1.51		−3.56			1.63	3.03	1.40
Isobutyl formate[z]	2.05[x]		−1.24		−3.29			1.63	2.83	1.20
Isobutyl acetate[z]	1.91[x]		−1.72		−3.63			1.73	3.180	1.45
Isoamyl formate[z]	2.14[x]		−1.95		−4.09			1.56	3.35	1.79
Isoamyl acetate[z]	2.06[x]		−2.48		−4.54			1.62	3.74	2.12
Isobutyl isobutyrate[z]	2.59[w]		−2.67		−5.25			1.24	3.88	2.64
Methyl benzoate	−0.01[x]	−12.44[t]	−3.70	−11.56	−3.69	0.88	15.3	3.14	4.634	1.49
Ethyl benzoate	0.63[y]							2.67		
Propylene carbonate	−3.29[aa]	0.39[ab]						5.54		
Water	−2.05[ac]	−10.51[ac]	2.26[ad]	−8.44[ae]	4.31	2.07	−7.5	4.64	0.260	−4.38
Methanol	−0.83	−10.78[p]	1.36	−3.19	2.19	7.59	18.1	3.74	0.922	−2.82
Ethanol	−0.73	−12.58[p]	0.59	−3.90	1.32	8.68	24.7	3.67	1.485	−2.19
Propan-1-ol	−0.56	−13.77[p]	−0.24	−5.06	0.34	8.71	28.1	3.56	2.097	−1.46
Butan-1-ol	−0.45	−14.75[p]	−0.93	−6.71	−0.48	8.04	28.6	3.46	2.601	−0.86
Pentan-1-ol	−0.30	−15.48[p]	−1.62	−7.46	−1.32	8.02	31.3	3.35	3.106	−0.24
Hexan-1-ol	−0.14	−16.28[p]	−2.31	−9.51	−2.17	6.77	30.0	3.23	3.610	0.38
Heptan-1-ol	0.06	−17.24[p]	−2.99	−10.62[q]	−3.05	6.62	32.4	3.09	4.115	1.02

Table 1 (*continued*)

Solute	Water[a]		Hexadecane[b]		Water ⟶ Hexadecane					
	ΔG°_s	ΔH°_s	ΔG°_s	ΔH°_s	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}	log L_W	log L_{16}	log P_{16}
Octan-1-ol	0.18	−17.72[p]	−3.68	−11.73	−3.86	5.99	33.0	3.00	4.619	1.62
Nonan-1-ol	0.39		−4.37		−4.76			2.85	5.124	2.27
Decan-1-ol	0.63		−5.06		−5.69			2.67	5.628	2.96
Propan-2-ol	−0.48[e,f]	−14.05[i]	0.14	−5.35	0.62	8.70	27.1	3.48	1.821	−1.66
Butan-2-ol	−0.35[e,f]	−15.00[j]	−0.57		−0.22			3.39	2.338	−1.05
2-Methylpropan-1-ol	−0.23[e,f]	−14.38[j]	−0.65		−0.42			3.30	2.339	−0.90
2-Methylpropan-2-ol	−0.20[e,f]	−15.39[f]	−0.13	−5.50	0.07	9.89	32.9	3.28	2.018	−1.26
Pentan-2-ol	−0.12[k]		−1.26		−1.14			3.22	2.840	−0.38
2-Methylbutan-1-ol	−0.15[k]		−1.49		−1.34			3.24	3.011	−0.23
2-Methylbutan-2-ol	−0.16[k]	−16.44[e,g]	−0.97		−0.86			3.25	2.630	−0.62
Pentan-3-ol	−0.08[j]	−15.77[j]						3.19		
3-Methylbutan-1-ol	−0.15[j]		−1.49					3.24	3.011	−0.23
Hexan-3-ol	0.20[j]	−16.63[j]	−2.07					2.98	3.440	0.46
4-Methylpentan-2-ol	0.53[k]							2.74		
2-Methylpentan-2-ol	0.34[k]		−1.72					2.88	3.181	0.30
2-Methylpentan-3-ol	0.38[k]							2.85		
Cyclopentanol	−1.22[j]	−15.98[j]	−1.84		−0.62			4.03	3.270	−0.76
Cyclohexanol	−1.20[j]	−16.85[j]	−2.39		−1.19			4.01	3.671	−0.34
Cycloheptanol	−1.21[j]	−17.82[j]						4.02		
Allyl alcohol	−0.76[k]		−0.10		0.66			3.69	1.996	−1.69
2,2,2-Trifluoroethanol	−0.03[j]	−12.01[i]	0.95	−4.99	0.98	7.02	20.3	3.15	1.224	−1.93
Hexafluoropropan-2-ol	0.51[j]	−13.65[j]	0.72	−5.28	0.21	8.37	27.4	2.76	1.392	−1.37
Benzyl alcohol	−2.07[j]	−16.00[i]	−3.44	−10.13	−1.37	5.87	24.3	4.65	4.443	−0.21
Phenol	−2.00[a,h]	−13.65[a,i]	−2.64		−0.64			4.60	3.856	−0.74
o-Cresol	−1.60[a,i]	−14.52[a,i]	−3.17		−1.57			4.30	4.242	−0.06
m-Cresol	−1.23[a,j]		−3.29		−2.06			4.03	4.329	0.30
p-Cresol	−1.86[a,i]	−14.29[a,i]	−3.26		−1.40			4.50	4.307	−0.19
4-*t*-Butylphenol	−1.65[a,i]	−15.25[a,i]						4.34		
4-Bromophenol	−2.86[a,i]	−16.27[a,i]						5.23		
2-Nitrophenol	−0.15[a,k]	−11.47[a,k]	−3.77		−3.62			3.24	4.684	1.44
3-Nitrophenol	−5.36[j]	−16.18[j]						7.06		
4-Nitrophenol	−6.38[a,i]	−18.04[a,i] −16.40[j]						7.81		
3-Cyanophenol	−5.24[j]	−16.90[j]						6.97		
4-Cyanophenol	−5.90[j]	−16.80[j]						7.46		
3-Hydroxybenzaldehyde	−5.24[j]	−16.00[j]						6.97		
4-Hydroxybenzaldehyde	−6.20[j]	−16.30[j]						7.68		
2-Chlorophenol									4.937	
3-Chlorophenol		−12.03[j]								
4-Chlorophenol		−8.58[j]								
Formic acid		−11.09								
Acetic acid	−2.43[a,l]	−12.28	0.23		2.66			4.91	1.75	−3.16
Propanoic acid	−2.20[a,l]	−13.45	−0.50		1.70			4.74	2.29	−2.45
Butanoic acid	−2.08[a,l]	−14.50	−1.24		0.84			4.66	2.83	−1.83
Pentanoic acid	−1.90[a,m]	−15.32	−1.99		−0.09			4.52	3.38	−1.14
Hexanoic acid	−1.95[a,n]	−16.08	−2.72		−0.77			4.56	3.92	−0.64
Heptanoic acid	−1.89[a,n]	−16.96	−3.47		−1.58			4.52	4.46	−0.06
Octanoic acid	−1.78[e]	−17.75	−4.20		−2.42			4.44	5.00	0.56
3-Methylbutanoic acid	−1.82[n]		−1.88		−0.06			4.47	3.30	−1.17
Ammonia	−0.03[a,o]	−8.42[a,o]	2.25		2.28			3.15	0.269	−2.88
Methylamine	−0.29	−10.82						3.34		
Ethylamine	−0.23	−12.83	0.33		0.56			3.30	1.677	−1.62
Propylamine	−0.12	−13.38	−0.30	−5.73	−0.18	7.65	26.3	3.22	2.141	−1.08
Butylamine	0.03	−14.15	−0.95	−7.03	−0.98	7.12	27.2	3.11	2.618	−0.49
Pentylamine	0.18	−14.85	−1.59		−1.77			3.00	3.086	0.09
Hexylamine	0.32	−15.76	−2.23	−9.43	−2.55	6.33	29.8	2.90	3.557	0.66
Heptylamine	0.48		−2.91		−3.39			2.78	4.050	1.27
Octylamine	0.62		−3.55		−4.17			2.68	4.520	1.84
Isopropylamine		−13.37[a,o]								
t-Butylamine		−14.16[a,o]	−0.78	−6.25		7.91			2.493	
Cyclohexylamine	−0.32[n]							3.37		
Dimethylamine	−0.03[a,o]	−12.69[a,o]	0.44		0.47			3.15	1.60[q]	−1.55
Diethylamine	0.19[a,o]	−15.37[i]	−0.65	−5.88	−0.84	9.49	34.6	2.99	2.395	−0.60
Dipropylamine	0.62[a,o]	−17.26[a,o]	−1.98		−2.60			2.68	3.372	0.69
Dibutylamine	1.03[a,o]	−18.89[a,o]						2.38		
Di-isopropylamine	1.06[a,o]	−16.81[a,o]	−1.33		−2.39			2.36	2.893	0.53
Trimethylamine	1.03[a,o]	−12.60[a,o]	0.41		−0.62			2.35	1.620	−0.73
Triethylamine	1.05[a,p]	−16.64[a,p]	−1.58	−8.16	−1.58	8.48	33.7	2.36	3.077	0.72
Aniline	−1.23[j]	−12.87[i]	−2.83	−9.99	−1.60	2.88	15.0	4.03	3.923	−0.04

Table 1 (*continued*)

	Water^{a}		Hexadecane^{b}		Water → Hexadecane					
Solute	ΔG°_s	ΔH°_s	ΔG°_s	ΔH°_s	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}	log L_W	log L_H	log P_H
N,*N*-Dimethylaniline	0.82^{y}		−3.87	−11.56	−4.69			2.53	4.754	2.22
Pyridine	−0.42^{ee}	−11.93^{j}	−1.48	−7.80	−1.06	4.13	17.4	3.44	3.003	−0.44
2-Methylpyridine	−0.35^{ee}	−13.18^{j}	−2.07	−8.58	−1.72	4.60	21.2	3.39	3.437	0.05
3-Methylpyridine	−0.50^{ee}	−13.08^{j}	−2.30	−8.96	−1.80	4.12	19.9	3.50	3.603	0.10
4-Methylpyridine	−0.66^{ee}	−13.15^{j}	−2.28	−8.79	−1.62	4.36	20.1	3.61	3.593	−0.02
2-Ethylpyridine	−0.05^{ee}	−13.31^{em}	−2.70		−2.65			3.17	3.90	0.73
3-Ethylpyridine	−0.33^{ee}	−12.78^{em}	−3.01		−2.68			3.37	4.13	0.76
4-Ethylpyridine	−0.46^{ee}	−12.48^{em}	−3.03		−2.57			3.47	4.14	0.67
2,3-Dimethylpyridine	−0.55^{ee}	−13.79^{em}						3.53		
2,4-Dimethylpyridine	−0.59^{ee}	−14.51^{j}	−2.91		−2.32			3.56	4.05	0.49
2,5-Dimethylpyridine	−0.44^{ee}	−14.54^{j}	−2.91		−2.47			3.45	4.05	0.60
2,6-Dimethylpyridine	−0.32^{ee}	−14.81^{j}	−2.65		−2.33			3.37	3.86	0.49
3,4-Dimethylpyridine	−0.94^{ee}	−13.54^{em}	−3.33		−2.35			3.82	4.36	0.54
3,5-Dimethylpyridine	−0.56^{ee}	−14.46^{j}	−3.18		−2.62			3.54	4.25	0.71
4-*t*-Butylpyridine	−0.19^{j}	−13.83^{j}	−3.86		−3.67			3.27	4.75	1.48
Nitromethane	0.25^{er}	−8.54^{j}	0.04	−6.06	−0.21	2.48	9.0	2.95	1.892	−1.06
Nitroethane	0.56^{x}		−0.61		−1.17			2.72	2.367	−0.35
1-Nitropropane	0.93^{x}		−1.27		−2.20			2.45	2.85	0.40
1-Nitrobutane	1.18		−1.92		−3.10			2.27	3.33	1.06
1-Nitropentane	1.45^{w}		−2.59		−4.04			2.07	3.82	1.75
2-Nitropropane	1.14		−0.86		−2.00			2.30	2.550	0.25
Nitrobenzene	0.15^{x}	−11.60^{t}	−3.46	−10.91	−3.61	0.60	14.4	3.02	4.460	1.44
2-Nitrotoluene	0.68^{x}		−3.90		−4.58			2.63	4.78	2.15
3-Nitrotoluene	0.82		−4.16		−4.98			2.53	4.97	2.44
4-Nitrotoluene			−4.23						5.02	
Acetonitrile	0.38^{x}	−8.37^{t}	0.49	−4.56	0.11	3.81	12.4	2.85	1.560	−1.29
Propanonitrile	0.43^{x}	−9.48^{j}	−0.18		−0.61			2.82	2.050	−0.77
Butanonitrile	0.63^{x}	−10.15^{t}	−0.85		−1.48			2.67	2.540	−0.13
Pentanonitrile	0.75^{w}		−1.55		−2.30			2.58	3.057	0.48
Benzonitrile	0.16^{y}	−11.59^{t}	−2.84	−9.86	−3.00	1.73	15.9	3.01	4.004	0.99
Chloromethane	3.72	−5.53^{as}	1.03		−2.69			0.40	1.163	0.76
Chloroethane	3.64		0.33		−3.31			0.46	1.678	1.22
1-Chloropropane	3.94		−0.38		−4.32			0.24	2.202	1.96
1-Chlorobutane	4.11	−6.92^{at}	−1.09	−7.38	−5.20	−0.46	15.9	0.12	2.722	2.60
1-Chloropentane	4.21	−9.39^{at}	−1.78		−5.99			0.05	3.223	3.17
1-Chlorohexane	4.27	−8.86^{at}	−2.44		−6.71			0.00	3.71	3.71
1-Chloroheptane	4.56		−3.12		−7.68			−0.21	4.21	4.42
2-Chloropropane	4.03^{x}		−0.07		−4.10			0.18	1.970	1.79
2-Chlorobutane	4.27^{at}	−8.94^{at}						0.00		
1-Chloro-2-methylpropane			−0.88						2.566	
2-Chloro-2-methylpropane	5.36^{au}	−4.88^{av}	−0.41		−5.77			−0.80	2.217	3.02
2-Chloropentane	4.34^{x}							−0.05		
3-Chloropentane	4.31^{x}							−0.03		
Dichloromethane	2.96^{k,x,at}	−7.24^{at}	−0.14	−5.54	−3.10	1.70	16.1	0.96	2.019	1.06
Trichloromethane	3.20^{k,x,at}	−7.99^{f}	−0.76	−6.71	−3.96	1.28	17.6	0.79	2.480	1.69
Tetrachloromethane	4.35^{at}	−8.77^{at}	−1.23	−7.39	−5.58	1.38	23.3	−0.06	2.823	2.88
1,2-Dichloroethane	2.48^{at,aw}	−8.54^{av}	−0.89		−3.37			1.31	2.573	1.26
1,1-Dichloroethane	3.42^{k,x,aw}		−0.59		−4.01			0.62	2.350	1.73
1,1,1-Trichloroethane	4.08^{x,at,aw}		−1.05		−5.20			0.14	2.690	2.55
1,1,2-Trichloroethane	2.28^{x,at}		−1.87		−4.15			1.46	3.29	1.83
1,1,2,2-Tetrachloroethane	1.80^{at,aw}		−2.60		−4.48			1.81	3.826	2.02
1,1,1,2-Tetrachloroethane	2.99^{k}		−2.22		−5.21			0.94	3.55	2.61
Pentachloroethane	2.88^{k,x}							1.02		
Hexachloroethane	2.87^{x} 3.89^{k}									
1,2-Dichloropropane	3.01^{x,at}	−8.61^{at}	−1.27		−4.28			0.93	2.85	1.92
1,3-Dichloropropane	2.38^{x,at}	−7.78^{at}	−1.74		−4.12			1.39	3.194	1.80
1,4-Dichlorobutane	1.95^{at}	−6.22^{at}	−2.53		−4.48			1.70	3.775	2.08
Bromomethane	3.46	−6.10^{as}						0.60		
Bromoethane	3.54		−0.14		−3.68			0.54	2.020	1.48
1-Bromopropane	3.71		−0.95		−4.66			0.41	2.620	2.21
1-Bromobutane	3.87		−1.62		−5.49			0.29	3.105	2.82
1-Bromopentane	4.18		−2.31		−6.49			0.07	3.611	3.54
1-Bromohexane	4.45		−3.01		−7.46			−0.13	4.13	4.26
1-Bromoheptane	4.61		−3.66		−8.27			−0.25	4.60	4.85
1-Bromo-octane	4.79		−4.32		−9.11			−0.38	5.09	5.47
2-Bromopropane	3.79^{x}		−0.64		−4.43			0.35	2.391	2.04
2-Bromobutane			−1.38						2.933	
1-Bromo-2-methylpropane	4.24^{x}		−1.42		−5.66			0.02	2.961	2.94

Table 1 (*continued*)

Solute	Water[a] ΔG_s°	ΔH_s°	Hexadecane[b] ΔG_s°	ΔH_s°	Water → Hexadecane ΔG_{tr}°	ΔH_{tr}°	ΔS_{tr}°	log L_W	log L_H	log P_H
2-Bromo-2-methylpropane	5.12[au]	−6.07[au]	−0.95		−6.07			−0.62	2.616	3.24
Dibromomethane	2.31[x]		−1.27		−3.58			1.44	2.849	1.41
Tribromomethane	2.14[y]		−2.51		−4.65			1.56	3.747	2.19
1,2-Dibromoethane	1.94[x]		−2.01		−3.95			1.71	3.999	1.69
Iodomethane	3.37	−6.19[j]								
Iodoethane	3.54		−0.89		−4.43			0.54	2.573	2.04
1-Iodopropane	3.74		−1.65		−5.39			0.39	3.130	2.74
1-Iodobutane	4.03		−2.33		−6.36			0.18	3.628	3.45
1-Iodopentane	4.14		−3.01		−7.15			0.10	4.13	4.03
1-Iodohexane	4.35		−3.68		−8.03			−0.06	4.62	4.68
1-Iodoheptane	4.54		−4.32		−8.86			−0.20	5.09	5.29
Di-iodomethane	1.77[y]		−2.64	−9.31	−4.41			1.84	3.853	2.01
Fluoromethane	4.06[at]	−4.33[as]								
CCl_2FCClF_2	6.05[x]		−0.28		−6.33			−1.30	2.123	3.42
CF_3CHFBr (Tefluorane)	4.78[ax]		0.74		−4.04			−0.37	1.37	1.74
$CF_3CHClBr$ (Halothane)	4.13[ax]		−0.35		−4.51			0.08	2.177	2.10
CHF_2OCF_2CHFCl (Enfluorane)			0.36						1.653	
$CH_3OCF_2CHCl_2$ (Methoxyfluorane)	3.15[ax]		−1.29		−4.44			0.82	2.864	2.04
$CHF_2OCHClCF_3$ (Isofluorane)	4.37[ax]		0.47		−3.90			−0.07	1.576	1.65
$CF_3CH_2OCH{=}CH_2$ (Fluoroxene)	4.14[ax]		0.71		−3.43			0.10	1.40	1.30
Chloroethene	4.20[as]	−5.87[as]						0.05		
1,1-Dichloroethene	4.52[at]	−9.18[at]	−0.26		−4.78			−0.18	2.110	2.29
cis-1,2-Dichloroethene	3.57[ax]		−0.72		−4.29			0.51	2.450	1.94
trans-1,2-Dichloroethene	3.50[ax]		−0.59		−4.09			0.57	2.350	1.78
Trichloroethene	3.83[ax]	−9.23[at]	−1.47		−5.30			0.32	2.997	2.68
Tetrachloroethene	4.37[ax]	−9.41[at]	−2.27	−9.18	−6.64	0.23	23.0	−0.07	3.584	3.65
Allyl chloride	3.69[x]		−0.26		−3.95			0.42	2.109	1.69
Allyl bromide	3.42[y]		−0.80		−4.22			0.63	2.510	1.88
Allyl iodide			−1.49						3.01	
Benzyl chloride	2.35[y]	(3.47)[ay]	−3.23	(1.62)	−5.58	−1.85	12.5	1.41	4.290	2.88
Benzyl bromide	1.90[y]		−3.74		−5.64			1.74	4.66	2.92
Fluorobenzene	3.48[az]	−7.53[l]	−1.26	−7.42	−4.74	0.11	16.3	0.58	2.84	2.26
Chlorobenzene	3.13[k]	−10.40[av]	−2.35	−9.14	−5.48	1.26	22.6	0.84	3.640	2.80
2-Chlorotoluene	3.13[cl]		−3.06		−6.19			0.84	4.16	3.32
3-Chlorotoluene									4.16	
4-Chlorotoluene									4.19	
1,2-Dichlorobenzene	2.77[k]		−3.39		−6.16			1.10	4.405	3.30
1,3-Dichlorobenzene	3.14[k]		−3.37		−6.51			0.83	4.39	3.56
1,4-Dichlorobenzene	2.95[k,x]		−3.38		−6.33			0.97	4.40	3.43
Bromobenzene	2.81[k]		−2.89		−5.80			1.07	4.035	2.97
2-Bromotoluene			−3.55						4.52	
3-Bromotoluene			−3.57						4.54	
4-Bromotoluene	2.88[x]		−3.57		−6.45			1.02	4.54	3.52
Iodobenzene	2.53[k]		−3.63		−6.16			1.28	4.58	3.30
Methanethiol[be]	2.91	−6.16						1.00		
Ethanethiol[be]	3.13	−6.80	−0.34		−3.47			0.84	2.173	1.34
Propanethiol[be]	3.21	−7.10	−1.04		−4.25			0.78	2.685	1.91
Butanethiol[be]	3.27	−7.58	−1.31		−4.58			0.73	2.880	2.15
Dimethyl sulphide[be]	2.72	−7.49	−0.43		−3.15			0.63	2.238	1.61
Diethyl sulphide[be]	2.81	−8.87	−1.62		−4.43			1.07	3.104	2.03
Dipropyl sulphide[be]	2.99	−7.58	−3.00		−5.99			0.94	4.120	3.18
Di-isopropyl sulphide[be]	3.06	−9.56	−2.29		−5.35			0.89	3.600	2.71
Dimethyl disulphide[be]	2.43	−7.58	−2.22		−4.65			1.35	3.549	2.20
Diethyl disulphide[be]	2.63	−7.36	−3.12		−5.75			1.20	4.210	3.01
Thiophene[be]	2.85	−7.15	−1.40	−7.15	−4.25	0.00	14.3	1.04	2.943	1.90
2-Methylthiophene[be]	2.90	−7.55	−1.89		−4.79			1.01	3.302	2.30
Thiophenol	1.72[x]		−3.00		−4.72			1.87	4.118	2.25

[a] Values of ΔG_s° and ΔH_s°, in kcal mol^{-1} mole fraction scale, for gaseous solutes taken from refs. 8 and 9 unless shown otherwise [b] This work, or from ref. 4, unless shown otherwise. [c] M. H. Abraham and E. Matteoli, unpublished survey. [d] S. F. Dec and S. J Gill, *J. Solution Chem.*, 1984, **13**, 27. [e] Note that van't Hoff enthalpies from A. Kuantes and G. W. A. Rijinders in 'Gas Chromatography 1958,' ed D. H. Desty, Butterworths, London, 1958, are −5.95 and −6.87, respectively. [f] From data given by M. H. Abraham, P. L. Grellier, and R. A McGill, *J Chem Soc., Perkin Trans. 2*, 1987, 797. [g] Value for solution in dodecane by the van't Hoff method. Data from A. Sahgad, H. M. La, and W. Hayduk, *Can. J. Chem. Eng.*, 1978, **56**, 354. [h] By the van't Hoff method, P. J. Lin and J. F. Parcher, *J. Chromatogr. Sci*, 1982, **20**, 33 [i] By the van't Hoff method, data from Y. Migano and W. Hayduk, *Can. J. Chem. Eng.*, 1981, **59**, 746. [j] Ref. 7. [k] Ref. 10. [l] G. L. Amidon and S. T. Anik, *J. Chem. Eng. Data*, 1981, **26**, 28. [m] J. W. Owens, S P. Wasik, and H. De Voe, *J. Chem. Eng. Data*, 1986, **31**, 47. [n] I. Sanemasa, M. Araki, T. Deguchi, and H. Nagai, *Bull. Chem. Soc. Jpn*, 1982, **55**, 1054. [o] R. D. Wauchope and R. Haque, *Can. J. Chem*, 1972, **50**, 133. [p] Data from ref. 8 slightly adjusted using more recent ΔH_v° values from V. Majer and V. Svoboda, 'Enthalpies of Vaporization of Organic Compounds,' Blackwell, Oxford, 1985 [q] Estimated

Table 1 (*continued*)

value, this work. [r] Estimated value by J. P. Guthrie and P. A. Cullimore, *Can. J. Chem.*, 1979, 57, 240. [s] K. R. Brower, J. Peslak, and J. Elrod, *J. Phys. Chem.*, 1969, 73, 207. [t] This work. [u] C. J. Marsh and R. C. Pemberton, *National Physical Laboratory, Report Chem. III*, 1980. [v] R. G. Buttery, L. C. Ling, and D. G. Guadagni, *J. Agric. Food Chem.*, 1969, 17, 385. These values are for the unhydrated aldehydes, see ref. in footnote *u*. [w] J. E. Amoure and R. G. Buttery, *Chem. Senses Flavour*, 1978, 3, 57. [x] Ref. 6. [y] From liquid solubilities and vapour pressures as calculated in this work. [z] Isobutyl is 2-methylpropyl, isoamyl is 3-methylbutyl; isobutyrate is 2-methylpropanoate. [aa] Calculated from vapour–liquid equilibria. [ab] Enthalpy of solution of the pure liquid from B. C. Cox, A. J. Parker, and W. E. Waghorne, *J. Am. Chem. Soc.*, 1973, 95, 1010. [ac] Parameters for the vaporisation of pure water. [ad] Value from ref. 2. Other values that may be calculated are 2.17 from S. D. Christian, R. French, and K. O. Yeo, *J. Phys. Chem.*, 1973, 74, 813, and 2.27 from P. Schatzberg, *J. Phys. Chem.*, 1963, 67, 776. [ae] H. Saito and K. Shinoda, *J. Colloid Interfac. Chem.*, 1970, 32, 647. [af] J. H. Rytting, L. P. Huston, and T. Higuchi, *J. Pharm. Sci.*, 1978, 67, 615. [ag] K. Bocek, *J. Chromatogr.*, 1979, 162, 209. [ah] M. F. Abd-El-Bary, M. F. Hamoda, S. Tanisho, and N. Wakao, *J. Chem. Eng. Data*, 1986, 31, 229. [ai] G. H. Parsons, C. H. Rochester, and C. E. Wood, *J. Chem. Soc., Perkin Trans. 2*, 1972, 136. [aj] Calculated from the known partition coefficient and log L_H values. [ak] K. Schoene and J. Steinhanses, *Fresenius Z. Anal. Chem.*, 1985, 321, 538. The ΔH° value is by the van't Hoff method. [al] J. A. V. Butler and C. N. Ramchandani, *J. Chem. Soc.*, 1935, 952. [am] Average of values from ref. in footnote *w* (−1.88) and calculated from partition coefficients of R. Aveyard and R. W. Mitchell, *Trans. Faraday Soc.*, 1970, **66**, 37, corrected in this work for dimerization in hexadecane (−1.92). [an] From partition coefficients, see ref. in footnote *am*. [ao] E. M. Arnett and F. M. Jones, *Prog. Phys. Org. Chem.*, 1974, 11, 263. [ap] M. H. Abraham and A. Nasehzadeh, *J. Chem. Thermodyn.*, 1981, 13, 549. [aq] R. J. L. Andon, J. D. Cox, and E. F. G. Herington, *J. Chem. Soc.*, 1954, 3118. [ar] J. H. Park, A. Hussam, P. Couasnon, D. Fritz, and P. W. Carr, *Anal. Chem.*, 1987, 59, 1970. [as] E. Wilhelm, R. Battino, and R. J. Wilcock, *Chem. Rev.*, 1977, 77, 219. [at] D. L. Leighton and J. M. Cole, *J. Chem. Eng. Data*, 1981, 26, 382. [au] M. H. Abraham, P. L. Grellier, A. Nasehzadeh, and R. A. C. Walker, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1717. [av] From ΔH°_s (liq) by J. W. Larsen and L. Magid, *J. Phys. Chem.*, 1974, 78, 834, and R. de Lisi, M. Goffredi, and V. T. Liveri, *J. Chem. Soc., Faraday Trans. 1*, 1980, 1660, together with ΔH°_v. [aw] R. S. Barr and D. M. T. Newshan, *Fluid Phase Eq.*, 1987, 35, 189. [ax] M. H. Abraham, M. J. Kamlet, R. W. Taft, R. M. Doherty, and P. K. Weathersby, *J. Med. Chem.*, 1985, **28**, 865. [ay] This is ΔH°_s (liq) from R. Ohnishi and K. Tanabe, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2647, by the van't Hoff method. Our own listed value for ΔH°_s in hexadecane is also for the liquid solute. [az] P. Bernal, S. D. Christian, and E. E. Tucker, *J. Solution Chem.*, 1986, 15, 947. [ba] A. Przyjazny, W. Janicki, W. Chrzanowski, and R. Staszewski, *J. Chromatogr.*, 1983, **280**, 249.

ception of methanol (3A), nitromethane (3A), and water. ΔH°_s values were independent of concentration in the measurement range.

Discussion

Most of the gas solubility data in water were taken from key references,[6–8] two of which [7,8] include values for the enthalpy of solution in water. The L_H values used were mostly those we have determined either previously[4] or in this work, but we also calculated a number of values using literature data for closely related solvents such as squalane,[15–17] $C_{87}H_{176}$,[18,19] octacosane,[20] and heptadecane.[21] In Table 1 are collected values of log L_W and log L_H, together with the calculated log P_H values, *via* equation (1). The log P_H values all refer to the molar concentration scale, as is usual for partition coefficients. We have, where necessary, recalculated gas solubilities using standard states of 1 atm (gas) and unit mole fraction (solution), so that the ΔG°_{tr} values in Table 1 refer to the mole fraction concentration scale, a more appropriate scale when calorimetrically determined enthalpies of solution are involved. Our enthalpies of solution of liquid solutes were converted into ΔH°_s values for gaseous solutes, using enthalpies of vaporization at 298 K, care being taken to ensure that the same ΔH°_v values were used for solution into water and hexadecane. The observed ΔH°_s values, and the deduced ΔH°_{tr} and ΔS°_{tr} are collected in Table 1. Additional log P_H values are given in Table 2.

The expected error in the log L_H values is very small, probably no more than 0.03 log unit, However, there are substantial differences in recorded values for log L_W, even for moderately volatile solutes. Thus for halogenated alkanes, the log L_W values given by Hine and Mookerjee[6] and by Mackay and Shiu[10] differ randomly by *ca.* 0.1 log unit, and for hexachloroethane the two recorded values differ by a full log unit (2.87 and 3.89, respectively). Enthalpies of solution, although in the best instances* capable of leading to ΔH°_{tr} values with an error of only some 0.05 kcal mol^{-1}, can also be subject to very large errors. We can suggest that the expected error in ΔG°_{tr} will be *ca.* 0.2 kcal mol^{-1}, that in ΔH°_{tr} around 0.5 kcal mol^{-1}, and that in ΔS°_{tr} *ca.* 2 cal K^{-1} mol^{-1}. However, occasionally much larger experimental errors may arise, and this should be borne in mind when results are discussed. We note that the thermodynamics of transfer from water to hexadecane are very similar to those for transfer to 2,2,4-trimethylpentane, as found by Tomlinson *et al.*[12] A comparison for a number of solutes is in Table 3. Within any reasonable error, it seems as though ΔH°_{tr} values are identical for the two transfers, and that ΔG°_{tr} values average at about the same, with rather more random variation. It seems that without introducing too much error, values of ΔH°_{tr} and ΔG°_{tr} for transfer to 2,2,4-trimethylpentane, Table 3, could be taken as those for transfer to hexadecane.

Tomlinson *et al.*[12] examined the possibility of enthalpy–entropy correlations for transfer to 2,2,4-trimethylpentane through the statistically correct method of plotting ΔG°_{tr} *vs.* ΔH°_{tr}. They found that there was no general correlation between ΔG°_{tr} and ΔH°_{tr}, although linear relationships were observed for various homologous series. Using a more extended data set, we can confirm the findings of Tomlinson *et al.*[12] Aliphatic series such as the alkanes, ketones, and alcohols form separate linear plots. However, aromatic or halogeno-substituted compounds always lie off the plots for the unsubstituted series. This rather complicated enthalpy–Gibbs energy interplay is hardly surprising in view of the varied solute–solvent interactions that are possible.

One method for the examination of solute–solvent interactions is that of multiple linear regression analysis, especially as developed by Abraham, Doherty, Kamlet, Taft, and their coworkers.[22–25] The solubility of a gaseous solute in a solvent is regarded as being made up of an endoergic cavity term, that arises through breaking of solvent–solvent interactions, together with a number of exoergic terms that arise through different solute–solvent interactions. For a number of solutes in a given solvent phase, equations (2) and (3) are valid.[22–25]

$$SP = c + d\delta_2 + s\pi^*_2 + a\alpha_2 + b\beta_2 + vV_2 \qquad (2)$$

$$SP = c + d\delta_2 + s\pi^*_2 + a\alpha_2 + b\beta_2 + l\log L_H \qquad (3)$$

Equation (2) is recommended for processes within condensed phases, such as the water–hexadecane partition coefficients we

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* These are nearly always with calorimetrically determined enthalpies of solution of liquid solutes that dissolve readily in water and hexadecane and are not subject to extensive self-association. Note that any error in ΔH°_v cancels out. 1 kcal = 4.184 kJ.

Table 2. Directly determined log $P_{\rm H}$ values for compounds not in Table 1.[a]

Solute	$\Delta G^{\circ}_{\rm tr}$/kcal mol^{-1}	log $P_{\rm H}$	Ref.
Butane-1,4-diol	4.30	−4.37	2
Hexane-1,6-diol	2.80	−3.27	2
Formamide	5.31	−5.10	2
Acetamide	4.73	−4.68	2
Butyramide	3.05	−3.44	2
Isobutyramide	3.03	−3.43	2
Urea	5.79	−5.46	2
4-Pentylpyridine	−5.26	2.64	*b*
4-Hexylpyridine	−6.12	3.27	*b*
4-Heptylpyridine	−7.00	3.92	*b*
4-Octylpyridine	−7.89	4.57	*b*
4-Nonylpyridine	−8.76	5.21	*b*
4-Decylpyridine	−9.62	5.84	*b*
Paraldehyde	−1.98	0.24	3
2-Chlorophenol	(−1.52) −1.45	−0.15	*c*
4-Chlorophenol	(−0.70) −0.63	−0.75	*c*
4-Chloro-3-methylphenol	(−2.14) −2.07	0.31	*c*
2-Iodophenol	(−2.28) −2.21	0.41	*c*
o-Toluidine	−2.17	0.38	*d*
p-Toluidine	−2.14	0.36	*d*
2-Methoxyaniline	−2.10	0.33	*d*
4-Methoxyaniline	−0.92	−0.54	*d*
2-Chloroaniline	−3.11	1.07	*d*
3-Chloroaniline	−2.53	0.64	*d*
4-Chloroaniline	−2.42	0.56	*d*
2-Nitroaniline	−1.95	0.22	*e*
Acetophenone	−3.18	1.12[g]	*f*
4-Methoxyacetophenone	−2.88	0.90	*f*
3-Methylacetophenone	−4.00	1.72	*f*
4-Methylacetophenone	−3.88	1.63	*f*
4-Fluoroacetophenone	−3.29	1.20	*f*
3-Chloroacetophenone	−4.40	2.01	*f*
4-Chloroacetophenone	−3.89	1.85	*f*
3-Trifluoromethylacetophenone	−4.49	2.08	*f*
3-Nitroacetophenone	−2.38	0.53	*f*
4-Nitroacetophenone	−2.59	0.69	*f*
Biphenyl	−7.37	4.19	5

[a] Values of log $P_{\rm H}$ on the molar scale and $\Delta G^{\circ}_{\rm tr}$ on the mol fraction scale as in Table 1. [b] K. C. Yeh and W. I. Higuchi, *J. Pharm. Sci.*, 1976, 65, 82. [c] Parenthesised values are for transfer to dodecane, from D. E. Burton, K. Clarke, and G. W. Gray, *J. Chem. Soc.*, 1964, 1314. The listed values for $\Delta G^{\circ}_{\rm tr}$ and log P have been slightly adjusted to correspond to transfer to hexadecane, by comparison for phenols for which both transfers are known. [d] W. Kemula, H. Buchowski, and W. Pawlowski, *Rocz. Chem.*, 1968, 48, 1951. [e] W. Kemula, H. Buchowski, and J. Terepat, *Bull. Acad. Sci. Polon.*, 1961, 9, 595. [f] Values for transfer to dodecane, from J. Toullec, M. El-Alaoui, and P. Kleffert, *J. Org. Chem.*, 48, 4808. [g] Note the same value (Table 1) for transfer to hexadecane.

wish to analyse. We shall therefore consider only equation (2) and not equation (3), preferred for gas–solvent partition coefficients. In equation (2), δ_2 is a solute polarisability correction term taken as zero except for polyhalogeno aliphatics (0.5) and aromatics (1.0), π^*_2 is the solute dipolarity, α_2 the solute hydrogen-bond acidity, β_2 the solute hydrogen-bond basicity, and V_2 is the solute volume. The constants *c*, *d*, *s*, *a*, *b*, and *v* are found by multiple linear regression analysis, and can be used to deduce the factors that are important in the particular process. If we consider specifically the water–hexadecane partition, with SP = log $P_{\rm H}$ as defined *via* equation (1), then the values of the *s*-constant will depend on the differences in dipolarity between water and hexadecane; a negative *s*-constant will indicate that water is more dipolar than hexadecane and hence more able to undergo solvent–solute dipole–dipole interactions. In a similar vein, the *a*-constant will reflect the hydrogen-bond basicity of water, that is its ability to hydrogen bond with solutes that are hydrogen-bond acids (hexadecane cannot), whilst the *b*-constant will reflect the hydrogen-bond acidity of water. The vV_2 term covers cavity effects, the larger the solute the more solvent–solvent interactions must be broken to make a suitably sized cavity. Hence the *v*-constant should provide an assessment of the difference in cavity effects between water and hexadecane.

In equation (2), the solute explanatory variables were taken as follows: δ_2 defined as above; π^*_2 as listed before;[22–25] α_2 as $\alpha^{\rm H}_2$, the new solute hydrogen-bond acidity parameter;[26] β_2 as $\beta^{\rm H}_2$, the new solute hydrogen-bond basicity parameter,[27,28] supplemented by a few recently determined[29] 'effective' or 'summation' $\beta^{\rm H}_2$ values for multifunctional bases; V_2 as McGowan's intrinsic volume V_x.[30] The equation that we use to correlate log $P_{\rm H}$ and also the thermodynamic functions of transfer is therefore as follows, where V_x is in units of (cm^3 mol^{-1})/100.

$$\mathrm{SP} = c + d\delta_2 + s\pi^*_2 + a\alpha^{\rm H}_2 + b\beta^{\rm H}_2 + vV_x \qquad (4)$$

If we include all of the data of Tomlinson *et al.*[12] in Table 3, as well as our calculated values in Tables 1 and 2, we have 270 compounds for which we have all the required explanatory variables. Details of the regression equations are in Table 4, where *n* is the number of solutes, *r* the overall correlation coefficient, and sd the standard deviation. Bearing in mind the probable average experimental error in log $P_{\rm H}$ of about 0.1, and also the experimental errors in the various explanatory variables, an overall standard deviation of *ca.* 0.2 log units is as good as can be expected. Thus the regression equation for 270 compounds, with $r = 0.9884$ and sd = 0.28, is quite acceptable. The constants in equation (4) are all chemically reasonable, with *s*, *a*, and *b* all being very negative, and *v* being very positive. Thus solute dipolarity, hydrogen-bond acidity, and hydrogen-bond basicity, all lead to a preference for water, whereas solute volume leads to a preference for hexadecane. As mentioned in the introduction, we were interested in results for aliphatic compounds and aromatic compounds taken separately; details of the found regressions are also in Table 4. A comparison of the 'aliphatics only' with the 'aromatics only' regression does suggest that there are small, but possibly significant differences, with the constants *a*, *b*, and *v* all being numerically smaller for the aromatic regression. Interestingly, Kamlet and co-workers[31,32] found that for aqueous solubility of liquids and solids, different regression equations were required for aliphatic and aromatic compounds,[31] but for water–octanol partition coefficients (log $P_{\rm OCT}$)[32] the same regression equation could accommodate both types of solutes [equation (5)].

$$\log P_{\rm OCT} = 0.35 + 0.36\,\delta_2 - 1.04\,\pi^*_2 + 0.10\,\alpha_{\rm m} - 3.84\,\beta_{\rm m} + 5.35\,V_{\rm I} \qquad (5)$$

Because equation (5) is cast in terms of $\alpha_{\rm m}$ and $\beta_{\rm m}$ (related to $\alpha^{\rm H}_2$ and $\beta^{\rm H}_2$ but not entirely equivalent) and also of Leahy's intrinsic volume, $V_{\rm I}$,[33] we felt it useful to examine log $P_{\rm OCT}$ for the set of solutes assembled in Tables 1–3 using equation (4). The results are in Table 5. The *v*-constant in Table 5 is much smaller than in equation (5), but this is to be expected since $V_x/V_{\rm I}$ is only *ca.* 0.68.[30] The other constants in Table 5 are all reasonably consistent with those in equation (5), and, as found by Kamlet and co-workers,[32] there is little difference between aliphatic and aromatic solutes.

It is instructive to compare the constants in equation (4) for water–hexadecane with water–octanol, for the 'all solutes' correlations

	c	*d*	*s*	*a*	*b*	*v*
water–hexadecane	0.26	0.51	−1.45	−3.92	−5.21	4.32
water–octanol	0.20	0.49	−1.24	−0.28	−3.32	3.85

Table 3. Comparison of thermodynamics of transfer from water to hexadecane and to 2,2,4-trimethylpentane, molar scale at 298 K

Solute	Hexadecane[a]			2,2,4-Trimethylpentane[11,12]		
	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}
Butanone	0.59	4.58	13	0.25	4.54	14
Ethanol	2.99	8.68	19	2.72	8.36	19
Hexan-1-ol	−0.52	6.77	24	−0.74	6.57	24
Aniline	0.05	2.68	9	0.28	3.25	10
Nitrobenzene	−1.96	0.69	9	−1.95	0.67	9
Methyl benzoate	−2.03	0.88	10	−2.49	0.82	11
Phenol	1.01			1.31	4.64	11
p-Cresol	0.26			0.54	4.51	13
4-Chlorophenol	1.02			0.66	4.11	12
3-Methoxyphenol				1.48	4.46	10
4-Methylaniline				−0.46	3.53	13
4-Chloroaniline				−0.65	2.46	10
N-Methylaniline				−1.41	2.52	13
Methyl phenyl sulphone				1.25	3.21	7
Methyl phenyl sulphoxide				2.03	5.60	12
Ethyl benzoate				−2.76	0.74	12
Benzyl alcohol	0.29	5.87	19	1.04	6.15	17
2-Phenylethanol				0.49	6.03	19
3-Phenylpropan-1-ol				−0.25	6.41	22
Acetophenone	−1.53	1.32	10	−1.52	2.11	12
Benzaldehyde	−1.41	0.95	8	−1.43	0.99	8
Anisole	−2.90	0.00	10	−2.76	0.00	9
Pyridine	0.60	4.13	12	0.56	4.08	12

[a] From Tables 1 and 2, after conversion into the molar scale.

Table 4. Regression analysis of water–hexadecane partition coefficients, using equation (4).[a]

Solute set	*c*	*d*	*s*	*a*	*b*	*v*	*n*	*r*	sd
All solutes	0.26 ± 0.06	0.51 ± 0.05	−1.45 ± 0.09	−3.92 ± 0.11	−5.21 ± 0.09	4.32 ± 0.06	270	0.9884	0.28
Aliphatics only	0.27 ± 0.07	0.48 ± 0.17	−1.45 ± 0.10	−4.11 ± 0.14	−5.39 ± 0.13	4.39 ± 0.07	203	0.9890	0.28
Aromatics only	0.94 ± 0.19	—	−1.31 ± 0.17	−3.65 ± 0.13	−4.74 ± 0.17	3.85 ± 0.16	67	0.9913	0.21

[a] Compounds listed in Tables 1–3, with log P_H on the molar scale.

Table 5. Regression analysis of water–octanol partition coefficients,[a] using equation (4).

Solute set	*c*	*d*	*s*	*a*	*b*	*v*	*n*	*r*	sd
All solutes	0.20 ± 0.06	0.49 ± 0.04	−1.24 ± 0.08	−0.28 ± 0.08	−3.32 ± 0.08	3.85 ± 0.06	307	0.9790	0.26
Aliphatic only	0.28 ± 0.06	0.24 ± 0.15	−1.28 ± 0.09	−0.48 ± 0.13	−3.42 ± 0.11	3.84 ± 0.06	215	0.9740	0.27
Aromatic only	0.53 ± 0.17	—	−0.91 ± 0.15	−0.17 ± 0.09	−3.30 ± 0.14	3.74 ± 0.14	92	0.9782	0.22

[a] Compounds listed in Tables 1–3, with log P_{OCT} on the molar scale

The most striking features of the two sets of constants are (i) the dipolarity of wet octanol is surprisingly small, with *s* (octanol) almost as negative as *s* (hexadecane); (ii) the basicity of wet octanol must be almost the same as that of water, since *a* (octanol) is only −0.28 as compared with *a* (hexadecane) of −3.92; (iii) the hydrogen-bond acidity of wet octanol is appreciably less than that of water: *cf.* *b* (hexadecane) = −5.21, *b* (octanol) = −3.21; and (iv) the cavity effect (or probably a combined cavity effect plus dispersion interactions) for wet octanol is not far away from that for hexadecane. Obviously, results on more water–solvent partitions are needed to quantify these effects, but already it can be seen that equation (4) will yield information about various solute–solvent interactions.

Having now to hand not only values of log P_H (equivalent to ΔG°_{tr} on the molar scale) but also ΔH°_{tr}, we can now set out ΔG°_{tr}, ΔH°_{tr}, and ΔS°_{tr} on the mole fraction scale, Table 1, and regress a unified set of transfer parameters for the same solutes. We have 86 such solutes for which the required explanatory variables are known, and summarise results of the regressions in Table 6 The constants in the ΔG°_{tr} regression (other than *c*) then yield the log P_H constants on division by −1.364; there is reasonable agreement between the 86 solute correlation in Table 6 and the 270 solute correlation in Table 4 The sd values in Table 6 are roughly as expected for correlations of ΔH°_{tr} (±0.5 kcal mol^{-1}) and ΔS°_{tr} (±2 kcal K^{-1} mol^{-1}), being 0.94 kcal mol^{-1} and 2.7 cal K^{-1} mol^{-1} respectively.

There are a number of extraordinary features of the results given in Table 6; it is useful to take the main parameters in turn. The *s*-constants, viewed as dipolarity effects, are almost impossible to interpret. Whereas an increase in solute dipolarity (π_2^*) reduces transfer to hexadecane in terms of ΔG°_{tr} or log P_H, it actually aids transfer in terms of ΔH°_{tr}. One difficulty here is that the π_2^* parameter involves not only dipolarity, but also polarisability effects; furthermore, there is an interplay between δ_2, the polarisability correction term, and π_2^* The solute hydrogen-bond acidity term, $a\alpha_2^H$, can be plausibly interpreted

Table 6. Regression analysis of ΔG°_{tr}, ΔH°_{tr}, and ΔS°_{tr} for the water–hexadecane partition, mole fraction scale at 298 K [a]

Parameter	*c*	*d*	*s*	*a*	*b*	*l*	*n*	*r*	sd
ΔG°_{tr}	-1.90 ± 0.11	-0.69 ± 0.12	1.63 ± 0.23	5.44 ± 0.23	7.06 ± 0.25	-5.78 ± 0.15	86	0.9896	0.35
ΔH°_{tr}	2.81 ± 0.30	-1.73 ± 0.33	-2.08 ± 0.60	8.11 ± 0.62	10.05 ± 0.67	-2.43 ± 0.41	86	0.9451	0.94
ΔS°_{tr}	15.80 ± 0.88	-3.55 ± 0.95	-12.84 ± 1.74	9.23 ± 1.80	10.34 ± 1.95	11.28 ± 1.19	86	0.8766	2.73
$-T\Delta S^\circ_{tr}$ [b]	-4.71	1.06	3.83	-2.75	-3.08	-3.36			

[a] Values from Tables 1 and 3, ΔG°_{tr} and ΔH°_{tr} in kcal mol^{-1}; ΔS°_{tr} in cal K^{-1} mol^{-1}. [b] Calculated from the constants in the ΔS°_{tr} regression. The values do not quite yield the $\Delta H^\circ_{tr} - \Delta G^\circ_{tr}$ constants due to rounding-off errors.

as follows. Hydrogen-bonding from the solute acid to water base will be exothermic, and hence ΔH°_{tr} will be positive (as observed). But the creation of hydrogen bonds will be somewhat disfavoured in terms of entropy, leading to a positive ΔS°_{tr} value and to a ΔG°_{tr} value that is still positive, but less so than ΔH°_{tr}. An exactly similar argument can account for the positive *b*-constants in ΔG°_{tr}, ΔH°_{tr}, and ΔS°_{tr}. The breakdown of the vV_x 'cavity' term into enthalpic and entropic contributions is especially interesting in that any so-called 'hydrophobic effect' must reside in this vV_x term. Now on the scaled particle theory (SPT),[34] the free energy of cavity formation in water, G^{W}_{cav}, is much more positive than the corresponding value in a solvent such as hexadecane, G^{H}_{cav}. Hence $G^{H}_{cav} - G^{W}_{cav}$ is negative and will correspondingly contribute a negative quantity to ΔG°_{tr}. But the enthalpy of cavity formation in water is smaller than in solvents such as hexadecane, so that $H^{H}_{cav} - H^{W}_{cav}$ is actually positive.[35] We suggest that the vV_2 term in equation (2) and the vV_x term in equation (4) include not only cavity effects, but general dispersion interactions as well. These will always be more exoergic and exothermic in hexadecane than in water (note that water has a particularly low refractive index and molar refraction). Hence a combination of an exoergic interaction transfer with an exoergic cavity transfer will lead to a very negative vV_x term in ΔG°_{tr}. But combination of an exothermic interaction transfer with an endothermic cavity transfer can result in a vV_x term that is still negative, but not greatly so. This is exactly as observed, Table 6.

Our thermodynamic analysis thus reveals that the $s\pi^*_2$ term in equation (2) and equation (4) cannot easily be interpreted on its own, not even in conjunction with the correction term $d\delta_2$. The hydrogen-bond terms, however, seem to be quite straightforward, but the so-called cavity term vV_x (or vV_2) must include not only cavity effects but also general dispersion interactions as well. Our analysis also shows that because of the rather complicated interplay of the coefficients in the Gibbs energy and enthalpy of transfer, no simple relationship between ΔG°_{tr} and ΔH°_{tr} across families of solutes is expected. This is in agreement with the findings of Tomlinson *et al.*[12] and also our own observations.

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This paper is dedicated to the memory of Mortimer J. Kamlet.

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Our main preliminary aim, however, was to examine our LSER equations in order to see if parameters such as δ_2 or π^*_2 could be replaced by more suitable ones. In order to do this, it is necessary to examine data for a large number and wide variety of solutes. Gas liquid chromatography (GLC) is the obvious process to examine, since retention volumes or retention times can be used as the dependent variable SP (as log SP). We therefore analysed three sets of data, (1) the data of Laffort for 240 solutes on five stationary phases, (2) a selection of data for a variety of solutes on amide stationary phases, and (3) the extensive data of McReynolds on up to 367 solutes on 77 phases. We were able to develop a new solute parameter, R_2, to replace δ_2 in the general LSER equations. We define R_2 as an excess molar refraction of a solute over the molar refraction of an alkane of the same characteristic volume V_X. Hence our modified LSER equation is ±

$$\log SP = c + r.R_2 + s.\pi^*_2 + a.\alpha^H_2 + b.\beta^H_2 + l.\log L^{16} \qquad [9]$$

± Note that in Parts 13 and 14 we use SP instead of log SP.

Hydrogen Bonding. Part 13.† A New Method for the Characterisation of GLC Stationary Phases—The Laffort Data Set

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A number of equations for the correlation of retention data for a series of solutes on a given stationary phase (or solvent) have been investigated with the aim of characterising stationary phases. The two most successful equations are,

$$\mathrm{SP} = c + d\delta_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l \log L^{16} \qquad (a)$$

$$\mathrm{SP} = c + rR_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l \log L^{16} \qquad (b)$$

In the present case the dependent variable SP is $\log L - \log L^{\mathrm{Decane}}$ and the explanatory variables are solute parameters as follows: δ_2 is an empirical polarisability correction term, R_2 is a polarisability parameter that reflects the ability of a solute to interact with a solvent through π and n electron pairs, α_2^H is the solute hydrogen-bond acidity, β_2^H is the solute hydrogen-bond basicity, π_2^* is the solute dipolarity/polarisability, and L^{16} is the Ostwald solubility coefficient of the solute on n-hexadecane at 298 K. The constants c, r, s, a, b, and l in the more useful equation (b) are found by the method of multiple linear regression analysis, and serve to characterise a solvent phase in terms of specific solute/solvent interactions. Application of equation (b) to the five stationary phases examined by Laffort *et al.* shows that the magnitude of these constants is in accord with general chemical principles, and that the present procedure constitutes a new, general method for the characterisation of gas chromatographic stationary phases.

The most widely used method for the classification of stationary phases in gas-liquid chromatography (GLC), is that due to Rohrschneider,[1] either as such, or as subsequently modified by McReynolds.[2] Retention data of solutes are first expressed as Kovats retention indices[3] calculated according to equation (1):

$$I^i = 100\left(\frac{\log \tau^i - \log \tau^m}{\log \tau^{m+1} - \log \tau^m}\right) + 100m \qquad (1)$$

Here, I^i is the retention index of solute i on a given stationary phase at a given temperature, τ^i is the adjusted retention time of solute i, and τ^{m+1} and τ^m are the adjusted retention times of n-alkanes of carbon number $m + 1$ and m, respectivey. Rohrschneider[1] determined values of I^i for the selected solutes benzene, ethanol, butanone, nitromethane, and pyridine, on squalane (SQ), and on a stationary phase to be investigated (P), and defined a differential set of I^i values through equation (2),

$$\Delta I^i = I_P^{\,i} - I_{SQ}^{\,i} \qquad (2)$$

Then five 'Rohrschneider constants,' x, y, z, u, and s, one for each of the selected solutes, can be used to characterise the stationary phase, P, according to equation (3), illustrated for the selected solute benzene

$$x = \Delta I^{\mathrm{benzene}}/100 \qquad (3)$$

An 'overall' stationary phase polarity can also be obtained as the sum of the ΔI^i values for the five test solutes.

McReynolds[2] suggested the use of ten test solutes, rather than five, these being benzene (x'), butan-1-ol (y'), pentan-2-one (z'), nitropropane (u'), pyridine (s'), 2-methylpentan-2-ol (h'), 1-iodobutane (j'), oct-2-yne (k'), dioxane (l'), and *cis*-hydrindane (m'). Later workers tended to reduce the number of McReynolds test solutes, for example to the first five solutes.[4] An overall stationary phase polarity can again be calculated as the sum of ΔI^i values ($i = x', y', z', u'$, and s'); for an account of work in this area, the comprehensive review of Budahegyi *et al.*[5] is available.

However, although the Rohrschneider–McReynolds method is the basis of most approaches to the classification of stationary phases, quite recently Poole *et al.*[6] have severely criticised the method on a number of technical and theoretical grounds. Their main technical objection is that alkanes (necessary for the determination of I values) are sorbed onto polar stationary phases mainly by interfacial adsorption, rather than by true gas-liquid partitioning. If the I_P values are incorrect, then the whole procedure is invalid (for polar phases). A theoretical objection is that the 'overall' polarity, defined as above cannot be a true measure of polarity, since it depends principally on the solubility of the n-alkanes in the stationary phase.[6]

There are other difficulties over the Rohrschneider–McReynolds method Firstly, the method is entirely restricted to GLC retention data, so that there is no possibility of

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† Part 12 M. H Abraham, G. S. Whiting, Y Alarie, J. J. Morris, P J Taylor, R M. Doherty, R. W Taft, and G O. Nielsen, *QSAR*, 1990, 9, 6

Table 1. Some values of the gas ⟶ solvent methylene increment, $\Delta G_s^\circ(CH_2)$, in kcal mol^{-1} at 298 K [a]

Solvent	$\Delta G_s^\circ(CH_2)$	Solvent	$\Delta G_s^\circ(CH_2)$
Cyclohexane	−0.76	Propanone	−0.62
Hexadecane	−0.74	Ethanol	−0.61
Decane	−0.74	Dimethylformamide	−0.60
Hexane	−0.74	*N*-Methylpyrrolidi-2-none	−0.56
Benzene	−0.74	Methanol	−0.56
Chlorobenzene	−0.73	Propylene carbonate	−0.48
Tetrachloromethane	−0.71	Dimethyl sulphoxide	−0.48
Octan-1-ol	−0.68	Ethane-1,2-diol	−0.35
Butan-1-ol	−0.66	Water	+0.18
Nitrobenzene	−0.64		

[a] All values from data in ref. 11.

Table 2. Correlations of $\Delta G_s^\circ(CH_2)$ against some solvent parameters.[a]

Intercept	Slope	*n*	*R*	SD
(*a*) All solvents in Table 1				
−0.862	$0.188\ \delta_H^2/100$	19	0.981	0.04
−0.804	$0.370\ \pi_1^*$	19	0.673	0.17
−0.671	$0.043\ \mu_1$	19	0.328	0.21
−0.955	$0.949\ f(\varepsilon)$	19	0.554	0.19
−1.396	$0.019\ E_T$	16[b]	0.786	0.15
0.058	$-2.529\ f(\eta)$	19	0.376	0.21
−0.399	−0.089 MR	19	0.530	0.19
(*b*) Nonhydroxylic solvents in Table 1				
−0.890	$0.230\ \delta_H^2/100$	13	0.941	0.04
−0.758	$0.189\ \pi_1^*$	13	0.772	0.07
−0.746	$0.046\ \mu_1$	13	0.911	0.04
−0.877	$0.636\ f(\varepsilon)$	13	0.859	0.05
−1.273	$0.016\ E_T$	11[c]	0.911	0.04
−0.679	$0.082\ f(\eta)$	13	0.024	0.11
−0.570	−0.035 MR	13	0.437	0.10

[a] These are δ_H^2 the Hildebrand cohesive energy density, π_1^* the Kamlet–Taft solvent dipolarity, μ_1 the dipole moment, $f(\varepsilon)$ the dielectric constant function $(\varepsilon - 1)/(2\varepsilon + 1)$, E_T the Reichardt solvent parameter, $f(\eta)$ the refractive index function $(\eta^2 - 1)/(\eta^2 + 2)$, and MR a molar refraction we define as $10f(\eta)V_x$ where V_x is the intrinsic volume. [b] Excluding values for hexadecane, decane, and octan-1-ol. [c] Excluding values for hexadecane and decane.

comparing GLC stationary phases with common solvents. Secondly, the method is far too coarse to allow any analysis of solute-solvent interactions, which are actually the basis of gas-liquid partition, and hence of retention data

Poole *et al.*,[6] following several other workers,[7–10] suggested that the methylene increment to the gas ⟶ stationary phase transfer, as $\Delta G_s^\circ(CH_2)$ could be taken as a better measure of the overall polarity. Since $\Delta G_s^\circ(CH_2)$ can be obtained from a variety of homologous series, the difficulty over retention processes of alkanes is avoided. However, it is by no means obvious what a general polarity based on $\Delta G_s^\circ(CH_2)$ means. Abraham[11] has published data from which values of $\Delta G_s^\circ(CH_2)$ can be obtained for the n-alkanes in a number of common solvents (see Table 1). Note that since the original measurements were non-chromatographic, the n-alkane difficulty does not arise We can match the $\Delta G_s^\circ(CH_2)$ values against various solvent polarity parameters, and give simple regression constants in Table 2. For the nonhydroxylic solvents, there are reasonable correlations of $\Delta G_s^\circ(CH_2)$ with solvent dipole movement (μ), or with dielectric constant function $(\varepsilon - 1)/(2\varepsilon + 1)$, or with Reichardt's E_T parameter. But none of these are as good as the solvent cohesive energy density, as $\delta_H^2/100$, and for the total solvent list in Table 2(*a*), only the latter yields a reasonable correlation.* We have examined various double correlations amongst parameters that are not self-correlated, but the only one that is significantly better than the single correlation in $\delta_H^2/100$ is that in equation (4), for nonhydroxylic solvents, where the correlation coefficient, *R*, between δ_H^2 and $f(\eta)$ is only 0.265. Equation (4) can be

$$\Delta G_s^\circ(CH_2) = -0.679 + 0.246\,\delta_H^2/100 - 0.847f(\eta) \quad (4)$$

$$n = 13 \qquad R = 0.970 \qquad SD = 0.03$$

rationalised using a cavity theory of solution. In order to create a cavity in a solvent, solvent–solvent bonds must be broken in an endoergic process, modelled by δ_H^2. Then on insertion of the solute CH_2 group into the cavity, exoergic CH_2-solvent general dispersion interactions will be set up, modelled at least roughly by $f(\eta)$. The $\Delta G_s^\circ(CH_2)$ increment is therefore not a general polarity parameter in the sense of, say π_1^* or E_T, but reflects a combination of solvent–solvent bond breaking and CH_2-solvent dispersion interactions.

Other workers have moved away from the Rohrschneider–McReynolds method and have attempted to account for retention data on the basis of specific solute–solvent interactions. Ecknig *et al.*[12] characterised solute–solvent interactions in terms of two energy parameters a nonpolar or dispersion parameter and a polar parameter that includes hydrogen-bonding as an electrostatic effect. The calculation of these parameters, however, is not trivial, and application seems to be restricted to aliphatic solutes only.[13] The UNIFAC solution-of-groups method has been investigated also, but yielded only rough estimates of retention data.[14] A few workers have attempted to characterise stationary phases using indices that include stationary phase acidity and basicity as such. Burns and Hawkes,[15] for example, used retention data on the butan-1-ol–ethyl acrylate pair of solutes to obtain stationary phase basicities, and on pyridine–benzene to obtain stationary phase acidities, but conceded that the obtained indices were rather 'shaky.' Hawkes *et al.*[16] later carried out various spectroscopic studies of solutes in stationary phases and tabulated indices of dispersion forces, polarity, acidity, and basicity for a number of stationary phases (but note that acidity was obtained from retention data on the n-butylamine–n-butyl chloride pair of solutes).

It seems, therefore, to be acknowledged that factors such as dispersion, polarity, acidity, and basicity are important in solute–stationary phase interactions.[13,15,16] In order to quantify these effects, some general system in which both solute and stationary phase are characterised is necessary. The pur-

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* The units of δ_H^2 are cal cm^{-3}, where 1 cal = 4.184 J, and the units of μ are Debyes, where 1 D ≡ 3.336×10^{-30} C m

pose of this paper is to give one set of examples of such a system that can be used for GLC stationary phases, common solvents, and, indeed, any condensed phase.

We start with two equations suggested by Abraham, Doherty, Kamlet, and Taft, and their co-workers,[17-20]

$$\mathrm{SP} = c + d\delta_2 + s\pi_2^* + a\alpha_2 + b\beta_2 + mV_2 \quad (5)$$

$$\mathrm{SP} = c + d\delta_2 + s\pi_2^* + a\alpha_2 + b\beta_2 + l\log L^{16} \quad (6)$$

In equations (5) and (6),* SP denotes some property of a series of solutes, for example log V_G or log τ for solutes on a given stationary phase under the same set of conditions. The explanatory variables are δ_2, a polarisability correction term taken as zero except for polyhalogenated aliphatic compounds (0.5) and for aromatic compounds (1.0), π_2^* the solute dipolarity, α_2 the solute hydrogen-bond acidity, β_2 the solute hydrogen-bond basicity, V_2 the solute volume, and log L^{16} where L^{16} is the solute Ostwald solubility coefficient on n-hexadecane at 298 K.[21] The constants c, d, s, a, b, m, and l are found by multiple linear regression analysis of SP against as many explanatory variables as are statistically significant.

The terms in equations (5) and (6) can be, for the most part, directly identified with particular solute–solvent interactions.[17,18] The $s\pi_2^*$ term arises through solute–solvent dipole–dipole or dipole-induced dipole interactions, and hence the magnitude of the s-constant will reflect the solvent (or stationary phase) dipolarity. The $a\alpha_2$ term reflects interactions between hydrogen-bond solute acids and a hydrogen-bond solvent base, so that the a-constant will now be a measure of the solvent hydrogen-bond basicity. Conversely, the b-constant in the $b\beta_2$ term will be a measure of hydrogen-bond solvent acidity. The V_2 and log L^{16} terms both involve composite interactions, and will include both an endoergic cavity term and an exoergic solute–solvent general dispersion interaction.

There are a number of GLC retention parameters that could be used as the dependent variable (SP) in equations (5) and (6). The standard Gibbs energy of solution of a gaseous solute is given by equation (7), where L is the Ostwald solubility

$$-\Delta G_s^\circ = RT\ln L = RT\ln(V_G\rho_1) = RT\ln V_G + RT\ln\rho_1 \quad (7)$$

coefficient of the solute in the given solvent, often referred to as K the gas-liquid partition coefficient; V_G is the retention volume of the solute at the column temperature,† and ρ_1 is the solvent or stationary phase density The standard states for ΔG_s° are unit concentration in the gas phase and unit concentration in solution The most useful dependent variable is log L; not only can this be obtained from log V_G values by GLC, but log L values can be derived for solution of gaseous solutes in simple solvents If values of ρ_1 are unavailable so that log V_G itself must be used, there is little problem—all the constants in equations (5) and (6) remain the same except for c which will alter by log ρ_1. Unfortunately, much retention data in GLC is expressed only as the retention index I, equation (1), which on its own is not connected directly to any physicochemical parameter such as log L (or log K) Only if the so-called b-coefficient, herein designated as B, is specified for the variation of log V_G with carbon number for n-alkanes can the retention index be reconverted into a suitable parameter for use in equations (5) and (6). Even adjusted retention times, such as log τ values, can be used in these equations since log L = log τ + constant.

Results and Discussion

One of the most extensive and carefully determined sets of data is that of Laffort *et al.*[22] who listed retention indices of 240 compounds on five stationary phases at 393 K. Since Laffort *et al.*[22] gave the necessary B-values,[23] we can convert the reported values of I into log L values *via* equation (8),

$$\log L - \log L^{\mathrm{Decane}} = \log L' = \left(\frac{I - 1000}{100}\right)B \quad (8)$$

The constant c in equations (5) and (6) is now of little significance, but all the other constants are unaffected by the use of log L' rather than log L itself. The five Laffort phases are Carbowax, diethyleneglycol succinate (DEGS), polyphenyl ether (PPE), tricyanoethoxypropane (TCEP), and an ester of 'pyromellitic acid and trihydrofluoro alcohol,' known as Zonyl E-7 (ZE7).

Of the explanatory variables, δ_2 is trivial, π_2^* the Kamlet–Taft dipolarity parameter was as before,[17-20] whilst for α_2 and β_2 we used our new α_2^H and β_2^H hydrogen-bond solute parameters.[24-27] For a few difunctional bases such as anisole we used recently determined 'effective' or 'summation' $\Sigma\beta_2^H$ values.[28] The solute volume was taken as McGowan's intrinsic volume,[29] V_x, which has the merit that it can be calculated for any compound of known structure, and values of L^{16} were as before, supplemented by a number of additional values.[28] The general equations (5) and (6) thus take the specific formulation,

$$\log L' = c + d\delta_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + mV_x \quad (9)$$

$$\log L' = c + d\delta_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad (10)$$

We had available a complete set of explanatory variables for 168 solutes out of the 240. Details of the solutes and parameters are in Table 3, and the regressions based on equations (9) and (10) are summarised in Tables 4 and 5. The overall correlation coefficients, R, and standard deviations, SD, are not particularly good, but we stress that these refer to 'all solute' regressions We wish to point out that the purpose of constructing these regressions is to characterise the statinary phases, and not to provide equations that can be used to predict further retention values. The obtained regression equations summarised in Tables 4 and 5 are adequate for the former, but not for the latter, purpose We note also that as we have found before,[20] equation (10) yields much better regressions than does equation (9) for gas/liquid partition coefficients.‡

We can now examine the constants in equations (9) and (10) to check whether they are chemically reasonable. All five phases are to some extent dipolar, so that the s-constant in $s\pi_2^*$ should be positive, as observed. The order of stationary phase dipolarity, as measured by the s-constant, is TCEP > DEGS > Carbowax > ZE7 ⩾ PPE on equation (10), and almost the same on equation (9), this seems chemically quite reasonable Again, all five phases are hydrogen-bond bases, so that the a-constant in $a\alpha_2^H$ should be positive The order of stationary phase basicity is Carbowax > DEGS ⩾ TCEP > ZE7 ⩾ PPE on both equation (9) and equation (10). As might be expected, the fluoroester ZE7 is both less dipolar and less basic than the ester DEGS Nominally, the five phases are all non-hydrogen-bond acids, so that the b-constant in $b\beta_2^H$ should be near zero

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* We denote solute properties by subscript 2 and solvent properties by subscript 1

† It is of no value to use V_G°, the specific retention volume corrected to 273 K, because V_G° must be converted back to V_G for use in equation (7)

‡ Except for gas water partitions, but in this case neither V_x nor log L^{16} are very significant.[20]

There is a difficulty here, in that over the 168 solute set, the explanatory variable β_2^H is not independent, there being a cross correlation coefficient of 0.673 between β_2^H and π_2^* The total correlation matrix in terms of *R* is as follows:

	δ_2	π_2^*	α_2^H	β_2^H
π_2^*	0.302			
α_2^H	−0.188	0.059		
β_2^H	−0.164	0.673	0.373	
$\log L^{16}$	0.052	0.073	−0.032	0.075

We therefore repeated the regressions, excluding the β_2^H parameter, and we conclude that none of the stationary phases has any significant hydrogen-bond acidity [see Tables 5(*a*) and 5(*b*)]

The *l*-constants in $l \log L^{16}$ are all much lower than unity. Part of this will certainly be due to the operating temperature of 393 K instead of 298 K, but part is probably also due to the lessening of general solute–solvent dispersion interactions by comparison to n-hexadecane solvent (at 298 K).

We can conclude that equation (9) and particularly equation (10) are suitable for the characterisation of GLC stationary phases through a set of constants *c*, *d*, *s*, *a*, *b*, and *l*. Unlike Rohrschneider–McReynolds constants, however, those derived from equation (10) yield quantitative information on the propensity of the phase to take part in given solute-stationary phase interactions. The difficulty over n-alkanes on polar phases does not apply to the application of equation (10), because incorporation of alkanes into the solute data set is not essential. Furthermore, an additional advantage of the present method is that it is now possible to compare GLC stationary phases with other condensed phases, for example common solvents. From preliminary regressions[20] we know that the *s*-constant for ethyl acetate is *ca.* 1.8, so that the dipolarity of tricyanoethoxypropane at 393 K is no more than that of a simple ester at 298 K. We hope to apply equation (10) to a variety of solvents, as well as to other GLC stationary phases, in order to obtain a general classification of condensed phases.

There are disadvantages in the use of equations (9) and (10). In order to obtain suitability firm regressions with five explanatory variables, it is necessary to obtain retention data for not less than about 30 solutes. However, since only $\log\tau$ values are needed in order to determine all the constants except *c*, this is not an onerous task. A more important disadvantage is revealed by an examination of the origin of the explanatory variables in equations (9) and (10). The dependent variable is ideally $\log L$ (or $\log K$), *i.e.*, a Gibbs energy related quantity *via* an equilibrium constant. If $\log V_G$, $\log L'$ or $\log\tau$ are used, these quantities are still equivalent to the use of $\log L$ as far as all the terms except the *c*-constant are concerned. Hence for thermodynamic consistency, all the explanatory variables should be Gibbs energy related. There is no difficulty over α_2^H, β_2^H, and $\log L^{16}$ since these are all derived from equilibrium constants, as $\log K$ values.[21,24–27] The variable V_X is not a Gibbs energy term, but since we prefer equation (10) to equation (9) this does not concern us overmuch. A more pressing problem is the δ_2/π_2^* formulism: the δ_2 parameter is simply an empirical correction factor, whilst the π_2^* parameter originates as a spectroscopically determined solvent π_1^* parameter, and is certainly not a Gibbs energy related quantity. Furthermore, π_1^* can only be determined for compounds that are liquids at room temperature, and can be equated to π_2^* only for nonassociated liquids. All other π_2^* values have either been estimated or have been obtained *via* various π_2^*/dipole moment correlations.[10] Because of the indeterminate nature of π_2^*, it becomes impossible to connect the $s\pi_2^*$ term in a regression equation with any specific solute–solvent interaction. In the above discussion we have used the *s*-constant as a measure of 'dipolarity', but more correctly it will represent some blend of polarisability and dipolarity. We set out now our attempts to resolve these difficulties by replacement of the δ_2/π_2^* parameters in equation (10).

Construction of a New General Equation.—We first examine the terms in equation (10), in order to specify more exactly the parameters required to take the place of δ_2 and π_2^*. The α_2^H and β_2^H parameters take care of hydrogen-bond interactions, as spelt out above, and will be retained in any new equation. As we have seen in the introduction, the $\log L^{16}$ parameter is very useful in that it accounts for cavity effects, together with general dispersion interactions of the solute-nonpolar solvent (hexadecane) type. We are then left with solute solvent dipole–dipole and dipole-induced dipole effects, together with additional dispersion interactions that may loosely be described as polarisability effects. The obvious solute parameter needed to describe dipole–dipole type interactions is the dipole moment (μ_2). Following Kirkwood,[30] we use μ_2^2, which has the advantage that it is very nearly a free energy related quantity † Various physical quantities can be used to model dispersion polarisability interactions. We have briefly investigated both the solute molar refraction, MR, and the solute polarisability, but found neither satisfactory when used in combination with μ_2^2, α_2^H, β_2^H, and $\log L^{16}$. The refractive index function, $f(\eta)$, has been used by Fuchs *et al.*[31] with some success, and we give in Table 6 details of regressions using equation (11), with $f(\eta)$ defined by equation (12)

$$\log L' = c + jf(\eta) + q\mu_2^2 + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad (11)$$

$$f(\eta) = (\eta^2-1)/(\eta^2+2) \quad (12)$$

The regression equations based on equation (11) are appreciably poorer than those using equation (10). Not only are *R* and SD poorer, but significant *b*-constants are produced, surely as artifacts. Part of this difficulty may be due to cross-correlations between μ_2^2 and β_2^H ($R = 0.556$) and also between $f(\eta)$ and $\log L^{16}$ ($R = 0.534$), that could be overcome by a more suitable selection of solutes. But $f(n)$ must include interactions already dealt with by the $\log L^{16}$ parameter, hence the coefficients of $\log L^{16}$ in equation (11) are always less than those in equation (10). What is required is a parameter that is more specifically related to the polarisability of the solute as regards interactions due to the presence of polarisable electrons. We start with the solute molar refraction, but for convenience defined in terms of

$$MR_X = 10(\eta^2-1)V_X/(\eta^2+2) = 10f(\eta)\,V_X \quad (13)$$

the characteristic volume. With V_X in units of (cm^3 mol^{-1})/100, equation (13) will yield MR_X in the more convenient units of (cm^3 mol^{-1})/10 Note that η is taken at 293 K with the sodium-D line Unlike $f(\eta)$ itself, the molar refraction has the interesting property of being the same (within a few per cent) for a given solute in the gas phase and in solution. Hence although $f(\eta)$ is most conveniently measured on bulk liquids, MR (and MR_X) can be taken as a property of an isolated molecule ‡ In order to

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† Kirkwood[30] showed that the Gibbs energy of a dipole in a dielectric continuum was proportional to μ^2/r^3 where *r* is the radius of a sphere containing the dipole. Now many functional groups contain a dipole within a sphere of a similar radius, so that the Gibbs energy is approximately proportional to μ^2

‡ We have confirmed that MR is essentially the same in the gas phase and bulk liquid even for associated compounds such as water and alcohols The one exception we have noted is acetic acid, probably due to the extensive dimerisation that takes place in the gas phase

Table 3. The 168 compounds and the parameters used in the regressions

No	Compound	δ_2	$f(n)$	R_2	π_2^*	μ_2^2	α_2^H	β_2^H	V_X	$\log L^{16}$
3352	Methanol	0.00	0.203	0.278	0.40	2.890	0.37	0.41	0.308	0.922
3353	Ethanol	0.00	0.221	0.246	0.40	2.856	0.33	0.44	0.449	1.485
3354	Propan-1-ol	0.00	0.234	0.236	0.40	2.822	0.33	0.45	0.590	2.097
3355	Propan-2-ol	0.00	0.230	0.212	0.40	2.756	0.32	0.47	0.590	1.821
3473	Prop-2-en-1-ol, allyl-OH	0.00	0.250	0.341	0.45	2.560	0.33	0.41	0.547	1.996
3356	Butan-1-ol	0.00	0.242	0.224	0.40	2.756	0.33	0.45	0.731	2.601
3358	2-Methylpropan-1-ol	0.00	0.240	0.217	0.40	2.670	0.33	0.45	0.731	2.399
3357	Butan-2-ol	0.00	0.241	0.217	0.40	2.723	0.32	0.47	0.731	2.338
3359	t-Butyl alcohol	0.00	0.236	0.180	0.40	2.657	0.32	0.49	0.731	2.018
3360	Pentan-1-ol	0.00	0.248	0.219	0.40	2.756	0.33	0.45	0.872	3.106
3361	2-Methylbutan-1-ol	0.00	0.248	0.219	0.40	2.890	0.33	0.45	0.872	3.011
3362	3-Methylbutan-1-ol	0.00	0.245	0.192	0.40	2.560	0.33	0.45	0.872	3.011
3440	Cyclopentanol	0.00	0.270	0.427	0.40	2.890	0.32	0.48	0.763	3.270
3368	Hexan-1-ol	0.00	0.252	0.210	0.40	2.890	0.33	0.45	1.013	3.610
3490	(*E*)-Hex-2-en-1-ol	0.00	0.263	0.294	0.45	2.560	0.33	0.41	0.970	3.510
3369	Hexan-2-ol	0.00	0.250	0.187	0.40	2.890	0.32	0.47	1.013	3.340
3370	Hexan-3-ol	0.00	0.251	0.200	0.40	2.890	0.32	0.47	1.013	3.440
3372	2-Methylpentan-2-ol	0.00	0.248	0.169	0.40	2.890	0.32	0.49	1.013	3.181
3374	3-Methylpentan-3-ol	0.00	0.252	0.210	0.40	2.890	0.32	0.49	1.013	3.277
3389	Heptan-1-ol	0.00	0.256	0.211	0.40	2.924	0.33	0.45	1.154	4.115
3492	(*E*)-Hept-2-en-1-ol	0.00	0.267	0.281	0.45	2.560	0.33	0.41	1.111	4.010
3405	Octan-1-ol	0.00	0.258	0.199	0.40	2.958	0.33	0.45	1.295	4.619
3494	(*E*)-Oct-2-en-1-ol	0.00	0.273	0.270	0.45	2.560	0.33	0.41	1.252	4.520
3410	2-Methylheptan-2-ol	0.00	0.256	0.169	0.40	2.890	0.32	0.49	1.295	3.990
3416	Nonan-1-ol	0.00	0.260	0.193	0.40	2.958	0.33	0.45	1.435	5.124
3426	Decan-1-ol	0.00	0.262	0.191	0.40	2.592	0.33	0.45	1.576	5.628
3429	Undecan-1-ol	0.00	0.263	0.181	0.40	2.890	0.33	0.45	1.717	6.130
3430	Dodecan-1-ol	0.00	0.265	0.175	0.40	2.890	0.33	0.45	1.858	6.640
1551	Acetaldehyde	0.00	0.205	0.208	0.67	7.236	0.00	0.40	0.406	1.230
1552	Propionaldehyde	0.00	0.223	0.196	0.65	6.350	0.00	0.40	0.547	1.815
1569	Propenal, acrolein	0.00	0.243	0.324	0.65	9.734	0.00	0.40	0.504	2.110
1553	Butyraldehyde	0.00	0.234	0.187	0.65	7.398	0.00	0.40	0.688	2.270
1554	Isobutyraldehyde	0.00	0.228	0.146	0.65	7.290	0.00	0.40	0.688	2.060
1570	(*E*)-But-2-en-1-al	0.00	0.262	0.387	0.75	12.532	0.00	0.40	0.645	2.570
1556	3-Methylbutanal	0.00	0.237	0.144	0.65	6.859	0.00	0.40	0.829	2.620
1558	Hexanal	0.00	0.244	0.146	0.65	7.290	0.00	0.40	0.970	3.370
1560	Heptanal	0.00	0.248	0.140	0.65	7.290	0.00	0.40	1.111	3.860
1561	Octanal	0.00	0.254	0.160	0.65	7.398	0.00	0.40	1.252	4.380
1590	Benzaldehyde	1.00	0.317	0.820	0.92	7.563	0.00	0.42	0.873	3.985
1651	Propan-2-one	0.00	0.220	0.179	0.71	8.294	0.04	0.50	0.547	1.760
1652	Butan-2-one	0.00	0.231	0.166	0.67	7.618	0.00	0.48	0.688	2.287
1653	Pentan-2-one	0.00	0.237	0.143	0.65	7.290	0.00	0.48	0.829	2.755
1706	Cyclopentanone	0.00	0.262	0.373	0.76	10.890	0.00	0.52	0.720	3.120
1659	Hexan-2-one	0.00	0.243	0.136	0.65	7.023	0.00	0.48	0.970	3.262
1660	Hexan-3-one	0.00	0.243	0.136	0.65	7.290	0.00	0.48	0.970	3.310
1708	Cyclohexanone	0.00	0.269	0.403	0.76	9.000	0.00	0.52	0.861	3.615
1664	Heptan-2-one	0.00	0.247	0.123	0.65	6.812	0.00	0.48	1.111	3.760
1712	Cycloheptanone	0.00	0.274	0.436	0.76	9.610	0.00	0.52	1.002	4.110
1675	Octan-2-one	0.00	0.250	0.108	0.65	7.398	0.00	0.48	1.252	4.257
1713	Cyclo-octanone	0.00	0.279	0.474	0.76	8.762	0.00	0.52	1.143	4.610
1750	Acetophenone	1.00	0.312	0.818	0.90	9.000	0.00	0.51	1.014	4.483
1685	Nonan-2-one	0.00	0.254	0.119	0.65	7.301	0.00	0.48	1.392	4.755
1714	Cyclononanone	0.00	0.280	0.490	0.76	8.123	0.00	0.52	1.284	5.110
1690	Decan-2-one	0.00	0.256	0.108	0.65	7.290	0.00	0.48	1.533	5.260
1715	Cyclodecanone	0.00	0.284	0.527	0.76	7.840	0.00	0.52	1.425	5.610
1722	Carvone	0.00	0.294	0.674	0.80	10.049	0.00	0.49	1.339	5.330
1691	Undecan-2-one	0.00	0.258	0.101	0.65	7.290	0.00	0.48	1.674	5.760
1716	Cycloundecanone	0.00	0.288	0.557	0.76	7.840	0.00	0.52	1.566	6.110
1692	Dodecan-2-one	0.00	0.260	0.103	0.65	7.290	0.00	0.48	1.815	6.260
1717	Cyclododecanone	0.00	0.293	0.588	0.76	7.840	0.00	0.52	1.707	6.600
1352	Diethyl ether	0.00	0.217	0.041	0.27	1.323	0.00	0.45	0.731	2.061
1355	Di-n-butyl ether	0.00	0.242	0.000	0.27	1.369	0.00	0.45	1.294	4.001
1414	Furan	1.00	0.254	0.369	0.50	0.436	0.00	0.15	0.536	1.830
1450	Methyl phenyl ether	1.00	0.303	0.708	0.73	1.904	0.00	0.33	0.916	3.926
2101	Nitromethane	0.00	0.233	0.313	0.85	11.972	0.12	0.25	0.424	1.892
2102	Nitroethane	0.00	0.238	0.270	0.80	13.323	0.00	0.25	0.565	2.367
2103	1-Nitropropane	0.00	0.243	0.242	0.79	13.396	0.00	0.25	0.706	2.850
2143	3-Nitrotoluene	1.00	0.317	0.874	0.97	16.000	0.00	0.34	1.032	4.970
2201	Acetonitrile	0.00	0.212	0.237	0.75	15.366	0.09	0.44	0.404	1.560
2203	1-Cyanopropane	0.00	0.234	0.188	0.68	16.557	0.00	0.44	0.586	2.540

Table 3 (*continued*)

No.	Compound	δ_2	$f(n)$	R_2	π_2^*	μ_2^2	α_2^H	β_2^H	V_x	$\log L^{16}$
2205	1-Cyanobutane	0.00	0.241	0.177	0.68	16.974	0.00	0.44	0.827	3.057
2241	Benzonitrile	1.00	0.308	0.742	0.90	17.472	0.00	0.42	0.871	4.004
2701	Pyridine	1.00	0.299	0.794	0.87	4.796	0.00	0.62	0.675	3.003
2952	Acetic acid	0.00	0.227	0.265	0.60	2.890	0.55	0.43	0.465	1.750
2953	Propanoic acid	0.00	0.235	0.233	0.60	2.890	0.54	0.43	0.606	2.290
2954	Butanoic acid	0.00	0.241	0.210	0.60	2.820	0.54	0.42	0.747	2.830
2956	Pentanoic acid	0.00	0.247	0.205	0.60	2.590	0.54	0.41	0.887	3.380
2957	3-Methylbutanoic acid	0.00	0.244	0.178	0.60	2.790	0.54	0.41	0.887	3.300
2959	Hexanoic acid	0.00	0.251	0.174	0.60	2.490	0.54	0.39	1.028	3.920
2964	Heptanoic acid	0.00	0.251	0.149	0.60	2.790	0.54	0.38	1.169	4.460
2969	Octanoic acid	0.00	0.258	0.150	0.60	2.890	0.54	0.36	1.310	5.000
2975	Nonanoic acid	0.00	0.261	0.132	0.60	2.790	0.54	0.34	1.451	5.550
1860	Methyl acetate	0.00	0.220	0.142	0.60	2.958	0.00	0.40	0.606	1.960
1861	Ethyl acetate	0.00	0.227	0.106	0.55	3.168	0.00	0.45	0.747	2.376
1881	Methyl propanoate	0.00	0.230	0.128	0.55	2.890	0.00	0.45	0.747	2.459
1853	Propyl formate	0.00	0.230	0.132	0.61	3.648	0.00	0.38	0.747	2.413
1862	n-Propyl acetate	0.00	0.234	0.092	0.55	3.419	0.00	0.45	0.887	2.878
1864	n-Butyl acetate	0.00	0.239	0.071	0.55	3.240	0.00	0.45	1.028	3.379
1889	Propyl butanoate	0.00	0.249	0.068	0.55	3.063	0.00	0.45	1.169	3.810
1867	Pentyl acetate	0.00	0.244	0.067	0.55	3.063	0.00	0.45	1.169	3.810
1870	Isopentyl acetate	0.00	0.240	0.051	0.55	3.312	0.00	0.45	1.169	3.740
1892	Isobutyl isobutanoate	0.00	0.242	0.000	0.55	3.240	0.00	0.45	1.310	3.880
1896	Isopentyl isopentanoate	0.00	0.248	0.000	0.55	3.240	0.00	0.45	1.592	4.580
553	Trichloromethane	0.50	0.267	0.425	0.58	1.020	0.20	0.02	0.617	2.480
554	Tetrachloromethane	0.50	0.274	0.458	0.28	0.000	0.00	0.00	0.739	2.823
557	1,2-Dichloroethane	0.50	0.266	0.416	0.81	1.638	0.10	0.05	0.635	2.573
586	1,1,2-Trichloroethene	0.50	0.283	0.524	0.53	0.721	0.12	0.03	0.715	2.997
1038	Benzyl chloride	1.00	0.313	0.821	0.71	3.385	0.00	0.31	0.980	4.290
579	1-Chlorohexane	0.00	0.253	0.201	0.39	3.803	0.00	0.15	1.077	3.710
1002	1,2-Dichlorobenzene	1.00	0.319	0.870	0.80	5.153	0.00	0.03	0.961	4.405
605	Bromoethane	0.00	0.255	0.366	0.48	4.121	0.00	0.17	0.565	2.120
624	1-Bromopentane	0.00	0.266	0.356	0.48	4.840	0.00	0.17	0.988	3.611
637	2-Bromo-octane	0.00	0.267	0.322	0.48	4.000	0.00	0.17	1.411	5.110
651	Iodomethane	0.00	0.313	0.675	0.40	2.624	0.00	0.18	0.508	2.106
670	1-Iodobutane	0.00	0.294	0.628	0.50	4.494	0.00	0.18	0.930	3.628
671	2-Iodobutane	0.00	0.294	0.610	0.50	4.000	0.00	0.18	0.930	3.390
3552	Ethanethiol	0.00	0.259	0.392	0.35	2.459	0.00	0.16	0.554	2.172
3553	n-Propylthiol	0.00	0.263	0.385	0.35	2.280	0.00	0.16	0.695	2.685
3554	Isopropylthiol	0.00	0.256	0.336	0.35	2.560	0.00	0.16	0.695	2.406
3569	Prop-2-en-1-thiol	0.00	0.285	0.542	0.40	2.403	0.00	0.20	0.652	2.510
3555	n-Butylthiol	0.00	0.266	0.382	0.35	2.369	0.00	0.16	0.836	3.243
3556	Isobutylthiol	0.00	0.260	0.356	0.35	2.403	0.00	0.16	0.836	2.780
3558	t-Butylthiol	0.00	0.254	0.281	0.35	2.403	0.00	0.16	0.836	2.558
3601	Thiophene	1.00	0.308	0.684	0.60	0.325	0.00	0.16	0.641	2.943
3559	n-Pentylthiol	0.00	0.269	0.369	0.35	2.403	0.00	0.16	0.977	3.720
3560	Isopentylthiol	0.00	0.272	0.343	0.35	2.403	0.00	0.16	0.977	3.360
3602	2-Methylthiophene	1.00	0.304	0.688	0.40	0.449	0.00	0.14	0.782	3.302
3561	n-Hexylthiol	0.00	0.271	0.361	0.35	2.403	0.00	0.16	1.118	4.220
3603	2,5-Dimethylthiophene	1.00	0.301	0.690	0.40	0.260	0.00	0.16	0.923	3.806
3550	n-Heptanethiol	0.00	0.273	0.357	0.35	2.403	0.00	0.16	1.258	4.720
3562	n-Octylthiol	0.00	0.271	0.353	0.35	2.403	0.00	0.16	1.399	5.310
3563	n-Nonylthiol	0.00	0.271	0.347	0.35	2.403	0.00	0.16	1.540	5.890
3564	n-Decylthiol	0.00	0.270	0.342	0.35	2.403	0.00	0.16	1.681	6.480
3579	Dimethyl sulphide	0.00	0.261	0.404	0.36	2.250	0.00	0.29	0.554	2.238
3580	Diethyl sulphide	0.00	0.265	0.373	0.36	2.310	0.00	0.29	0.836	3.104
3581	Di-n-propyl sulphide	0.00	0.268	0.358	0.36	2.430	0.00	0.29	1.117	4.120
3587	Isopentyl sulphide	0.00	0.272	0.300	0.36	2.560	0.00	0.29	1.681	5.540
3610	Diethyl disulphide	0.00	0.298	0.670	0.64	3.960	0.00	0.22	0.999	4.210
3589	Di-n-butyl sulphide	0.00	0.290	0.345	0.36	2.592	0.00	0.29	1.400	4.950
3585	Methyl-n-propyl sulphide	0.00	0.266	0.380	0.36	2.560	0.00	0.29	0.836	3.240
371	Propene	0.00	0.196	0.103	0.08	0.134	0.00	0.07	0.488	0.946
373	But-1-ene	0.00	0.216	0.100	0.08	0.116	0.00	0.07	0.629	1.491
380	Pent-1-ene	0.00	0.277	0.093	0.08	0.116	0.00	0.07	0.770	2.013
392	Hex-1-ene	0.00	0.234	0.078	0.08	0.116	0.00	0.07	0.911	2.547
406	Hept-1-ene	0.00	0.242	0.092	0.08	0.116	0.00	0.07	1.052	3.063
409	Oct-1-ene	0.00	0.247	0.094	0.08	0.116	0.00	0.07	1.192	3.591
412	(*Z*)-Oct-2-ene	0.00	0.250	0.135	0.08	0.090	0.00	0.07	1.192	3.650
413	2-Ethylhex-1-ene	0.00	0.251	0.139	0.08	0.116	0.00	0.07	1.192	3.510
468	Oct-1-yne	0.00	0.251	0.155	0.20	0.656	0.13	0.20	1.150	3.480
469	Oct-2-yne	0.00	0.257	0.226	0.20	0.656	0.00	0.20	1.150	3.850

Table 3 (*continued*)

No	Compound	δ_2	$f(n)$	R_2	π_2^*	μ_2^2	α_2^H	β_2^H	V_X	$\log L^{16}$
751	Benzene	1.00	0.295	0.610	0.59	0.000	0.00	0.14	0.716	2.803
752	Toluene	1.00	0.292	0.601	0.55	0.130	0.00	0.14	0.857	3.344
766	Ethylbenzene	1.00	0.292	0.613	0.53	0.348	0.00	0.15	0.998	3.765
843	Styrene	1.00	0.317	0.848	0.55	0.063	0.00	0.18	0.955	3.908
795	Phenylethyne	1.00	0.300	0.679	0.55	0.533	0.12	0.21	0.912	3.715
753	2-Xylene	1.00	0.297	0.663	0.51	0.384	0.00	0.17	0.998	3.937
754	3-Xylene	1.00	0.293	0.623	0.51	0.160	0.00	0.17	0.998	3.864
755	4-Xylene	1.00	0.292	0.613	0.51	0.000	0.00	0.17	0.998	3.858
758	Mesitylene	1.00	0.294	0.649	0.47	0.000	0.00	0.20	1.139	4.399
442	α-Pinene	0.00	0.277	0.446	0.10	0.130	0.00	0.10	1.257	4.200
52	Propane	0.00	0.181	0.000	0.00	0.000	0.00	0.00	0.531	1.050
53	n-Butane	0.00	0.205	0.000	0.00	0.000	0.00	0.00	0.672	1.615
54	Isobutane	0.00	0.197	0.000	0.00	0.000	0.00	0.00	0.672	1.409
55	n-Pentane	0.00	0.219	0.000	0.00	0.000	0.00	0.00	0.813	2.162
58	n-Hexane	0.00	0.229	0.000	0.00	0.000	0.00	0.00	0.954	2.688
287	Cyclohexane	0.00	0.257	0.305	0.00	0.000	0.00	0.00	0.845	2.913
63	n-Heptane	0.00	0.236	0.000	0.00	0.000	0.00	0.00	1.095	3.173
73	2-Methylheptane	0.00	0.240	0.000	0.00	0.000	0.00	0.00	1.236	3.480
74	3-Methylheptane	0.00	0.242	0.000	0.00	0.000	0.00	0.00	1.236	3.510
69	2,3-Dimethylpentane	0.00	0.232	0.000	0.00	0.000	0.00	0.00	1.095	2.841
72	n-Octane	0.00	0.241	0.000	0.00	0.000	0.00	0.00	1.236	3.677
91	n-Nonane	0.00	0.245	0.000	0.00	0.000	0.00	0.00	1.377	4.182
112	2,2,5-Trimethylhexane	0.00	0.242	0.000	0.00	0.000	0.00	0.00	1.377	3.530
126	n-Decane	0.00	0.248	0.000	0.00	0.000	0.00	0.00	1.518	4.686
162	n-Undecane	0.00	0.263	0.000	0.00	0.000	0.00	0.00	1.658	5.191
168	n-Dodecane	0.00	0.254	0.000	0.00	0.000	0.00	0.00	1.799	5.696
174	n-Tridecane	0.00	0.256	0.000	0.00	0.000	0.00	0.00	1.940	6.200
180	n-Tetradecane	0.00	0.258	0.000	0.00	0.000	0.00	0.00	2.081	6.705

Table 4. Regression analysis using equation (9), $n = 168$, $\log L' = c + d\delta_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + mV_X$.

Phase		c	d	s	a	b	m	SD[a]	R[b]
Carbowax		−2.33	0.20	2.29	2.37	−0.53	1.57	0.22	0.960
	SD[c]	0.07	0.06	0.12	0.12	0.17	0.05		
	CL[d]	1.00	0.99	1.00	1.00	0.99	1.00		
DEGS		−2.04	0.25	2.41	2.05	−0.20	1.40	0.24	0.955
	SD	0.07	0.07	0.13	0.13	0.18	0.05		
	CL	1.00	1.00	1.00	1.00	0.74	1.00		
PPE		−2.90	0.22	1.93	0.84	−0.38	1.98	0.22	0.959
	SD	0.07	0.06	0.12	0.12	0.17	0.05		
	CL	1.00	1.00	1.00	1.00	0.97	1.00		
TCEP		−1.95	0.20	2.67	2.02	−0.02	1.32	0.23	0.961
	SD	0.07	0.07	0.13	0.13	0.18	0.05		
	CL	1.00	1.00	1.00	1.00	0.08	1.00		
ZE7		−2.43	0.09	1.91	0.81	0.21	1.59	0.16	0.975
	SD	0.05	0.04	0.09	0.08	0.12	0.04		
	CL	1.00	0.96	1.00	1.00	0.91	1.00		

[a] Overall standard deviation [b] Overall correlation coefficient. [c] Standard deviation in the constant. [d] Confidence level 1.00 signifies >0.99

remove the dispersive part already incorporated in $\log L^{16}$, we then subtract out the value of MR_X for an alkane of the same

$$R_2 = MR_X(\text{observed}) - MR_X(\text{alkane of same } V_X) \quad (14)$$

characteristic volume, equation (4) The latter quantity is readily obtained through an excellent linear regression for the n-alkanes,

$$MR_X(\text{alkane}) = -0.525\,53 + 2.831\,95V_X \quad (15)$$
$$n = 13, R = 0.999\,99, SD = 0.0078$$

Hence knowing $f(\eta)$ and V_X for any solute, MR_X and then R_2 can be calculated *via* equations (13)–(15). For convenience we tabulate R_2 in units of 10^{-1} cm^3, and give a number of typical values in Table 7. Note that by definition $R_2 = 0$ for all n-alkanes, and by calculation R_2 is also zero for branched chain alkanes and for the rare gases as well.

We now use the new polarisability parameter, R_2, in conjunction with μ_2^2, to construct equation (16), that we apply to the same set of 168 solutes as before. Details are in Table 8

$$\log L' = c + rR_2 + q\mu_2^2 + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad (16)$$

The quality of the regressions in Table 8 is slightly better than those in Table 6, based on equation (11), but significantly poorer than those in Table 5, based on equation (10). For purposes of characterisation, this might not matter too much, but unfortunately the regressions in Table 8(*a*) show larger dependences on β_2^H that are probably artifacts [compare Table 8 (*a*) with Table 8 (*b*)]. Although there is no significant cross-correlation between R_2 and any other explanatory variable in equation (16), there still remains the connection between μ_2^2 and β_2^H, $r = 0.556$, referred to above It is possible that for a better selection of solutes without the μ_2^2/β_2^H cross-correlation, equation (16) might perform as well as equation (10), and we intend to investigate this further.

Finally, we suggest that our calculated R_2 values (Table 7) can replace the empirical δ_2 values in equation (10) to yield equation (17). Details of regressions using equation (17) are in

$$\log L' = c + rR_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad (17)$$

Table 9. In terms of overall standard deviation and correlation coefficient, these regressions are the best we have obtained, being slightly better than those given in Table 5. We have also investigated replacement of δ_2 by R_2 in equation (9), but, as usual, find that equations using V_X are considerably poorer than those using $\log L^{16}$

Table 5. Regression analysis using equation (10), $n = 168$, $\log L' = c + d\delta_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l\log L^{16}$

Phase		c	d	s	a	b	l	SD	R
(*a*) Carbowax		−2.07	0.05	1.55	2.13	−0.17	0.446	0.14	0.985
	SD	0.04	0.04	0.07	0.07	0.10	0.008		
	CL	1.00	0.83	1.00	1.00	0.89	1.00		
DEGS		−1.81	0.12	1.76	1.84	0.11	0.399	0.16	0.978
	SD	0.04	0.05	0.09	0.09	0.12	0.010		
	CL	1.00	0.99	1.00	1.00	0.64	1.00		
PPE		−2.54	0.04	1.01	0.53	0.08	0.554	0.11	0.990
	SD	0.03	0.03	0.06	0.06	0.08	0.007		
	CL	1.00	0.77	1.00	1.00	0.66	1.00		
TCEP		−1.74	0.07	2.06	1.82	0.28	0.380	0.16	0.981
	SD	0.04	0.05	0.09	0.09	0.12	0.010		
	CL	1.00	0.88	1.00	1.00	0.98	1.00		
ZE7		−2.10	−0.05	1.17	0.56	0.59	0.434	0.13	0.984
	SD	0.03	0.04	0.07	0.07	0.10	0.008		
	CL	1.00	0.84	1.00	1.00	1.00	1.00		
(*b*) Carbowax		−2.06	0.08	1.46	2.08		0.446	0.14	0.985
	SD	0.04	0.03	0.05	0.07		0.008		
	CL	1.00	0.98	1.00	1.00		1.00		
DEGS		−1.81	0.10	1.82	1.87		0.400	0.16	0.978
	SD	0.04	0.04	0.06	0.08		0.010		
	CL	1.00	0.98	1.00	1.00		1.00		
PPE		−2.54	0.02	1.05	0.55		0.555	0.11	0.990
	SD	0.03	0.03	0.04	0.05		0.007		
	CL	1.00	0.61	1.00	1.00		1.00		
TCEP		−1.73	0.02	2.21	1.90		0.382	0.16	0.981
	SD	0.04	0.04	0.06	0.08		0.010		
	CL	1.00	0.40	1.00	1.00		1.00		
ZE7		−2.09	−0.16	1.50	0.72		0.438	0.14	0.980
	SD	0.04	0.03	0.05	0.07		0.009		
	CL	1.00	0.99	1.00	1.00		1.00		

[a] These are the preferred equations

Table 6. Regression analysis using equation (11), $n = 168$; $\log L' = c + ff(\mathrm{n}) + q\mu_2^2 + a\alpha_2^H + b\beta_2^H + mV_X$.

Phase		c	f	q	a	b	l	SD	R
Carbowax		−3.48	7.61	0.59	2.34	0.55	0.370	0.19	0.971
	SD	0.16	0.67	0.005	0.11	0.12	0.014		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
DEGS		−3.62	9.56	0.67	2.06	0.92	0.304	0.22	0.961
	SD	0.18	0.77	0.006	0.13	0.14	0.016		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
PPE		−3.56	5.37	0.038	0.66	0.56	0.500	0.14	0.985
	SD	0.11	0.48	0.004	0.08	0.09	0.010		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
TCEP		−3.67	10.26	0.080	2.09	1.21	0.278	0.23	0.961
	SD	0.19	0.81	0.006	0.13	0.15	0.017		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
ZE7		−2.55	2.84	0.051	0.72	1.04	0.409	0.17	0.972
	SD	0.14	0.58	0.005	0.10	0.11	0.012		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		

Table 7. Some values of the molar refraction parameter, R_2, and the 'correction factor', δ_2

Solute	R_2/10^{-1} cm^3	δ_2
Rare gases	0	0
Alkanes	0	0
Cyclohexane	0.305	0
But-1-ene	0.100	0
But-1-yne	0.178	0
Benzene	0.610	1
1-Chlorobutane	0.210	0
1-Bromobutane	0.360	0
1-Iodobutane	0.628	0
Dichloromethane	0.387	0.5
Tetrachloromethane	0.458	0.5
Chlorobenzene	0.718	1
Butan-2-one	0.166	0
Diethyl ether	0.041	0
Ethyl acetate	0.106	0
Dimethylformamide	0.367	0
Butan-1-ol	0.224	0
n-Butylamine	0.224	0
Acetophenone	0.818	1
Methyl phenyl ether	0.708	1
Ethyl benzoate	0.663	1
Phenol	0.805	1
Aniline	0.955	1

Table 8. Regression analysis using equation (16), $n = 168$, $\log L' = c + rR_2 + q\mu_2^2 + a\alpha_2^H + b\beta_2^H + l\log L^{16}$.

Phase		c	r	q	a	b	l	SD	R
(*a*) Carbowax		−1.98	0.86	0.052	2.30	0.53	0.438	0.17	0.976
	SD	0.05	0.06	0.005	0.10	0.10	0.011		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
DEGS		−1.74	1.10	0.059	2.03	0.89	0.389	0.19	0.971
	SD	0.05	0.07	0.005	0.11	0.12	0.012		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
PPE		−2.50	0.62	0.033	0.64	0.55	0.548	0.12	0.988
	SD	0.03	0.04	0.003	0.07	0.08	0.008		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
TCEP		−1.67	1.16	0.071	2.05	1.19	0.369	0.20	0.970
	SD	0.05	0.07	0.006	0.12	0.13	0.013		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
ZE7		−1.99	0.34	0.048	0.71	1.04	0.434	0.16	0.974
	SD	0.04	0.06	0.004	0.09	0.10	0.010		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
(*b*) Carbowax		−1.92	0.85	0.068	2.56		0.444	0.18	0.972
	SD	0.05	0.07	0.004	0.09		0.011		
	CL	1.00	1.00	1.00	1.00		1.00		
DEGS		−1.63	1.08	0.084	2.47		0.398	0.22	0.961
	SD	0.06	0.08	0.005	0.11		0.014		
	CL	1.00	1.00	1.00	1.00		1.00		
PPE		−2.44	0.61	0.049	0.91		0.553	0.14	0.984
	SD	0.03	0.05	0.003	0.07		0.009		
	CL	1.00	1.00	1.00	1.00		1.00		
TCEP		−1.50	1.14	0.105	2.64		0.382	0.25	0.954
	SD	0.06	0.09	0.005	0.12		0.016		
	CL	1.00	1.00	1.00	1.00		1.00		
ZE7		−1.88	0.32	0.078	1.22		0.445	0.21	0.956
	SD	0.05	0.07	0.004	0.10		0.013		
	CL	1.00	1.00	1.00	1.00		1.00		

Table 9. Regression analysis using equation (17), $n = 168$, $\log L = c + rR_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l\log L^{16}$

Phase		c	r	s	a	b	l	SD	R
(*a*) Carbowax		−2.07	0.25	1.40	2.13	−0.05	0.442	0.13	0.986
	SD	0.03	0.06	0.08	0.07	0.10	0.008		
	CL	1.00	1.00	1.00	1.00	0.42	1.00		
DEGS		−1.84	0.43	1.53	1.83	0.28	0.393	0.15	0.982
	SD	0.04	0.07	0.09	0.08	0.11	0.009		
	CL	1.00	1.00	1.00	1.00	0.98	1.00		
PPE		−2.56	0.25	0.85	0.53	0.21	0.550	0.10	0.991
	SD	0.03	0.05	0.06	0.05	0.08	0.006		
	CL	1.00	1.00	1.00	1.00	0.99	1.00		
TCEP		−1.76	0.36	1.84	1.81	0.45	0.374	0.15	0.984
	SD	0.04	0.07	0.09	0.08	0.11	0.009		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
ZE7		−2.08	−0.24	1.31	0.56	0.48	0.438	0.12	0.985
SD		0.03	0.06	0.07	0.06	0.09	0.008		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
(*b*)[a] Carbowax		−2.07	0.26	1.37	2.11		0.442	0.13	0.986
	SD	0.03	0.05	0.05	0.06		0.008		
	CL	1.00	1.00	1.00	1.00		1.00		
DEGS		−1.83	0.35	1.70	1.92		0.396	0.15	0.981
	SD	0.04	0.06	0.06	0.07		0.009		
	CL	1.00	1.00	1.00	1.00		1.00		
PPE		−2.55	0.19	0.98	0.59		0.552	0.11	0.991
	SD	0.03	0.04	0.04	0.05		0.007		
	CL	1.00	1.00	1.00	1.00		1.00		
TCEP		−1.75	0.23	2.12	1.94		0.379	0.16	0.982
	SD	0.04	0.06	0.06	0.08		0.010		
	CL	1.00	1.00	1.00	1.00		1.00		
ZE7		−2.07	0.38	1.61	0.70		0.442	0.13	0.983
	SD	0.03	0.05	0.05	0.06		0.008		
	CL	1.00	1.00	1.00	1.00		1.00		

[a] These are the preferred equations

In our view, equation (17) represents the most satisfactory regression equation we have been able to construct. Analysis of the constants follows closely our analysis using equation (10). Although the analysis *via* equation (17) is only slightly better than that through equation (10), we prefer the former because the R_2 parameter is a well-defined explanatory variable that refers to a specific type of solute–solvent phase interaction. From the method of determination of R_2, as well as from inspection of R_2 values, it follows that the rR_2 term in equation (17) is a quantitative measure of the ability of a solute to interact with the solvent through solute π (mainly) or n-electron pairs. Furthermore, R_2 is a reasonably independent explanatory variable; cross-correlation coefficients between R_2 and the other explanatory variables in equations (16) and (17) are:

π_2^*	μ_2^2	α_2^H	β_2^H	$\log L^{16}$
0.503	0.175	0.152	0.025	0.124

There is bound to be some correlation between R_2 and π_2^* because we have still not succeeded in subtracting all the polarisability contribution from π_2^*. However, equation (17) does go some way to so doing.

Table 10. The characterisation of stationary phases at 393 K

Phase	c[a]	d	s	a	l
Carbowax	−2.06	0.08	1.46	2.08	0.445
DEGS	−1.81	0.10	1.82	1.87	0.400
PPE	−2.54	0.02	1.05	0.55	0.555
TCEP	−1.73	0.02	2.21	1.90	0.382
ZE7	−2.54	0.16	1.50	0.72	0.438
	c	r	s	a	l
Carbowax	−2.07	0.26	1.37	2.11	0.442
DEGS	−1.83	0.35	1.70	1.92	0.396
PPE	−2.55	0.19	0.98	0.59	0.552
TCEP	−1.75	0.23	2.12	1.94	0.379
ZE7	−2.07	−0.38	1.61	0.70	0.442
	c	r	q	a	l
Carbowax	−1.92	0.85	0.068	2.56	0.444
DEGS	−1.63	1.08	0.084	2.47	0.398
PPE	−2.44	0.61	0.049	0.91	0.553
TCEP	−1.50	1.14	0.105	2.64	0.382
ZE7	−1.88	0.32	0.078	1.22	0.445

[a] Note that this constant includes the term $\log L^{\text{Decane}}$, see equation (8)

Conclusions

A number of equations can be constructed for the characterisation of gas chromatographic phases, and, indeed, any solvent phase, through a series of constants that refer to specific solute–solvent interactions. Our preferred equation (17) leads to a set of constants c, r, s, a, b, and l of which r refers to interactions through solute π- and n- electron pairs, s to interactions of the dipole–dipole and dipole-induced dipole type (together with some polarisability effects), a to solute hydrogen bond acid solvent hydrogen-bond base interactions, b to solute hydrogen-bond base/solvent hydrogen-bond acid interactions and l to a combination of general dispersion forces plus cavity effects. The methodology does not suffer from the technical deficiences of the Rohrschneider–McReynolds method, as outlined by Poole *et al.*,[6] and can be applied to any condensed phase. We list in Table 10, the characteristic constants for the Laffort phases, using equations that omit the β_2^H explanatory variable. The dipolarity of the three phases, using either π_2^* or μ^2 as a probe, is always in the order.

TCEP > DEGS > ZE7 > Carbowax > PPE

and the hydrogen-bond basicity of the phases, as given by the *a*-constant, is best represented by the order,

Carbowax > TCEP ≥ DEGS > ZE7 > PPE

The ability of the phase to interact with solutes specifically through π- and n- solute electron pairs is given by the *r*-constant in the rR_2 term. There is not very good quantitative agreement between equations (16) and (17), but both equations show that the fluorinated solvent ZE7 has the least ability to take part in π- and n-interactions.

We aim to extend this method of characterisation to other stationary phases and to common solvents, and hope to report further in the near future.

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Hydrogen Bonding. Part 14.† The Characterisation of Some *N*-Substituted Amides as Solvents: Comparison with Gas–Liquid Chromatography Stationary Phases

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Equations previously used for the characterisation of GLC stationary phases have been found to be equally suitable for the characterisation of common solvents. Thus equation (a) has been applied to solubility data for series of solutes on *N*-formylmorpholine (NFM), *N*-methylpyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA).

$$SP = c + r \cdot R_2 + s \cdot \pi_2^* + a \cdot \alpha_2^H + b \cdot \beta_2^H + l \cdot \log L^{16} \qquad (a)$$

In equation (a), SP can be log V_G° or log L for a series of solutes on a given solvent where V_G° is the specific retention volume and L is the Ostwald solubility coefficient. The solute parameters are R_2, a polarisability parameter; π_2^*, the solute dipolarity; α_2^H, the solute hydrogen-bond acidity; β_2^H, the solute hydrogen-bond basicity; and log L^{16} where L^{16} is the solute Ostwald solubility coefficient on n-hexadecane at 298 K.

It is shown that at 298 K all four amides have about the same dipolarity, as judged by the *s*-constant, and have nearly the same hydrogen-bond basicity, as judged by the $a \cdot \alpha_2^H$ term: all have zero hydrogen-bond acidity so that $b = 0$ in equation (a). Comparison can be made between results for NFM and NMP at 393 K and results for some GLC stationary phases. The two amides are less dipolar than tricyano(ethoxy)propane and diethyleneglycol succinate, about the same as Zonyl E-7® and Carbowax®, and more dipolar than poly(phenyl ether). The amides, however, have rather more hydrogen-bond basicity than any of the above five GLC phases. It is suggested that equation (a) can be used as the basis of method for characterising condensed phases, such that common solvents as well as GLC stationary phases can be included within the scope of the method.

A number of amides are industrially important solvents, and there are several reports dealing with vapour–liquid equilibria (VLE) of *N*-substituted amides, especially.[1–6] A particularly convenient method of obtaining VLE data for a series of solutes in a given amide is the gas-chromatographic procedure in which the amide acts as the stationary phase [1,3–6] The obtained specific retention volumes, either at the column temperature (V_G) or corrected to 273 K (V_G°), can be converted into infinite dilution activity coefficients of the solute in the amide solvent, γ_2^∞, at the column temperature, through well established equations [1,3–5] Alternatively, values of V_G can be transformed into Ostwald solubility coefficents, L_2, defined by equation (1), through the very simple equation (2) in which ρ_1 is the density

$$L_2 = \frac{\text{concentration of solute in solution}}{\text{concentration of solute in the gas phase}} \qquad (1)$$

$$L_2 = V_G\,\rho_1 \qquad (2)$$

of the amide at the column temperature. For measurements at essentially zero solute concentration, L_2 is effectively L_2°, and the concentration of solute in solution becomes identical with the concentration of solute in the pure solvent.

Medina and co-workers[3] used both their own gas–liquid chromatographic (GLC) measurements and literature data to obtain γ^∞-values for hydrocarbons in *N*-methylpyrrolidinone (NMP) and were able to account rather well for these γ^∞-values using the group contribution method, UNIFAC. A much more extensive set of solutes was studied by Gmehling and co-workers[4,6] with both the amides NMP and *N*-formylmorpholine (NFM). They obtained V_G°-values for a set of hydrocarbons, esters, aldehydes, ketones, and alcohols at various temperatures, and listed both V_G°- and γ^∞-values.

Now although the calculation of γ^∞-values using methods such as UNIFAC, UNIQUAT, and ASOG is well established, there is always an over-riding difficulty in the interpretation of parameters that refer to γ^∞: since γ^∞ is an equilibrium constant (or partition coefficient) between the bulk liquid solute and the solute at infinite dilution in the solvent, γ^∞ will contain not only contributions from solute–solvent interactions, but also those from solute–solute interactions. As has been pointed out before,[7] gas–liquid partition coefficients contain only the solute–solvent interaction terms, and hence are inherently easier to interpret than quantitites that refer to partition between the bulk liquid and the solvent. Since gas–liquid partition coefficients, either as values of L or as Henry's constants K^H, are convertible into γ^∞-values through the solute vapour pressure, P°, and since, in any case, P°-values are needed to obtain γ^∞

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† Part 13 is ref 10

Table 1. Solutes used in the correlations with V_G^o, Tables 2–5.

NFM	NMP
n-Pentane	n-Pentane
n-Hexane	n-Hexane
n-Heptane	n-Heptane
n-Octane	n-Octane
2,2,4-Trimethylpentane	2,2,4-Trimethylpentane
n-Decane	Cyclopentane
Cyclopentane	Cyclohexane
Methylcyclopentane	Methylcyclopentane
Cyclohexane	Methylcyclohexane
Methylcyclohexane	Benzene
Ethylcyclohexane	Toluene
1,4-*trans*-Dimethylcyclohexane	Hex-1-ene
1,4-*cis*-Dimethylcyclohexane	Oct-1-ene
1,2-*trans*-Dimethylcyclohexane	Methanol
1,2-*cis*-Dimethylcyclohexane	Ethanol
Benzene	Propan-2-ol
Toluene	t-Butyl alcohol
2-Xylene	Methyl acetate
3-Xylene	n-Propyl acetate
4-Xylene	Ethyl propanoate
Ethylbenzene	Ethyl butanoate
Isopropylbenzene	Vinyl acetate
Hex-1-ene	Acetone
Oct-1-ene	Butan-2-one
Methanol	Pentan-2-one
Ethanol	Pentan-3-one
Propan-2-ol	Butanal
Propan-1-ol	2-Methylpropanal
t-Butyl alcohol	Pentanal
Methyl acetate	(*E*)-But-2-enal
Ethyl acetate	Thiophene
n-Propyl acetate	
Ethyl propanoate	
Ethyl butanoate	
Vinyl acetate	
Acetone	
Butan-2-one	
Pentan-2-one	
Pentan-3-one	
4-Methylpentan-2-one	
Butanal	
2-Methylpropanal	
Pentanal	
(*E*)-But-2-enal	
Thiophene	

from V_G, it seems a theoretically simpler matter to deal with gas–liquid parameters (such as *L*, K^H, or V_G) than with γ^∞.

A number of equations have already been derived for the correlation of gas–liquid partition coefficients, as log *L* or log V_G, for a series of solutes in a given liquid phase.[8–10]

$$SP = c + d\cdot\delta_2 + s\cdot\pi_2^* + a\cdot\alpha_2^H + b\cdot\beta_2^H + l\cdot\log L^{16} \quad (3)$$

$$SP = c + r\cdot R_2 + s\cdot\pi_2^* + a\cdot\alpha_2^H + b\cdot\beta_2^H + l\cdot\log L^{16} \quad (4)$$

$$SP = c + r\cdot R_2 + q\cdot\mu_2^2 + a\cdot\alpha_2^H + b\cdot\beta_2^H + l\cdot\log L^{16} \quad (5)$$

In these equations SP can be log *L* or log V_G, *etc.*,† and the various explanatory variables are as follows: δ_2 is an empirical solute polarisability correction term taken as zero except for aromatic solutes ($\delta_2 = 1$) and polyhalogenated solutes ($\delta_2 = 0.5$), π_2^* is the solute dipolarity/polarisability, α_2^H and β_2^H are respectively the solute hydrogen-bond acidity and hydrogen-bond basicity, L^{16} is the solute Ostwald solubility coefficient on n-hexadecane at 298.15 K, R_2 is the solute molar refraction less that of an alkane of the same characteristic volume, and μ_2 is the solute dipole moment.[10] Equations (3) and (4) have usually given better correlations than has equation (5)

We start with the results of Gmehling and co-workers on NFM,[4] where V_G^o-values were obtained for 45 solutes at various temperatures, ranging from 303.4 to 373.4 K. Not all solutes were studied at all temperatures, and so we have interpolated values, and have also extrapolated values from either 303.4 K or 313.3 K down to 298.15 K to obtain a

Table 2. Correlations of log V_G^o for 45 solutes in NFM[4] by using equations (3) and (4)

T/K	*c*	*s*	*a*	*l*	*SD*[a]	*R*[b]
298.2	−0.313	2.311	4.335	0.708	0.122	0.985
	0.107[c]	0.069	0.216	0.031		
313.3	−0.349	2.153	3.916	0.656	0.114	0.985
	0.101	0.065	0.204	0.029		
332.7	−0.386	1.966	3.430	0.594	0.104	0.985
	0.091	0.059	0.184	0.026		
352.5	−0.425	1.811	2.998	0.536	0.099	0.983
	0.088	0.056	0.177	0.025		
373.4	−0.459	1.645	2.582	0.487	0.094	0.982
	0.083	0.053	0.167	0.024		

[a] Overall standard deviation in log V_G^o. [b] Overall correlation coefficient. [c] These are the standard deviations in the various constants.

Table 3. Correlations of log V_G^o for 45 solutes in NFM[4] by using equation (5).

T/K	*c*	*r*	*q*	*a*	*l*	*SD*	*R*
298.2	−0.040	1.756	0.159	4.156	0.621	0.330	0.890
313.3	−0.095	1.659	0.149	3.742	0.572	0.302	0.892
332.7	−0.155	1.534	0.136	3.266	0.516	0.271	0.895
352.5	−0.215	1.432	0.126	2.843	0.464	0.245	0.897
373.4	−0.264	1.337	0.114	2.425	0.417	0.217	0.902

Table 4. Correlations of log V_G^o for 31 solutes in NMP[4] by using equations (3) and (4).

T/K	*c*	*s*	*a*	*l*	*SD*	*R*
298.2	−0.159[a]	2.103	5.049	0.779	0.107	0.988
	0.141	0.073	0.241	0.046		
323.4	−0.212	1.883	4.298	0.680	0.096	0.987
	0.126	0.066	0.216	0.041		
333.2	−0.220	1.803	4.016	0.644	0.093	0.986
	0.121	0.063	0.208	0.040		
343.4	−0.246	1.730	3.777	0.612	0.092	0.986
	0.120	0.063	0.206	0.039		

[a] For log L_{NMP}, this constant takes the value −0.110

Table 5. Correlations of log V_G^o for 31 solutes in NMP[4] by using equation (5).

T/K	*c*	*r*	*q*	*a*	*l*	*SD*	*R*
298.2	−0.094[a]	1.422	0.142	5.172	0.785	0.300	0.902
323.4	−0.151	1.300	0.127	4.397	0.683	0.268	0.900
333.2	−0.164	1.254	0.121	4.109	0.647	0.255	0.900
343.4	−0.189	1.215	0.116	3.860	0.613	0.246	0.898

[a] For log L_{NMP}, this constant takes the value −0.045.

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† Note that log *L* and log V_G give rise to exactly the same constants in equations (3), (4), and (5) except for the *c*-constant which will differ by log ρ_1

Table 6. Values of log L at 298 K for solutes in NMP, DMF, and DMA.

Solute	NMP	DMF	DMA
Argon	−0.98[19]‡	−0.86[19]	
Hydrogen	−1.46[27]	−1.35[26,27]	
Nitrogen	−1.25[15]		
Ammonia	1.34[14]		
Carbon monoxide		−1.06[28]	
Methane	−0.61[16–19]	−0.52[19]	
Ethane	0.19[16,17,19]	0.22[14,19]	0.35[29]
Propane	0.65[14,16,17,19]	0.64[14]	0.81[29]
n-Butane	1.14[16,17,19]	1.08[14]	1.28[29]
Isobutane	0.88[14,16,17,19]		
n-Pentane	1.56[3,16,19]	1.51[19]	1.70[29]
2-Methylbutane	1.32[3]	1.39‡	1.45‡
n-Hexane	2.03[3,16,19]	1.99[19]	2.10[29]
n-Heptane	2.34[3,16,19]	2.36[19]	
n-Octane	2.77[3,16,19,20]	2.81[19,20]	2.90[20]
2,2,4-Trimethylpentane	2.29[3,21]	2.22[30]	
n-Nonane	3.05[3]		
Cyclopentane	1.92[3]		
Methylcyclopentane	2.20[3]		
Cyclohexane	2.33[3,16,21,22]	2.31[2,19]	
Methylcyclohexane	2.64[3,16]	2.58[19,30]	
Ethylcyclohexane	3.02[3]		
n-Propylcyclohexane	3.35[3]		
n-Butylcyclohexane	3.73[3]		
Ethene	0.29[16,18]		
Propene	0.91[18]		
But-1-ene		1.30[25]	
Pent-1-ene	1.65[1]	1.70[1,2,30]	1.72[1]
3-Methylbut-1-ene	1.50[1]	1.53[1]	1.56[1]
2-Methylbut-2-ene	1.86[1,22]	1.88[1]	1.89[1]
Hex-1-ene	2.06[4]	2.21[2]	
Oct-1-ene	2.91[4]		
Cyclopentene		2.22[2]	
Cyclohexene		2.68[2]	
Buta-1,3-diene	1.73[18]	1.68[24]	
2-Methylbuta-1,3-diene	2.14[1,22]	2.11[1,2]	2.12[1]
2,3-Dimethylbuta-1,3-diene		2.63[2]	
(*E*)-Penta-1,3-diene	2.24[1]	2.23[1]	2.25[1]
(*Z*)-Penta-1,3-diene	2.29[1]	2.27[1]	2.29[1]
Cyclopenta-1,3-diene		2.50[2]	
Pent-1-yne		2.54[2]	
Benzene	3.30[21,22]	3.26[31]	
Toluene	3.71[20]	3.64[20]	3.64[20]
Chloromethane		1.74[32]	
Chloroethane		2.01[29]	2.16[29]
Trichloromethane	3.84[24]		
Bromoethane		2.45[29,30]	2.53[29]
Iodomethane	2.76[23]	2.56[30]	2.66[23]
Iodoethane		2.86[29,30,33]	2.91[29]
Dimethyl ether		1.56[32]	
1,4-Dioxane	3.66[20]	3.72[20]	3.66[20]
Butanal	3.05[4]		
2-Methylpropanal	2.78[4]		
Pentanal	3.42[4]		
(*Z*)-But-2-enal	3.66[4]		
Acetone	2.77[4]		
Butan-2-one	3.42[20]	3.36[20]	3.28[20]
Pentan-2-one	3.47[4]		
Pentan-3-one	3.49[4]		
Methyl acetate	2.72[4]		
n-Propyl acetate	3.39[4]		
Ethyl propanoate	3.29[4]		
Ethyl butanoate	3.59[4]		
Vinyl acetate	3.05[4]		
Acetonitrile		3.41[34]	
Propanonitrile		3.67[29]	3.66[29]
Nitromethane		4.07[20]	4.02[20]
Methylamine		1.95[14]	
Dimethylamine		2.11[14]	
Trimethylamine		1.77[14]	
Triethylamine		2.62[33]	
Thiophene	3.43[4]		
Tetramethyltin	2.19[19]	2.15[19]	
Water		4.07[34]	
Methanol	3.43[4]		
Ethanol	3.78[20]	3.73[20]	3.82[20]
Propan-1-ol		4.08[a]	
Propan-2-ol	3.73[4]		
Butan-1-ol			4.84[a]
Butan-2-ol		4.16[a]	4.32[a]
t-Butyl alcohol	3.75[4]		
2,2,2-Trifluoroethanol		5.08[a]	4.99[a]
NMP	5.63§		
DMF		4.72§	
DMA			4.69§

[a] This work, see the text. ‡,§ — see footnotes in the text

coherent set of log V_G^o-values at five given temperatures. Explanatory variables are available for all 45 solutes,[9–13] and so we can apply equations (3), (4), and (5) at each temperature. Preliminary results suggested that the solute hydrogen-bond basicity, β_2^H was not important, as expected on general chemical grounds,† and so we can reduce the equations to four explanatory variables.

In the event, neither δ_2 in equation (3) nor R_2 in equation (4) were significant, and so both equations reduce to a three-parameter equation in π_2^*, α_2^H, and log L^{16}. The 45 solutes studied are listed in Table 1, and a summary of the regressions is in Table 2. Gmehling and co-workers[6] repeated some of their measurements of V_G^o but since there is excellent agreement between the old[4] and the new[6] sets, we took V_G^o all from the earlier set, for convenience. We also investigated use of equation (5), and details are collected in Table 3.

Equations (3) and (4), with δ_2, R_2, and β_2^H non-significant, reproduce the log V_G^o-values with an overall standard deviation of 0.1 log units, at the various temperatures given. Considering that this represents 'all solute' correlations, with no outliers at all, agreement between observed and calculated log V_G^o is quite satisfactory. These equations could therefore be used to predict further log V_G^o-values for a large number of solutes for which the necessary parameters are available.

Gmehling and co-workers also reported V_G^o-values in NMP for 31 solutes at 323.4, 333.2, and 343.4 K. We have similarly analysed these data, as log V_G^o, and have also extrapolated the V_G^o-values down to 298.2 K to obtain another regression equation. As with NFM, the parameters δ_2, R_2, and β_2^H in equations (3) and (4) were not significant, and the latter parameter was not significant in equation (5). Details are in Tables 4 and 5. Once again equations (3) and (4) reproduce the log V_G^o-values to *ca.* 0.1 log unit, with again no solutes being excluded. Thus equations (3) and (4) with the constants in Table 4 can be used to predict log V_G^o for further solutes.

In the case of NMP, there is a very considerable quantity of literature data available, mostly on vapour–liquid equilibria,[14–24] and we have recast these data in terms of log L_{NMP} at 298 K. Here, L_{NMP} refers to the Ostwald solubility coefficient of a solute in NMP solvent, see equation (1). Some of these data overlap with those of Gmehling and co-workers,[4,6] but in order to have as independent a set of results as possible,

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† Neither NFM nor NMP can act as hydrogen-bond acids, and hence solute hydrogen-bond basicity plays no part in any solute–solvent interactions.

‡ Calculated from high pressure data given in ref. 14.

§ Taking $\gamma' = 1$, by definition.

Table 7. Correlations of log L for 60 solutes[a] in NMP at 298 K

	c	d	r	s	q	a	l	SD	R
Equation (3)	−0.276	−0.170		2.157		5.134	0.870	0.148	0.995
	0.043	0.089		0.072		0.229	0.017		
Equation (4)	−0.283		0.454	1.998		5.085	0.851	0.137	0.996
	0.040		0.121	0.072		0.212	[illegible]		
Equation (5)	−0.195		1.458		0.126	5.676	0.839	0.247	0.985
	0.071		0.198		0.009	0.377	0.029		

[a] These are the 60 data entries in Table 6.

Table 8. Correlations of log L for 53 solutes[a] in DMF at 298 K.

	c	d	r	s	q	a	l	SD	R
Equation (3)	−0.231	−0.366		2.561		4.612	0.839	0.149	0.994
	0.047	0.109		0.090		0.165	0.021		
Equation (4)	−0.207			2.482		4.585	0.829	0.164	0.993
	0.051			0.096		0.182	0.023		
Equation (5)	−0.145		1.387		0.119	5.830	0.823	0.233	0.986
	0.072		0.193		0.008	0.244	0.034		

[a] These are the 53 data entries in Table 6

Table 9. Correlations of log L for 27 solutes[a] in DMA at 298 K.

	c	d	r	s	q	a	l	SD	R
Equation (3)	−0.045	−0.346		2.229		4.984	0.802	0.169	0.992
	0.114	0.168		0.128		0.261	0.052		
Equation (4)	−0.001			2.196		4.864	0.782	0.181	0.991
	0.120			0.136		0.271	0.054		
Equation (5)	−0.003		1.158		0.115	6.222	0.796	0.145	0.994
	0.096		0.153		0.006	0.201	0.044		

[a] These are the 27 data entries in Table 6

Table 10. Comparison of characteristic constants for solvents and GLC stationary phases, equation (4).

Solvent	T/K	$r \cdot R_2$	$s \cdot \pi_2^*$	$a \cdot \alpha_2^H$	$l \cdot \log L^{16}$
NFM[a]	298		2.31	4.33	0.708
NMP[b]	298	0.45	2.00	5.09	0.851
DMF[c]	298		2.48	4.58	0.829
DMA[d]	298		2.20	4.86	0.782
NFM[e]	393		1.52	2.24	0.442
NMP[e]	393		1.42	2.70	0.472
Carbowax[f]	393	0.26	1.37	2.11	0.442
DEGS[f]	393	0.35	1.70	1.92	0.396
PPE[f]	393	0.19	0.98	0.59	0.552
TCEP[f]	393	0.23	2.12	1.94	0.379
ZE7[f]	393	−0.38	1.61	0.70	0.442

[a] Table 2. [b] Table 7. [c] Table 8. [d] Table 9 [e] Extrapolated data from results in Tables 2 and 4. [f] From ref 10

we have used Gmehling's data as an additional source only.* Details of the log L_{NMP}-values are in Table 6, and a summary of our obtained regression equations is in Table 7. Bearing in mind the different set of solutes studied, there is quite good agreement between the various equations in Table 7 and those given before in Tables 4 and 5 (the 31 solutes of Tables 4 and 5 are a subset of the 60 solutes in Table 7).

We shall consider in more detail the actual constants listed in Table 7, but now set out values of log L for a range of solutes in N,N-dimethylformamide (DMF) and in N,N-dimethylacetamide (DMA). These are two additional N-substituted amides for which there are a large number of log L-values at 298 K that can be obtained from a variety of additional literature sources[25-34] Values of log L_{DMF} and log L_{DMA} are collected in Table 6. Although there are a reasonable number of hydrogen-bond bases in these two sets, there are but few hydrogen-bond acids. Since these are very important in characterising phases or solvents that are themselves hydrogen-bond bases, we determined a few values of log L_{DMF} and log L_{DMA} for alcohols by the method of headspace analysis, exactly as we have detailed before.[11]

We have to hand log L-values for 53 assorted solutes in DMF and for 27 solutes in DMA (Table 6), and give summaries of the obtained regression equations in Tables 8 and 9 Bearing in mind the diverse sources of the data used, the correlation equations (3) and (4) lead to quite satisfactory results These equations could be used as 'all solute' correlations to predict further log L-values for a variety of solutes For both DMF and DMA the $r \cdot R_2$ term in equation (4) is not significant, but this

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* We calculated log L_{NMP} at 298 K by using the equation log L_{NMP} = log V_G^0 + 0.0499

Table 11. Solute parameters used in the regressions

No	Compound	δ_2	R_2	μ_2^2	π_2^*	α_2^H	log L^{16}
3	Argon	0.00	0.000	0.000	0.00	0.00	−0.688
11	Hydrogen	0.00	0.000	0.000	0.00	0.00	−1.200
15	Nitrogen	0.00	0.000	0.000	0.00	0.00	−0.978
18	Ammonia	0.00	0.139	2.074	0.34	0.10	0.680
21	Carbon monoxide	0.00	0.000	0.010	0.02	0.00	−0.812
50	Methane	0.00	0.000	0.000	0.00	0.00	−0.323
51	Ethane	0.00	0.000	0.000	0.00	0.00	0.492
52	Propane	0.00	0.000	0.000	0.00	0.00	1.050
53	n-Butane	0.00	0.000	0.000	0.00	0.00	1.615
54	Isobutane	0.00	0.000	0.000	0.00	0.00	1.409
55	n-Pentane	0.00	0.000	0.000	0.00	0.00	2.162
56	2-Methylbutane	0.00	0.000	0.000	0.00	0.00	2.013
58	n-Hexane	0.00	0.000	0.000	0.00	0.00	2.668
63	n-Heptane	0.00	0.000	0.000	0.00	0.00	3.173
72	n-Octane	0.00	0.000	0.000	0.00	0.00	3.677
86	2,2,4-Trimethylpentane	0.00	0.000	0.000	0.00	0.00	3.120
91	n-Nonane	0.00	0.000	0.000	0.00	0.00	4.182
126	n-Decane	0.00	0.000	0.000	0.00	0.00	4.686
284	Cyclopentane	0.00	0.263	0.000	0.00	0.00	2.447
288	Methylcyclopentane	0.00	0.225	0.000	0.00	0.00	2.771
287	Cyclohexane	0.00	0.305	0.000	0.00	0.00	2.913
293	Methylcyclohexane	0.00	0.244	0.000	0.00	0.00	3.252
308	1,2-*trans*-Dimethylcyclohexane	0.00	0.227	0.000	0.00	0.00	3.550
307	1,2-*cis*-Dimethylcyclohexane	0.00	0.281	0.000	0.00	0.00	3.760
312	1,4-*trans*-Dimethylcyclohexane	0.00	0.191	0.000	0.00	0.00	3.550
311	1,4-*cis*-Dimethylcyclohexane	0.00	0.204	0.000	0.00	0.00	3.700
313	Ethylcyclohexane	0.00	0.263	0.000	0.00	0.00	3.590
314	n-Propylcyclohexane	0.00	0.257	0.000	0.00	0.00	3.930
315	n-Butylcyclohexane	0.00	0.255	0.000	0.00	0.00	4.270
370	Ethene	0.00	0.107	0.000	0.08	0.00	0.289
371	Propene	0.00	0.103	0.134	0.08	0.00	0.946
373	But-1-ene	0.00	0.100	0.116	0.08	0.00	1.491
380	Pent-1-ene	0.00	0.093	0.116	0.08	0.00	2.013
383	3-Methylbut-1-ene	0.00	0.063	0.250	0.08	0.00	1.910
379	2-Methylbut-2-ene	0.00	0.159	0.116	0.08	0.00	2.190
392	Hex-1-ene	0.00	0.078	0.116	0.08	0.00	2.547
409	Oct-1-ene	0.00	0.094	0.116	0.08	0.00	3.591
387	Buta-1,3-diene	0.00	0.320	0.068	0.20	0.00	1.543
389	2-Methylbuta-1,3-diene	0.00	0.313	0.144	0.20	0.00	2.130
390	2,3-Dimethylbuta-1,3-diene	0.00	0.352	0.270	0.20	0.00	2.690
385	(*E*)-Penta-1,3-diene	0.00	0.385	0.342	0.20	0.00	2.250
384	(*Z*)-Penta-1,3-diene	0.00	0.345	0.250	0.20	0.00	2.280
427	Cyclopentadiene	0.00	0.417	0.281	0.35	0.00	2.222
454	Pent-1-yne	0.00	0.172	0.740	0.20	0.13	2.010
751	Benzene	1.00	0.610	0.000	0.59	0.00	2.803
752	Toluene	1.00	0.601	0.130	0.55	0.00	3.344
753	2-Xylene	1.00	0.663	0.384	0.51	0.00	3.937
754	3-Xylene	1.00	0.623	0.160	0.51	0.00	3.864
755	4-Xylene	1.00	0.613	0.000	0.51	0.00	3.858
766	Ethylbenzene	1.00	0.613	0.348	0.53	0.00	3.765
768	Isopropylbenzene	1.00	0.602	0.152	0.53	0.00	4.105
551	Chloromethane	0.00	0.249	3.764	0.40	0.00	1.163
552	Dichloromethane	0.50	0.387	2.624	0.82	0.13	2.019
553	Trichloromethane	0.50	0.425	1.020	0.58	0.20	2.480
605	Bromoethane	0.00	0.366	4.121	0.48	0.00	2.120
651	Iodomethane	0.00	0.676	2.624	0.40	0.00	2.106
655	Iodoethane	0.00	0.640	2.924	0.50	0.00	2.573
1351	Dimethyl ether	0.00	0.000	1.664	0.27	0.00	1.090
1421	1,4-Dioxane	0.00	0.329	8.500	0.67	0.00	2.797
1553	Butanal	0.00	0.187	7.398	0.65	0.00	2.270
1554	2-Methylpropanal	0.00	0.144	7.290	0.65	0.00	2.060
1555	Pentanal	0.00	0.163	6.760	0.65	0.00	2.770
1570	(*E*)-But-2-enal	0.00	0.387	12.530	0.75	0.00	2.570
1651	Acetone	0.00	0.179	8.294	0.71	0.04	1.760
1653	Pentan-2-one	0.00	0.143	7.290	0.65	0.00	2.755
1654	Pentan-3-one	0.00	0.154	7.398	0.65	0.00	2.811
1662	4-Methylpentan-2-one	0.00	0.111	7.290	0.65	0.00	3.050
1860	Methyl acetate	0.00	0.142	2.958	0.60	0.00	1.960
1861	Ethyl acetate	0.00	0.106	3.168	0.55	0.00	2.376
1862	n-Propyl acetate	0.00	0.092	3.420	0.55	0.00	2.878
1882	Ethyl propanoate	0.00	0.087	3.240	0.55	0.00	2.881

Table 11 (*continued*)

No	Compound	δ_2	R_2	μ_2^2	π_2^*	α_2^H	log L^{16}
1888	Ethyl butanoate	0.00	0.106	3.240	0.55	0.00	3.379
1880	Vinyl acetate	0.00	0.223	2.890	0.55	0.00	2.600
2201	Acetonitrile	0.00	0.237	15.366	0.75	0.09	1.560
2202	Propanonitrile	0.00	0.162	16.000	0.70	0.00	2.050
2101	Nitromethane	0.00	0.313	11.972	0.85	0.12	1.892
2301	Methylamine	0.00	0.250	1.664	0.32	0.00	1.300
2321	Dimethylamine	0.00	0.189	0.941	0.25	0.00	1.600
2340	Trimethylamine	0.00	0.140	0.375	0.15	0.00	1.620
2346	Triethylamine	0.00	0.101	0.490	0.15	0.00	3.077
3601	Thiophene	1.00	0.687	0.325	0.60	0.00	2.943
4561	Tetramethyltin	0.00	0.000	0.000	0.00	0.00	2.920
3351	Water	0.00	0.000	3.497	0.43	0.65	0.260
3352	Methanol	0.00	0.278	2.890	0.40	0.37	0.922
3353	Ethanol	0.00	0.246	2.856	0.40	0.33	1.485
3354	Propan-1-ol	0.00	0.236	2.822	0.40	0.33	2.097
3355	Propan-2-ol	0.00	0.212	2.756	0.40	0.32	1.821
3356	Butan-1-ol	0.00	0.224	2.756	0.40	0.33	2.601
3357	Butan-2-ol	0.00	0.217	2.723	0.40	0.32	2.338
3359	t-Butyl alcohol	0.00	0.180	2.657	0.40	0.32	2.018
3497	2,2,2-Trifluoroethanol	0.50	0.015	4.121	0.73	0.57	1.224
2854	*N*-methylpyrrolidin-2-one	0.00	0.481	16.728	0.92	0.00	4.320
2503	*N*,*N*-dimethylformamide	0.00	0.367	14.900	0.88	0.00	3.173
2509	*N*,*N*-dimethylacetamide	0.00	0.363	13.838	0.88	0.00	3.717

may be due to lack of solutes with high R_2-values in the correlations. In general, however, the correlation equations for DMF and DMA follow closely those for NMP (*cf.* Tables 8 and 9 with Table 7) This is exactly as expected, because all three of these amides are quite dipolar and all three are quite strong hydrogen-bond bases. From the results shown in Tables 7–9, the amides NMP, DMF, and DMA are of quite similar dipolarity with *s*-constants 2.00, 2.48, and 2.20, respectively, in equation (4), and *q*-constants 0.126, 0.119, and 0.115, respectively, in equation (5). The hydrogen-bond basicities of these amides are also very similar, being for NMP, DMF, and DMA in the sequence of *a*-values 5.09, 4.58, and 4.86 (compare the solvent hydrogen-bond β_1 basicity values of 0.77, 0.69, and 0.76, respectively)[35] The other amide studied, NFM, is of about the same dipolarity but of somewhat lower basicity than NMP, DMF, and DMA, see the collected results in Table 10.

We have previously[10] characterised a number of stationary phases used in gas–liquid chromatography (GLC), and it would be of considerable interest to compare such phases with common solvents. The GLC phases were studied at 393 K, but we have found that the constants in equation (4) obtained for NFM and NMP at lower temperatures can be extrapolated to 393 K through excellent plots against $1/T$(K); see Table 10

It is quite clear from results in Table 10, and from results in Tables 2–5, that characteristic constants in equations such as (4) alter markedly with temperature In general, it is to be expected that solute solvent interactions would decrease with a rise in temperature, simply as a result of increased thermal motion. Indeed, hydrogen-bond complexation constants between a given acid and a given base do invariably decrease with increase in temperature. In the present case, any decrease in solute–solvent interactions could be due both to effects on the solute and on the solvent. We have no means of separating these, and hence adopt the convention that any change in a characteristic constant with temperature is due to a change in solvent property only This does not matter as regards inter-solvent comparisons, which is what we are concerned with, but it would be important if absolute values of solvent properties were required

In Table 10 we report constants in equation (4) at 393 K for NFM and NMP, together with those for five GLC phases[10]

Table 12. Calculation of the solute–solvent interactions that influence log L-values in DMF at 298 K, *via* equation (4)

Solute	$s\ \pi_2^*$	$a\ \alpha_2^H$	l log L^{16}	Dispersion[a]	Cavity[a]
Butane	0	0	1.35	3.38	−1.47
Octane	0	0	3.05	6.42	−2.69
Benzene	1.46	0	2.32	4.29	−1.56
Propanone	1.76	0	1.46	2.65	−1.19
Propan-1-ol	0.99	1.51	1.74	2.86	−1.29

[a] Obtained by analysis of the l log L^{16} term according to Abraham and Fuchs[36] The two effects do not exactly add up to l log L^{16} because of omission of a constant term, and a small dipole-induced dipole term

Our above-stated comments on temperature effects are very relevant: at 298 K both NFM and NMP appear to be more dipolar and very much more basic than any of the GLC phases However, at a common temperature of 393 K, NFM and NMP are somewhat less dipolar than tricyano(ethoxy)propane (TCEP), diethyleneglycol succinate (DEGS), and Zonyl E-7® (ZE7), although more dipolar than poly(phenyl ether) (PPE). At 393 K, the hydrogen-bond basicity of NFM and NMP is not a great deal larger than that of the more basic GLC phases: Carbowax®, TCEP, and DEGS The l-constant represents a combination of cavity effects and general dispersion interactions,[10] but as regards GLC separations its importance lies in the separation of members of homologous series The larger the l-constant, the greater will be the separation. There are no very remarkable values of the l-constant in Table 10 as might be expected, PPE has a reasonably high value of 0.55, DEGS and TCEP the lowest values, with the amides and the other GLC phases in between.

We can conclude that equations (3)–(5) yield useful information on solute–solvent interactions and that the constants in equation (4), especially, can be used to characterise solvents in terms of such interactions Together with previous results,[10] we can demonstrate that the constants in equation (4) are useful in a general method for characterising condensed phases, and lead, for the first time, to a comparison of GLC stationary phases with common solvents

Finally, we collect in Table 11 all the solute parameters used in the regression analysis. Note that, for 1,4-dioxane, an 'effective' value of 8.5 is used for μ_2^2 and one of 0.67 for π_2^*.

Solute–Solvent Interactions.—Our preferred equation (4) can be used to separate out the various contributions to the observed log *L*-values for any particular solute. Details for solutes in DMF at 298 K are in Table 12, with a number of compounds taken as examples. The $l \cdot \log L^{16}$ term is always very large, and only if the solute π_2^*-value or α_2^H-value is substantial do the $s \cdot \pi_2^*$ and $a \cdot \alpha_2^H$ terms make comparable contributions. Abraham and Fuchs[36] separated out various contributions to the $\log L^{16}$ term itself, the two main ones being an exoergic dispersion interaction that leads to an increase in $\log L^{16}$, and an endoergic cavity term that leads to a decrease in $\log L^{16}$. If we assume that, as a first approximation, the relative sizes of these effects is the same in DMF, we can further subdivide the $l \cdot \log L^{16}$ term into dispersion and cavity effects; see Table 12. The results show very clearly that, of the exoergic solute–solvent effects we have considered, the general dispersion interaction is always the most important.

In terms of GLC analyses, separations of adjacent members of an homologous series will be governed by differences in dispersion interactions and cavity effects. These two influences are together contained in the $l \cdot \log L^{16}$ term—the larger the value of *l*, the greater will be the separation between members of a homologous series. Interactions of the dipole–dipole and hydrogen-bonding types will obviously influence separations of solutes of different functionalities, even though in general they are not so large as general dispersion effects.

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Hydrogen bonding

XV. A new characterisation of the McReynolds 77-stationary phase set

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ABSTRACT

The following equation has been applied to all the phases in the McReynolds 77-stationary phase set

$$\log V_G^0 = c + rR_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l\log L^{16}$$

In this equation, V_G^0 is the specific retention volume for a series of solutes on a given stationary phase, and the explanatory variables are R_2 a modified solute molar refraction, π_2^* the solute dipolarity, α_2^H the solute hydrogen-bond acidity, β_2^H the solute hydrogen-bond basicity, and $\log L^{16}$ where L^{16} is the solute Ostwald absorption coefficient on hexadecane at 25°C. The constants in the equation are obtained by multiple linear regression analysis, using about 150 data points in each regression, and values of r, s, a, b and l are regarded as characteristic constants of the phases that serve to classify the 77-phase set. It is shown that the classification of the phases into clusters is in accord with chemical principles, and is in excellent agreement with previous work using hierarchical clustering, minimum spanning tree techniques, and pattern cognition methods. The above equation allows the factors that lead to gas–liquid chromatographic separations to be identified, and provides quantitative information on the various solute–solvent interactions that give rise to these factors.

INTRODUCTION

The largest sets of gas chromatographic retention data are those of McReynolds, who determined retention volumes (V_G^0) and retention indices (I) of 376 solutes on 77 phases at two temperatures [1], and retention indices of 10 solutes on 226 phases at 120°C [2]. Numerous workers have classified both the 77-phase set and the 226-phase set by various methods. McReynolds himself [2] assigned a single polarity index to the 226 stationary phases, using the sum of the ΔI values for benzene, butanol, 2-pentanone, nitropropane and pyridine Later workers refined this method [3] and also calculated a polarity index from the Gibbs energy of solvation of the methylene increment, $\Delta G_s^0(CH_2)$, on a given stationary phase [4]. Other workers assigned a number of characteristic parameters to phases. Thus Figgins *et al.* [5] derived ΔG_s^0 values for six functional groups on 75 of the 226-phase set, and Fellous *et al.* [6] assigned a polarity index (ρ^*) to the same six functional groups on 72 of the 226-phase set.

Various sophisticated methods have been used to classify the McReynolds phases into groups. They include nearest neighbour techniques [7], information theory [8], numerical taxonomy [8,9], principal components analysis [10], pattern cognition methods [11,12] and factor analysis [13]. All these methods reduce the 226-phase set or the 77-phase set to a smaller number of clusters each of which represents a collection of similar phases. This is a very useful and helpful outcome, but, in addition, several of these methods lead to the estimation of the number of factors that influence chromatographic retention data. Wold and Andersson [10] suggested three main factors, (1) polarity, (2) a factor difficult to identify and (3) a factor that was due to hydrogen-bonding of the phase with alcohols. Chastrette [13] showed that five factors accounted for 99% of the total variance: three factors were difficult to account for, and the other two were polarity and a factor connected to, but not identical with, hydrogen-bonding. A polarity factor was identified by McCloskey and Hawkes [14], who also suggested that a factor related to the ability of a phase to retain *cis*-hydrindane was important.

It seems, therefore, that although a single "polarity" parameter is still often used to characterise stationary phases [4,15], analytical methods suggest that a number of factors must be involved, perhaps three [10] to five [13], although identification of these factors with particular chemical interactions has not proved possible. Our analysis starts with a model for solvation of a solute, and then deduces from the model various possible interactions. Once these interactions are set out, the necessary parameters required to quantify these interactions have to be obtained (from data other than the chromatographic results to be analysed). These parameters then, in effect, take the place of the various factors identified by methods such as principal components analysis [10] or factor analysis [13].

On our model, the process of dissolution of a gaseous solute into a liquid stationary phase or solvent can conceptually be broken down into a number of stages, *viz.* (1) the creation of a cavity in the phase of suitable size, (2) reorganisation of solvent molecules round the cavity and (3) introduction of the solute into the cavity. The first stage involves the endoergic breaking of solvent–solvent bonds: the larger the solute, the more bonds are broken to create a cavity, and the more endoergic is the process. On this step alone, the larger the solute the less soluble it would be, and the smaller would be the retention volume (V_G^0) or the Ostwald solubility coefficient (L). The second stage is not very important in terms of Gibbs energy, although it probably is in terms of enthalpy and entropy. In the third stage, various solute–solvent interactions will be set up, all of which will be exoergic and will lead to increased solubility of the solute. Possible interactions include: (i) General dispersion interactions that will invariably be larger or more exoergic the larger is the solute. It is these interactions that account for the solubility of inert solutes such as the alkanes. And since such solutes are more soluble the larger they are, these dispersion interactions must be strong enough to overcome the endoergic cavity effect. (ii) Dipolar interactions, including dipole–dipole or dipole–induced dipole effects. (iii) Hydrogen-bonding interactions between solute acid–solvent base and solute base–solvent acid. (iv) Possible specific interactions involving *π*- or *n*-electron pairs. In view of this complexity of solute–solvent systems, it is not surprising that only limited identification of the factors governing such systems has hitherto been made, but it is clearly of considerable importance if stationary phases could be characterised in terms of these fundamental interactions.

We have now developed solute parameters that, we believe, correspond to either simple fundamental properties, or to known combinations of properties [16–23]. These are as follows: R_2 a modified polarisability parameter that characterises the ability of a solute to interact via *π*- or *n*-electron pairs [16,17], δ_2 a polarisability correction term [18–20] taken as zero except for polyhalogenated aliphatics (0.5) or aromatics (1.0) and which is probably an approximation to R_2, π_2^* the solute dipolarity[a] [18–20], α_2^H the solute hydrogen-bond acidity [21], β_2^H the solute hydrogen-bond basicity [22] and log L^{16} where L^{16} is the solute Ostwald solubility coefficient on hexadecane at 25°C [23]. This latter parameter is a combination of a cavity term and a general dispersion interaction term [24]. Various multiple linear regression equations can then be constructed to account for solubility-related properties (SP) of a series of solutes in a given solvent or stationary phase, eqns. 1–3, where SP can be V_G^0, L (or K, the gas–liquid partition coefficient), but *cannot* be the retention index.

$$\log \mathrm{SP} = c + rR_2 + s\pi_2^* - a\alpha_2^H + b\beta_2^H + l \log L^{16} \qquad (1)$$

$$\log \mathrm{SP} = c + d\delta_2 + s\pi_2^* - a\alpha_2^H + b\beta_2^H + l \log L^{16} \qquad (2)$$

$$\log \mathrm{SP} = c + rR_2 + q\mu_2^2 - a\alpha_2^H + b\beta_2^H + l \log L^{16} \qquad (3)$$

In eqn. 3, μ_2 is the solute dipole moment. We have applied eqns. 1–3 to a number of sets of gas chromatographic retention data, and also to the solubility of gases and vapours in some common solvents, with considerable success [16,17,25]. Now since the parameters, or explanatory variables, in eqns. 1–3 represent solute properties, the various constants found by multiple linear regression analyses, will represent solvent or stationary phase properties. The most useful equation in this respect is eqn. 1 for which we have r the tendency of the phase to interact with *π*- and *n*-solute electron pairs, s the phase dipolarity, a the phase hydrogen-bond basicity (because basic phases will interact with acidic solutes), b the phase hydrogen-bond acidity, and l representing a combination of general dispersion interactions and cavity effects. These constants r, s, a, b and l (together with possibly q, another measure of phase dipolarity) thus serve to characterise the phase in terms of particular chemical interactions. That up to five constants are needed to characterise a given stationary phase reflects the complexity of solute–solvent interactions. The number of constants,

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[a] We use this term in the Kamlet–Taft sense [18] namely the ability of a molecule to undergo molecular interactions of a dipole–dipole or a dipole-induced dipole nature. Thus dioxane and 1,4-dichlorobenzene are regarded as "dipolar", even though they have no permanent dipole moment.

however, is certainly in accord with principal components analysis [10] and factor analysis [13], which both show that several factors are required to account for retention data.

RESULTS

We now apply eqns. 1-3 to the data of McReynolds [1] on 367 solutes on 77 phases. Of the solutes studied, we have all the necessary parameters for about 160, and our analysis uses up to 157 solutes on the 77 phases at two temperatures[a]. As pointed out, above, retention indices are not suitable for use as SP values in eqns. 1-3, and all our analyses are in terms of the log V_G^0 values reported by McReynolds [1]. We first test, as a necessary preliminary, whether the solute parameters used as explanatory variables are, indeed, independent. In Table I are given the correlation constants, R, between the explanatory variables in eqn. 1. It can be seen that the intercorrelations are insignificant, with the possible exception of that between π_2^* and β_2^H for which $R = 0.474$ (and $R^2 = 0.225$ only). We also test eqns. 1-3 for two typical phases, ethyleneglycol adipate and dibutyltetrachlorophthalate; results are in Table II. Both the overall correlation coefficient and the standard deviation, S.D., are almost identical for eqn. 1 and eqn. 2. Since the molar refraction parameter R_2 can be identified with a specific type of solute-solvent interaction, whereas the empirical δ_2 parameter cannot, we shall list results in terms of the preferred eqn. 1 only. Although the correlations in terms of eqn. 3 are quite useful, they are in all cases not as good as eqn. 1, and so we shall not give all the details of eqn. 3, but list where necessary values of the q constant only.

TABLE I

CORRELATION COEFFICIENTS BETWEEN THE EXPLANATORY VARIABLES, FOR THE 155-SOLUTE DATA SET USED FOR FLEXOL

	R_2	π_2^*	α_2^H	β_2^H
π_2^*	0.295			
α_2^H	0.111	−0.210		
β_2^H	−0.243	0.474	0.247	
log L^{16}	0.016	−0.171	−0.061	−0.169

The results of application of eqn. 1 to the entire set of stationary phases at 120°C are summarised in Table III, where also the q constant in eqn. 3 is given. For a few phases, data were available at 80 and 100°C only, and we have estimated the various constants at 120°C from values at the lower temperatures. For completeness, we applied the various equations to results at the other given temperatures used in the work of McReynolds [1], and details are shown in Table IV. Before attempting to

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[a] McReynolds studied a large number of difunctional compounds for which we lack most of the required parameters in eqns 1 and 2, these include many formals, acetals, dihydric alcohols, etc. Note that not all solutes were studied on all phases, so that the number of solutes used in our regressions varies from 130 to 157

TABLE II

COMPARISON OF EQNS 1–3 IN REGRESSIONS OF LOG V_G^0 AT 120°C

S.D. = Overall standard deviation, *R* = overall correlation coefficient, *n* = number of solutes

Eqn	*c*	*r*	*d*	*s*	*q*	*a*	*l*	S.D.	*R*	*n*
Ethyleneglycol adipate										
1	−0.900	0.357		1.425		1.720	0.443	0.093	0.9857	143
	0.038[a]	0.048		0.048		0.053	0.007			
2	−0.871		0.116	1.480		1.867	0.438	0.094	0.9849	143
	0.038		0.030	0.047		0.053	0.007			
3	−0.360	0.784			0.073	1.405	0.394	0.160	0.9476	143
	0.055	0.079			0.006	0.089	0.013			
Dibutyltetrachlorophthalate										
1	−0.615	0.249		0.692		0.600	0.600	0.048	0.9969	150
	0.019	0.025		0.025		0.028	0.004			
2	−0.615		0.112	0.752		0.687	0.599	0.050	0.9967	150
	0.020		0.016	0.025		0.029	0.004			
3	−0.410	0.547			0.038	0.420	0.586	0.070	0.9920	150
	0.024	0.039			0.003	0.040	0.006			

[a] These are the standard deviations in the constants

classify the phases, we note that the correlation eqn. 1 yields results that are reasonably good for "all solute" correlations, and, as we shall see, these results are chemically sensible. Thus the *s*, *a* and *b* constants, when statistically significant, are always positive, because increase in solute–solvent interactions must lead to an increase in solubility of the gaseous solute, and hence to an increase in V_G^0. The *r* constant is nearly always positive, except in the case of fluorinated phases, *e.g.* Dow fluid 1265, where the polarisability is even less than in hydrocarbon systems. As mentioned in the introduction, the *l* constant reflects a combination of an endoergic cavity term and an exoergic solute–solvent general dispersion interaction term. The latter always dominates, giving rise to positive *l* constants.

The effect of temperature is very important with regard to characterisation of solubility-related phenomena, although it has generally been overlooked as regards characterisation of stationary phases. In general, the main characteristic constants *s*, *a*, *b* and *l*, all decrease, often quite markedly, with temperature. Now if the relevant solute–solvent interactions are not only exoergic but are exothermic as well, the Van 't Hoff equation requires that these interactions will decrease with increase in temperature, hence leading to a decrease in the numerical values of the characteristic constants. On thermodynamic grounds it thus follows that any correlation equation set up in terms of solute–solvent or solute–stationary phase interactions must incorporate this temperature dependence. Our eqn. 1 does so via the characteristic constants.

As a final check on our method of analysis, we can compare regression equations obtained from the set of solutes used by McReynolds [1] with those [16] from the quite different set of solutes used by Patte *et al.* [26] for Carbowax 1540, diethyleneglycolsuccinate, polyphenyl ether and Zonyl-E7. Details are in Table V, and show that there is very good agreement between the two sets of regressions using eqn. 1.

TABLE III

CLASSIFICATION OF PHASES AT 120 °C

S.D. and *R* are the overall deviation and correlation coefficient on application of eqn 1 to log V_G^0. The number of data points is No. q = The coefficient of μ_2^2 in eqn 3

Group	Stationary phase	Characteristic constants in eqn 1					S.D.	*R*	No	*q*
		c	*r*	*s*	*a*	*l*				
1	Squalane[a]	−0.33	0.12	0.02	0.00	0.619	0.026	0.9990		0.001
2	Apiezon M	−0.45	0.26	0.10	0.11	0.600	0.035	0.9982	147	0.006
	Apiezon N	−0.48	0.27	0.12	0.10	0.601	0.037	0.9978	149	0.008
	Apiezon J	−0.48	0.27	0.13	0.13	0.594	0.034	0.9984	148	0.010
	Apiezon L	−0.48	0.27	0.14	0.13	0.596	0.036	0.9982	149	0.006
3	Versilube P50	−0.37	0.03	0.25	0.17	0.538	0.036	0.9978	149	0.010
	SE-31	−0.36	0.03	0.24	0.17	0.520	0.039	0.9971	156	0.012
	SE-30	−0.32	0.03	0.27	0.29	0.523	0.040	0.9971	152	0.014
	SE-30 NPGA	−0.40	0.06	0.27	0.33	0.525	0.042	0.9969	152	0.016
	SE-52	−0.38	0.06	0.32	0.22	0.532	0.041	0.9971	155	0.018
4	Dioctylsebacate	−0.35	0.12	0.49	0.79	0.594	0.047	0.9967	153	0.029
	Di-2-ethylhexylsebacate	−0.36	0.13	0.51	0.83	0.591	0.045	0.9969	153	0.028
	Tripelargonate	−0.42	0.16	0.53	0.82	0.583	0.051	0.9964	151	0.032
	Isooctyldecyladipate	−0.37	0.13	0.55	0.81	0.586	0.048	0.9964	154	0.031
	Di-2-ethylhexyladipate	−0.36	0.13	0.55	0.87	0.590	0.047	0.9967	150	0.030
	Diisodecylphthalate	−0.52	0.13	0.65	0.73	0.589	0.055	0.9958	155	0.038
	Dioctylphthalate	−0.52	0.14	0.67	0.77	0.587	0.053	0.9960	153	0.039
5	Ucon LB-1715	−0.56	0.18	0.71	1.22	0.543	0.072	0.9923	153	0.038
	Flexol 8N8	−0.48	0.11	0.73	1.27	0.573	0.065	0.9932	155	0.043
	Pluronic L81	−0.49	0.20	0.77	1.29	0.537	0.075	0.9913	152	0.040
6	Polyphenyl ether, 5 rings	−0.70	0.21	0.88	0.54	0.564	0.064	0.9940	155	0.048
	Polyphenyl ether, 6 rings	−0.74	0.21	0.90	0.56	0.563	0.066	0.9935	155	0.048
7	Tricresylphosphate	−0.68	0.15	1.06	1.23	0.550	0.074	0.9930	154	0.057
	Sucrose acetate isobutanoate	−0.56	0.05	1.05	1.29	0.509	0.071	0.9928	157	0.056
8	Hallcomid M18	−0.35	0.11	0.60	1.55	0.592	0.062	0.9947	154	0.037
	Hallcomid M18OL	−0.45	0.10	0.71	1.59	0.592	0.068	0.9930	153	0.040

9	Pluronic L42	−0.52	0.21	0.88	1.45	0.529	0.081	0.9898	154	0.045
	Pluronic L72	−0.54	0.17	0.89	1.41	0.531	0.077	0.9917	153	0.042
	Pluronic L61	−0.53	0.20	0.91	1.42	0.526	0.079	0.9905	151	0.044
	Pluronic L63	−0.54	0.24	0.92	1.46	0.519	0.080	0.9900	153	0.046
	Polytergent J300	−0.55	0.16	0.94	1.49	0.536	0.081	0.9901	154	0.052
	Pluronic P84	−0.57	0.20	0.94	1.44	0.516	0.079	0.9908	152	0.047
	Pluronic P85	0.57	0.28	0.94	1.46	0.512	0.082	0.9902	153	0.052
	Pluronic L44	−0.56	0.26	0.96	1.52	0.515	0.084	0.9899	154	0.049
	Oronite NIW	−0.62	0.25	0.96	1.46	0.524	0.085	0.9898	155	0.053
	Ucon HB-2000	−0.60	0.28	0.97	1.48	0.514	0.081	0.9907	154	0.053
	Ethofat 60-25	0.60	0.26	0.99	1.54	0.523	0.078	0.9916	154	0.052
	Pluronic P65	−0.60	0.28	1.01	1.50	0.513	0.086	0.9893	155	0.050
	Pluronic P46	−0.61	0.30	1.02	1.56	505	0.085	0.9893	154	0.052
	Tergitol NPX	−0.57	0.19	1.02	1.47	0.518	0.078	0.9917	154	0.058
10	Neopentylglycoladipate, term	−0.68	0.21	1.08	1.45	0.510	0.070	0.9929	152	0.057
	Ethyleneglycolsebacate	0.78	0.27	1.10	1.44	0.518	0.078	0.9911	145	0.054
	Diethyleneglycolsebacate	−0.76	0.32	1.14	1.45	0.498	0.074	0.9910	141	0.052
	Neopentylglycoladipate	−0.67	0.24	1.14	1.47	0.491	0.073	0.9916	150	0.060
	Neopentylglycolsuccinate	−0.71	0.23	1.24	1.49	0.466	0.082	0.9884	153	0.065
11	Pluronic F88	−0.63	0.34	1.10	1.60	0.483	0.086	0.9887	153	0.058
	Pluronic F68	−0.66	0.35	1.13	1.61	0.485	0.087	0.9884	154	0.059
	Pluronic F77	−0.63	0.32	1.09	1.61	0.496	0.083	0.9897	151	0.051
	Igepal CO 880	−0.66	0.28	1.16	1.61	0.488	0.084	0.9885	152	0.059
	Triton X 305	−0.83	0.29	1.17	1.65	0.492	0.086	0.9894	154	0.059
12	Ethyleneglycoladipate	−0.90	0.36	1.43	1.72	0.443	0.093	0.9857	143	0.073
	Diethyleneglycoladipate	−0.91	0.40	1.46	1.73	0.438	0.089	0.9847	139	0.065
13	XF-1150	−0.69	0.06	1.44	1.38	0.417	0.084	0.9856	150	0.092
	Sucrose octaacetate	−0.73	0.12	1.48	1.59	0.426	0.090	0.9852	154	0.071
14	Carbowax 20M	−0.73	0.40	1.23	1.78	0.465	0.091	0.9880	153	0.059
	Carbowax 6000	−0.75	0.40	1.28	1.80	0.469	0.090	0.9878	150	0.059
	Carbowax 4000	−0.76	0.32	1.31	1.85	0.470	0.090	0.9867	149	0.059
	Carbowax 1540	−0.75	0.31	1.34	1.87	0.457	0.093	0.9866	151	0.069
	Carbowax 1000	−0.76	0.29	1.37	1.89	0.457	0.094	0.9867	152	0.071

(Continued on p. 336)

TABLE III (continued)

Group	Stationary phase	Characteristic constants in eqn 1					S D	*R*	No	*q*
		c	*r*	*s*	*a*	*l*				
15	Carbowax 600	−0.82	0.31	1.46	2.12	0.455	0.093	0.9847	149	0.073
	Carbowax 400	−0.77	0.28	1.50	2.18	0.440	0.090	0.9883	149	0.077
	Carbowax 300	0.79	0.33	1.50	2.28	0.434	0.093	0.9877	149	0.071
	Quadrol	−0.77	0.07	1.47	2.38	0.471	0.103	0.9858	153	0.087
	Hyprose SP80	−0.87	0.11	1.53	2.40	0.414	0.103	0.9835	151	0.088
16	Triethyleneglycolsuccinate	−1.05	0.39	1.71	1.87	0.416	0.090	0.9858	145	0.078
	Diethyleneglycolsuccinate	−0.99	0.43	1.74	1.68	0.379	0.114	0.9755	145	0.073
	Dow Corning Fluid 550	−0.46	0.09	0.56	0.29	0.547	0.047	0.9963	152	0.032
	Casterwax	−0.45	0.10	0.63	1.09	0.562	0.060	0.9944	150	0.040
	Dibutyltetrachlorophthalate	−0.62	0.25	0.69	0.60	0.600	0.048	0.9969	150	0.038
	Citroflex A4[a]	−0.43	0.12	0.85	0.94	0.552	0.061	0.9951		0.046
	Bis(2-ethoxyethyl)phthalate	−0.64	0.13	1.23	1.25	0.529	0.074	0.9923	152	0.067
	Dow Corning Fluid FS 1265	−0.76	−0.25	1.29	0.29	0.451	0.083	0.9851	153	0.086
	Kroniflex THPP	−0.72	0.22	1.34	2.28	0.498	0.083	0.9913	152	0.071
	Zonyl E-7	−0.82	−0.28	1.63	0.69	0.449	0.071	0.9902	150	0.083

[a] Values extrapolated from 80 and 100 °C

CHARACTERISATION OF PHASES

Details of the application of eqn 1 to the 77 McReynolds phases are given in Tables III, IV, VI and VII In Table III are results at a common temperature of 120°C, with values for squalane and Citroflex A4 extrapolated from those at 80 and 100°C. Table IV contains results at temperatures other than 120°C, usually at 100 or at 140/160°C, so that all of McReynolds data sets have been analysed. We do not list the chemical formulation of the 77 phases, even though some of them are rather obscure, because Fellous *et al.* [illegible] have detailed the 77 stationary phases already. It should be noted that many of these phases contain a non-ionic surfactant (2%, w/w), and hence our obtained constants. Table III, refer to the phases as specifically formulated by McReynolds [1]. Although many of the McReynolds phases are no longer in current use, we list results for all the phases in order to show the utility of our method and in order to compare our classification with previous characterisation [12] of the total 77-phase set.

Furthermore, no corrections were made by McReynolds for effects such as interfacial adsorption, and his results for solutes such as alkanes in the more polar phases may be subject to additional error. We have no way of correcting the raw data of McReynolds, and rather than exclude particular subsets of compounds on some arbitrary basis, we have chosen to use all the available results. This may well account for part of the large standard deviations observed for regressions with phases such as diglycerol and sorbitol, and suggests also that the obtained constants for these phases should be viewed with some caution.

In principle, a given stationary phase at a given temperature is characterised by the six constants in eqn. 1. However, the constant c, although important as regards the absolute values of log V_G^0, is not a very useful characteristic constant, whilst the constant r plays only a minor role, at least for the present data set. We are thus left with the four constants s, a, b and l But we can effect further simplication by noting that only three out of the 77 phases give rise to statistically significant b constants, and hence show hydrogen-bond acidity. These are docosanol, diglycerol and sorbitol with b values of 0.34, 0.52 and 0 34 respectively at 120°C (see Table VI). A number of the other phases might be expected to show hydrogen-bond acidity, but the analysis given in Table VIII reveals that the $b\beta_2^H$ term is not significant. We can therefore regard docosanol, diglycerol and sorbitol as singular phases, and analyse the remaining 74 phases with the omission of the $b\beta_2^H$ term altogether (see Tables III and IV). For these 74 phases, the three major characteristic constants are thus s, a and l only.

We begin the analysis of the 74 phases in Table III by noting that there is some connection between s, a and l. In general, basic phases will also be dipolar, so that a and s will tend to run together. Furthermore, solvent–solvent interactions will be greater in dipolar, basic phases, thus giving rise to a larger endoergic cavity term, leading to a smaller value of the l constant. Since a and s are likely to be related, we can first group the 74 phases through a plot of a against s, shown in Fig. 1 Quite clearly, there are several groups or clusters of phases with about the same a and s values, and we have drawn up Table III to show the 16 clusters indicated in Fig. 1. Of course, there is an arbitrary element in the choice of clusters Thus groups 9 and 11 might be subsumed into a common group, or group 4 might be divided into two groups, but this is a feature of any method that reduces the 77 phases down to a

TABLE IV

REGRESSIONS AT VARIOUS TEMPERATURES

Stationary phase	*c*	*r*	*s*	*a*	*l*	S.D	*R*	No	Temperature (°C)
Squalane	−0.21	0.11	0.08	–	0.735	0.043	0.9970	133	80
	−0.27	0.12	0.05	–	0.674	0.034	0.9983	147	100
Apiezon M	−0.57	0.28	0.13	0.06	0.504	0.044	0.9971	153	160
Apiezon N	−0.62	0.28	0.15	0.09	0.504	0.045	0.9969	153	160
Apiezon J	−0.62	0.28	0.17	0.11	0.501	0.038	0.9977	150	160
Apiezon L	−0.57	0.29	0.10	0.05	0.502	0.037	0.9975	151	160
Versilube F50	−0.48	0.08	0.22	0.09	0.444	0.037	0.9972	152	160
SL-31	−0.48	0.05	0.22	0.14	0.430	0.038	0.9968	157	160
SE-30	−0.45	0.06	0.23	0.18	0.441	0.036	0.9968	154	160
SE-30 NPGA	−0.50	0.05	0.30	0.28	0.486	0.039	0.9970	139	140
SE-52	−0.51	0.07	0.29	0.17	0.442	0.040	0.9966	157	160
Dioctylsebacate	−0.31	0.13	0.55	0.94	0.646	0.049	0.9969	154	100
Di-2-ethylhexylsebacate	−0.31	0.13	0.55	0.95	0.646	0.050	0.9969	154	100
Tripelargonate	−0.53	0.15	0.49	0.65	0.486	0.051	0.9957	154	160
Isooctyldecyladipate	−0.33	0.11	0.60	0.96	0.645	0.054	0.9964	155	100
Di-2-ethylhexyladipate	−0.31	0.11	0.61	1.04	0.644	0.052	0.9966	152	100
Diisodecylphthalate	−0.55	0.14	0.59	0.62	0.537	0.050	0.9964	156	140
Dioctylphthalate	−0.55	0.15	0.61	0.64	0.532	0.052	0.9960	155	140
Ucon LB-1715	−0.69	0.20	0.61	0.88	0.459	0.061	0.9924	152	160
Flexol 8N8	−0.54	0.07	0.69	1.09	0.524	0.057	0.9953	157	140
Pluronic L81	−0.44	0.18	0.84	1.56	0.589	0.081	0.9910	151	100
Polyphenyl ether, 5 rings	−0.86	0.23	0.82	0.44	0.482	0.060	0.9936	156	160
Polyphenyl ether, 6 rings	−0.87	0.24	0.82	0.46	0.478	0.063	0.9929	156	160
Tricresylphosphate	−0.62	0.15	1.14	1.44	0.600	0.078	0.9920	142	100
Sucrose acetate isobutanoate	−0.65	0.06	0.86	0.99	0.429	0.060	0.9925	155	160
Hallcomid M18	−0.31	0.11	0.65	1.89	0.649	0.066	0.9943	141	100
Hallcomid M180L	−0.38	0.10	0.74	1.90	0.646	0.069	0.9934	141	100

Pluronic L42	0.59	0.20	0.82	1.26	0.486	0.074	0.9902	155	140
Pluronic L72	−0.61	0.23	0.81	1.23	0.489	0.072	0.9917	155	140
Pluronic L61	−0.50	0.21	1.02	1.67	0.581	0.088	0.9890	141	100
Pluronic L63	−0.47	0.17	1.01	1.71	0.571	0.083	0.9890	140	100
Polytergent J300	−0.49	0.15	1.01	1.76	0.584	0.089	0.9901	155	100
Pluronic P84	−0.52	0.25	1.00	1.70	0.564	0.090	0.9893	153	100
Pluronic P85	−0.52	0.27	1.03	1.71	0.562	0.091	0.9892	154	100
Pluronic L44	−0.62	0.25	0.89	1.31	0.473	0.078	0.9899	155	140
Oronite NIW	−0.81	0.20	0.90	1.12	0.458	0.071	0.9906	154	160
Ucon HB-2000	−0.52	0.29	1.03	1.67	0.560	0.094	0.9884	153	100
Ethofat 60-25	−0.57	0.19	1.08	1.78	0.575	0.086	0.9909	151	100
Pluronic P65	−0.50	0.27	1.05	1.76	0.560	0.090	0.9881	143	100
Pluronic P46	−0.46	0.30	0.94	1.38	0.466	0.079	0.9893	156	140
Tergitol NPX	−0.66	0.24	0.86	1.13	0.437	0.066	0.9916	152	160
Neopentylglycoladipate, term	−0.76	0.16	1.03	1.31	0.475	0.065	0.9928	140	140
Ethyleneglycolsebacate	0.81	0.22	1.02	1.32	0.478	0.067	0.9930	132	140
Diethyleneglycolsebacate	0.83	0.27	1.06	1.34	0.460	0.073	0.9909	136	140
Neopentylglycoladipate	−0.67	0.18	1.02	1.32	0.444	0.064	0.9926	140	140
Neopentylglycolsuccinate	−0.72	0.16	1.15	1.39	0.418	0.070	0.9905	139	140
Pluronic F88	−0.58	0.28	1.21	1.83	0.531	0.095	0.9878	153	100
Pluronic F68	−0.60	0.29	1.24	1.81	0.530	0.098	0.9878	156	100
Pluronic F77	−0.57	0.32	1.19	1.87	0.547	0.094	0.9871	141	100
Igepal CO 880	−0.66	0.27	1.28	1.88	0.540	0.096	0.9890	152	100
Triton X 305	−0.86	0.31	0.94	1.26	0.407	0.072	0.9890	152	160
Ethyleneglycoladipate	−0.97	0.24	1.37	1.68	0.412	0.083	0.9868	129	140
Diethyleneglycoladipate	−0.92	0.30	1.34	1.61	0.399	0.079	0.9865	130	140
XF-1150	−0.82	0.06	1.30	1.12	0.344	0.076	0.9843	152	160
Sucrose octaacetate	−0.84	0.12	1.29	1.30	0.362	0.076	0.9852	154	160
Carbowax 20M	−0.82	0.37	1.07	1.36	0.392	0.076	0.9879	151	160
Carbowax 6000	−0.79	0.40	1.15	1.56	0.431	0.083	0.9877	152	140
Carbowax 4000	−0.81	0.37	1.18	1.64	0.431	0.080	0.9889	150	140
Carbowax 1540	−0.71	0.38	1.42	2.17	0.499	0.100	0.9874	150	100
Carbowax 1000	−0.73	0.30	1.49	2.24	0.500	0.100	0.9875	149	100

(Continued on p 340)

TABLE IV (*continued*)

Stationary phase	*c*	*r*	*s*	*a*	*l*	S.D.	*R*	No.	Temperature (°C)
Carbowax 600	−0.78	0.29	1.61	2.39	0.496	0.104	0.9866	148	100
Carbowax 400	−0.73	0.28	1.60	2.44	0.481	0.104	0.9867	150	100
Carbowax 300	−0.76	0.26	1.64	2.56	0.476	0.106	0.9866	149	100
Quadrol	−0.72	0.12	1.50	2.76	0.521	0.106	0.9879	152	100
Hyprose SP80	−0.84	0.09	1.61	2.77	0.461	0.110	0.9848	150	100
Triethyleneglycolsuccinate	−1.06	0.33	1.57	1.67	0.381	0.086	0.9840	133	140
Diethyleneglycolsuccinate	−1.07	0.35	1.60	1.77	0.342	0.099	0.9746	133	140
Dow Corning Fluid 550	−0.56	0.11	0.47	0.20	0.456	0.041	0.9967	154	160
Casterwax	−0.56	0.13	0.60	0.93	0.519	0.053	0.9953	152	140
Dibutyltetrachlorophthalate	0.57	0.24	0.75	0.68	0.658	0.057	0.9956	142	100
Citroflex A4	{ 0.29	0.06	1.05	1.47	0.658	0.072	0.9923	136	80
	0.36	0.04	0.94	1.19	0.602	0.066	0.9938	150	100
Bis(2-ethoxyethyl)phthalate	−0.58	0.18	1.29	1.46	0.575	0.085	0.9899	143	100
Dow Corning Fluid FS 1265	−0.86	−0.21	1.13	0.27	0.367	0.071	0.9853	155	150
Kroniflex THF P	−0.79	0.23	1.25	2.02	0.461	0.082	0.9901	153	140
Zonyl E-7	−0.78	−0.29	1.78	0.78	0.494	0.077	0.9905	138	100

TABLE V

CHARACTERISATION OF PHASES USING EQN. 1 WITH McREYNOLDS AND LAFFORT'S DATA AT 120 °C

M = McReynold's set, this work; L = Laffort's set, ref. 16

Stationary phase	Set	r	s	a	l
Carbowax 1540	M	0.31	1.34	1.87	0.457
	L	0.26	1.37	2.11	0.442
Diethyleneglycolsuccinate	M	0.43	1.74	1.68	0.379
	L	0.35	1.70	1.92	0.396
Polyphenyl ether, 6 rings	M	0.21	0.90	0.56	0.563
	L	0.19	0.98	0.59	0.552
Zonyl E-7	M	−0.28	1.63	0.69	0.449
	L	−0.38	1.61	0.70	0.442

TABLE VI

STATIONARY PHASES WITH SIGNIFICANT HYDROGEN-BOND ACIDITY

Stationary phase	c	r	s	a	b	l	S.D.	R	No.	Temperature (°C)
Docosanol[a]	−0.41	0.13	0.29	0.75	0.34	0.603	–	–	–	120
	−0.37	0.15	0.30	1.13	0.39	0.657	0.061	0.9951	148	100
	−0.33	0.16	0.31	1.56	0.45	0.717	0.077	0.9925	134	80
Diglycerol	−1.26	0.55	1.63	2.77	0.52	0.225	0.148	0.9589	146	120
Sorbitol	−1.72	0.35	0.81	1.77	0.34	0.360	0.161	0.9217	130	120

[a] Extrapolated from results at 80 and 100 °C

TABLE VII

TEST FOR STATIONARY PHASE HYDROGEN-BOND ACIDITY

Stationary phase	c	r	s	a	b	l	S.D.	R
Castorwax	−0.47	0.13	0.59	1.06	0.08	0.563	0.059	0.9945
	−0.45	0.10	0.63	1.09	–	0.562	0.060	0.9944
Flexol 8N8	−0.49	0.12	0.71	1.25	0.03	0.573	0.065	0.9932
	−0.48	0.11	0.73	1.27	–	0.573	0.065	0.9932
Hyprose SP80	−0.86	0.09	1.56	2.42	0.05	0.414	0.103	0.9835
	−0.87	0.11	1.53	2.40	–	0.414	0.103	0.9835
Quadrol	−0.77	0.08	1.43	2.37	0.03	0.472	0.103	0.9858
	−0.77	0.07	1.47	2.38	–	0.471	0.103	0.9858

TABLE VIII

EFFECT OF CHAIN LENGTH ON THE CHARACTERISTIC CONSTANTS FOR SOME STATIONARY PHASE ESTERS

Stationary phase	*r*	*s*	*a*	*l*
Dioctylsebacate	0.12	0.49	0.79	0.594
Ethyleneglycolsebacate	0.27	1.10	1.44	0.518
Diethyleneglycolsebacate	0.32	1.14	1.45	0.498
Isooctyldecyladipate	0.13	0.55	0.81	0.586
Ethyleneglycoladipate	0.36	1.43	1.72	0.443
Diethyleneglycoladipate	0.40	1.46	1.73	0.438
Diethyleneglycolsebacate	0.32	1.14	1.45	0.498
Diethyleneglycoladipate	0.40	1.46	1.73	0.438
Diethyleneglycolsuccinate	0.43	1.74	1.68	0.379

relatively small number of clusters. We can then examine the 16 groups to see if any futher subdivision is necessary on the basis of the *r* and *l* constants. However, within each group, the *r* and *l* constants do not vary overmuch. Only in the case of group 7 and group 16 is there a clear subdivision into high and low values of *l*, although groups 10 and 15 do contain a rather wide spread of *l* values.

We can conclude that an analysis in terms of *s* and *a* (and also *b* for phases that are hydrogen-bond acids) enables us to group the 74 McReynolds phases into a number of clusters of similar phases, leaving some 11 stationary phases (8 in Table III plus the three acidic phases) as singular phases that cannot be substituted by any other of the 77-phase set. Our grouping is based entirely on chemical principles, and it

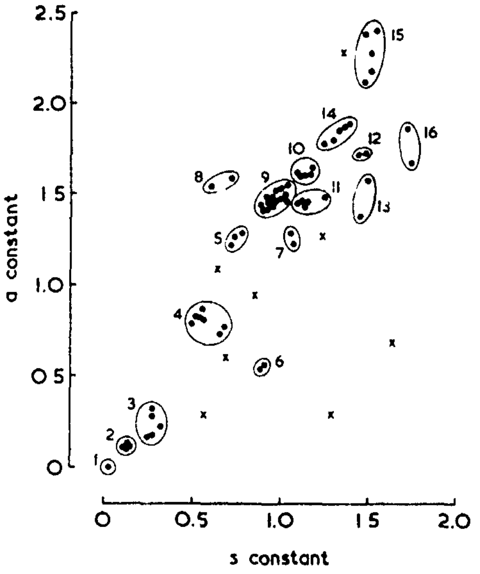

Fig 1 Classification of stationary phases according to the *a* constant and the *s* constant in eqn 1 ● = Groups as shown in Table III, × = singular phases

is very instructive to compare results with other work carried out on more mathematical lines.

Huber and Reich [12] have analysed the 77-phase set, using both hierarchical clustering and the minimum spanning tree method. Their results, especially by the latter technique, are almost identical to those we have obtained. Differences, such as there are, are trivial For example Huber and Reich [12] class Castorwax and our groups 5 and 8 together, but reference to Table III and Fig. 1 shows that this is quite reasonable on our analysis as well. Wold [11] used a pattern cognition method to group the 226-phase set into clusters. Where there are common phases between the 226- and the 77-phase sets, there is again excellent agreement between our result and those of Wold [11]. As pointed out by Wold, the nearest neighbour technique used by Leary *et al.* [7] leads to a rather peculiar set of clusters. However, the numerical taxonomy method of Massart *et al.* [9] applied to the 226-phase set leads to groups not too dissimilar to those in Table III. although there are some outstanding exceptions. Thus Massart *et al.* [9] class didecylphthalate and Flexol 8N8 in the same group, whereas we find the latter to be considerably more basic (a = 1.27 as against a = 0 73 for diisodecylphthalate). Our method of clustering, therefore, is in excellent agreement with results of Huber and Reich [12] and of Wold [11], but not so much with results of Leary *et al.* [7] or of Massart *et al.* [9].

A general survey of our classification, Table III, shows that it is completely consistent with the chemical formulation of the phases. Thus group 1 contains the saturated hydrocarbon squalane, and would include other hydrocarbons such as hexadecane (by definition), octacosane, $C_{87}H_{176}$ etc. The apiezons in group 2 are slightly dipolar and basic due to the presence of some aromatic groups, whilst the silicones in group 3 are rather more dipolar and basic through the silicon–oxygen bond. Thus the hydrogen-bond basicity of $(CH_3)_3SiOSi(CH_3)_3$ as a solute, β_2^H = 0.16, can be compared to values of β_2^H for di-*tert.*-butylether of 0.38, and values of around 0.45 for straight-chain aliphatic ethers [22]. All the simple esters of carboxylic acids cluster in group 4, the two amides appear in group 8, and so forth. The Carbowaxes fall into an exact sequence from Carbowax 20M to Carbowax 300, with values of s and a monotonically increasing along the series, where the cut-off point between groups 14 and 15 is clearly arbitrary. The sebacates (C_{10}), adipates (C_6) and succinates (C_4) are worthy of attention (see Table VIII). The sebacates are always less dipolar and less basic than the adipates or succinates, and the simple dialkylesters are always less dipolar and less basic than the corresponding ethyleneglycol or diethyleneglycol ester.

The constant r does not vary widely over the particular set of 77 phases, but, significantly, the r constant is negative in the case of the only fluorinated stationary phases in the set, *viz*. Dow Corning Fluid FS 1265 and Zonyl E-7. The ability of these phases to interact with solute π- and n-electron pairs is even less than that of a simple alkane.

Finally, we consider the characteristic constant l, a resultant of an endoergic solvent cavity term tending to decrease the value of l and an exoergic general dispersion interaction term tending to increase the value of l. We have previously shown [16] that the methylene increment for solvation of a homologous series[a] of gaseous

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[a] That is a series in which CH_2 groups are successively inserted at the same part of the molecule

TABLE IX

VALUES OF $\Delta\log V_G^0$ FOR 1-ALKANOLS ON SOME STATIONARY PHASES

R and No = Correlation coefficients and number of points in plots of $\log V_G^0$ against carbon number of the 1-alkanols

Stationary phase	Temperature (°C)	l	$\Delta\log V_G^0$	R	No
Squalane	80	0.735	0.398	0.9991	5
Squalane	100	0.674	0.358	0.9988	7
Squalane[a]	120	0.619	0.322	–	–
Apiezon N	120	0.601	0.314	0.9993	7
SE-30	120	0.523	0.280	0.9996	7
Carbowax 400	120	0.440	0.235	0.9998	7
Diethyleneglycolsuccinate	120	0.379	0.198	0.9989	7
Diglycerol	120	0.225	0.110	0.9987	7

[a] Extrapolated values

solutes in a given solvent, $\Delta G_s^0(\mathrm{CH_2})$, depends on a combination of a solvent cavity term and a general dispersion interaction term. Now $\Delta G_s^0(\mathrm{CH_2})$ is related to $\Delta\log V_G^0$, since $\Delta G_s^0(\mathrm{CH_2}) = -2.303RT\,\Delta\log V_G^0$, where $\Delta\log V_G^0$ is the average increase in $\log V_G^0$ along an homologous series. It therefore follows that the constant l must also be related to the important term $\Delta\log V_G^0$, or $\Delta G_s^0(\mathrm{CH_2})$.

In Table IX are given values of $\Delta\log V_G^0$ for the homologous series of 1-alkanols in a few representative stationary phases covering the range of l constants we have encountered. A plot of $\Delta\log V_G^0$ against the l constant (Fig. 2) yields an excellent straight line passing through the origin, since $\Delta\log V_G^0$ must approach zero as l approaches zero. We can thus show from experiment, as well as theory, that the l constant in eqn. 1 is a measure of the ability of a stationary phase to separate mem-

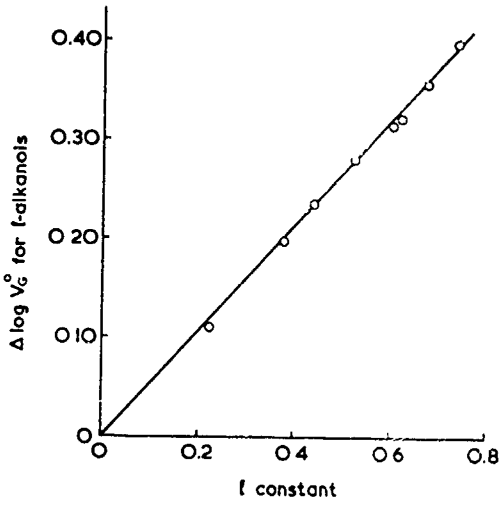

Fig. 2. Plot of $\Delta\log V_G^0$ against the l constant

TABLE X

CHARACTERISTIC CONSTANTS FOR OTHER PHASES AT 120°C

Phase	r	s	a	l
N-methylpyrrolidinone [17]	-	1.42	2.70	0.472
N-Formylmorpholine [17]	-	1.52	2.24	0.442
Tricyanoethoxypropane [16]	0.23	2.12	1.94	0.379

bers of an homologous series. The l constant is entirely equivalent to $\Delta G_s^0(CH_2)$, so that eqn. 1 actually incorporates this latter parameter.

We have not considered eqns. 2 and 3 other than to compare them with eqn. 1 in Table II. Eqn. 2 offers no advantage over eqn. 1 and suffers from the disadvantage of containing the empirical parameter δ_2. Eqn. 3, although giving rise to significantly worse fits than eqn. 1 has the advantage that the q constant, especially, can be related to a theoretical model of solute dipole–solvent interactions via the Kirkwood equation [27]. However, in practice the correlation constant between q and s is so high, 0.970 for the 77 stationary phases at 120°C, that no extra information is contained in q. At present, therefore, eqn. 3 is not necessary for the characterisation of stationary phases. However, the dipole moment term is theoretically very useful, and it might be possible to incorporate other solute parameters, and to obtain an improved version of eqn. 3 that retains the dipole moment as a dipolarity parameter.

In Table X we list a few phases that we have previously [16,17] characterised through eqn. 1. The two amides are highly basic, whilst tricyanoethoxypropane is the most dipolar phase we have examined to data. Finally, we give in Table XI a selection of phases to show how the characteristic constants s, a, b and l relate to the chemical

TABLE XI

CHEMICAL CHARACTERISTICS OF SOME PHASES

Phase	Polarity	Basicity	Acidity	Separation of homologues
Hexadecane Squalane	Zero	Zero	Zero	High
Apiezon	Low	Low	Zero	High
Polyphenylether	Medium	Low	Zero	High
Hallcomid Kroniflex THFP	Medium	High	Zero	Medium
Carbowax 300 Quadrol Hyprose SP80	High	High	Zero	Medium
Zonyl E-7	High	Low	Zero	Medium
N-Methylpyrrolidinone	High	Very high	Zero	Medium
Tricyanoethoxypropane	Very high	High	Zero	Low
Docosanol	Low	Medium	Low	High
Diglycerol	High	Very high	Medium	Very low

nature of the stationary phase. From such a list, it is easy to select a phase that will effect separations mainly through dipole–dipole interactions (e.g. Zonyl E-7), or a phase that will effect separations mainly through interactions of the type solute hydrogen-bond acid–solvent hydrogen-bond base (e.g. Hallcomid M18 or M180L). We have not been able to list any phase that leads mainly to interactions of the type solute hydrogen-bond base–solvent hydrogen-bond acid. The most acidic phase we have encountered is diglycerol with b = 0.52 at 120°C, but this phase is actually the strongest hydrogen-bond base of all the phases listed. In any case, diglycerol is unsuitable as a general stationary phase because of the very low l constant. We hope to report in the near future on our attempts to synthesise phases that are strong hydrogen-bond acids but weak hydrogen-bond bases.

In conclusion, we have been able to set up a new classification of stationary phases, based on fundamental chemical interactions. The characteristic constants r, s, a, b and l provide information on the propensity of a given phase to undergo specific interactions with solutes, and hence lead to criteria for the choice of a phase to effect particular separations. The method does not have the disadvantages of the McReynolds–Rohrschneider procedures, and although retention data on not less than about 25 solutes are required, it is necessary only to determine relative retention times. Another advantage of the present method is that eqn. 1 can be applied to equilibria involving any condensed phase, for example the solubility of gaseous solutes in simple organic solvents [17], or even the adsorption of gases on solids. We hope to report on these processes in the near future.

SOLUTE–SOLVENT INTERACTIONS

Our main aim in this paper has been to characterise the set of 77 McReynolds phases in terms of eqn. 1, where SP = I^0_G. However, we can now use the results given in Tables III–VI to analyse the factors that influence solute retention on stationary phases. We give in Table XII a breakdown of eqn. 1, term-by-term for two typical solutes, butanone and 1-butanol, in a variety of stationary phases. In the less polar

TABLE XII

ANALYSIS OF THE FACTORS THAT INFLUENCE LOG I^0_G, USING EQN. 1 AT 120°C

Solute	Phase	Term					Dispersion[a]	Cavity[a]
		rR_2	$s\pi_2^*$	$a\alpha_2^H$	$b\beta_2^H$	$l \log L^{16}$		
Butanone	Apiezon M	0.04	0.07	0	0	1.37	3.36	-1.93
	Hallcomid M18	0.02	0.40	0	0	1.35	3.26	-1.88
	Zonyl E-7	-0.05	1.09	0	0	1.03	1.90	-1.09
	Diglycerol	0.09	1.09	0	0.25	0.52	(0.48)	(-0.28)
1-Butanol	Apiezon M	0.06	0.40	0.04	0	1.56	4.10	-2.25
	Hallcomid M18	0.03	0.24	0.52	0	1.54	4.00	-2.20
	Zonyl E-7	-0.06	0.65	0.23	0	1.17	2.31	-1.27
	Diglycerol	0.12	0.65	0.91	0.23	0.59	(0.59)	(-0.32)

[a] See text. These do not add up to the $l \log L^{16}$ term because of a constant term and a small dipole–induced dipole term that have not been included.

phases, where the s constant is quite small, by far the main term is l log L^{16}. The term $a\alpha_2^H$ can be substantial for the combination of a hydrogen-bond acidic solute and a hydrogen-bond basic phase, but for the present set of solutes and phases the $b\beta_2^H$ term is never substantial. Of course, for more acidic phases than diglycerol, the $b\beta_2^H$ term could be much more significant.

In eqn. 1, the l log L^{16} term covers both general dispersion interactions that lead to positive values of log V_G^0, and the endoergic solvent–solvent cavity term that leads to negative values of log V_G^0. These two effects are very difficult to unravel quantitatively, hence we have had to use a combined term in eqn. 1. Abraham and Fuchs [24], however, managed to dissect the log L^{16} values themselves into mainly a cavity term and a general dispersion interaction term. If we assume, as before [25], that the ratio of these two terms remains the same, then we can roughly separate the total l log L^{16} term shown in Table XII into cavity and general dispersion effects. Given that these are only approximations, expecially in the case of diglycerol, we can still see that the largest interaction term corresponds to general solute solvent dispersion effects. It is these that control the separation of members of an homologous series. Eqn. 1 incorporates such an effect in the l log L^{16} term. Although dipolar and acid base interactions tend to be smaller than the general dispersion interactions, they control separations of dissimilar solutes. Eqn. 1 incorporates these effects in the first four terms.

Thus our preferred eqn. 1 not only forms the basis of a classification of stationary phases, but also leads to a rationale for the separation of solutes, based on a number of possible solute–solvent interactions

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CALCULATION OF SOLUTE PARAMETERS

(i) Calculation of Effective Hydrogen Bond Basicity, $\Sigma\beta^H_2$, from HPLC Data

As has been described in the project aims, an 'effective' hydrogen bond basicity, $\Sigma\beta^H_2$, can be calculated from chromatographic retention data, and some of these values were used in our characterisation of the Laffort phases[46]. At present, there seems no practical possibility of obtaining direct experimental complexation constants for multifunctional solutes, and hence some indirect method of evaluation of α_2 and β_2 is required. In addition, when LSER equations are applied to practical solubility situations, a given solute will be surrounded by an excess of solvent molecules, and hence multiple hydrogen bonding involving a number of solvent molecules can take place. This will not only take place with multifunctional solutes, but can also occur with certain solutes that are normally regarded as monofunctional. There are a very large number of literature reports of the determination of reversed phase HPLC (RP-HPLC) capacity factors, k'. Table 1 lists the variety of reversed-phase HPLC processes used in one of the first analyses attempted [47]. A number of series were analysed, where, in each case, the solvent composition is constant, and the general equation 8 (or the preferred equation 10, since the development of the R_2 parameter) were applied, where SP in this case is log k'. The use of δ_2 or R_2 in this analysis is to a great extent academic, because neither term is very important.

$$\log k' = c + d.\delta_2 + s.\pi^*_2 + a.\alpha^H_2 + b.\beta^H_2 + m.V_2 \qquad [8]$$

$$\log k' = c + r.R_2 + s.\pi^*_2 + a.\alpha^H_2 + b.\beta^H_2 + m.V_2 \qquad [10]$$

One method of dealing with the above problems of effetive basicities involves back-calculation of β_2 values via equations 8 and 10. $\Sigma\beta^H_2$ values can be back-calculated for solutes and $\Sigma\beta^H_2$ can be averaged for each solute where there are two or more values. These averaged $\Sigma\beta^H_2$ values are then used to generate a new set of equations of type 8 or 10, $\Sigma\beta^H_2$ are back-calculated, averaged, and the cycle repeated. This work is still continuing, but as an example, some work already done[47] is presented here. The final result is the set of correlation equations, using equation 8 in this case, which are given in Table 2, (note that the term $d.\delta_2$ is either not significant or small). Derived $\Sigma\beta^H_2$ values are given in Table 3. In addition, numerous $\Sigma\beta^H_2$ values calculated from only one result can be obtained, but these were not used to obtain the regression equations in Table 2.

Just as expected, the effective basicities values for phenols, anilines, and aromatic ethers are appreciably higher than the "monofunctional" β^H_2 values, (see Table 4 for a comparison of $\Sigma\beta^H_2$ from RP-HPLC back-calculations, and β^H_2 for representative solutes). It is rather unlikely that further cycles of this iterative process will appreciably alter the values listed in the final column of Table 3. However, it is possible to incorporate more solutes into the set of equations, and also to specify more exactly the HPLC solutes that are preferred for the back-calculation. A typical equation is that for system no. 33 (from Table 1) using equation 8, and V_X as a solute size term,

$$\log k' = -0.311 - 0.647\delta_2 + 0.308\pi^*_2 - 0.082\alpha^H_2 - 2.599\beta^H_2 + 1.4071V_X \quad [11]$$

$$R = 0.9981 \quad SD = 0.042 \quad N=48$$

The coefficient of β^H_2 in equation 11 is some eight times as large as that of π^*_2, with that of α^H_2 being negligible (the coefficient of the rather trivial δ_2 term is also small). Hence if π^*_2 or α^H_2 values have to be estimated, not much error in the back-calculated β^H_2 values will be introduced.

Such a method of calculation is an on-going project, since further literature data can be incorporated into a system of equations. However, results indicate that $\Sigma\beta^H_2$ values are firmly established for a number of key series of aromatic compounds where $\beta^H_2 \neq \Sigma\beta_2$. These include phenols, benzoic acids, benzyl alcohols, anilines, and aromatic ethers. In addition, $\Sigma\beta^H_2$ values have been established for a few aliphatic carboxylic acids, for which β^H_2 cannot be derived directly. The list of $\Sigma\beta^H_2$ values in Table 3 represents a very important advance in the characterisation of solutes, and enables us to extend considerably the nature of various regressions. It is still desirable to confirm and extend $\Sigma\beta^H_2$ values through back-calculations involving other processes. In particular, the pyridines still need to be further investigated, as so far, reliable values of $\Sigma\beta^H_2$ values have been difficult to obtain.

All in all, it is quite practical to obtain β^H_2 values for multifunctional solutes, and for other solutes for which direct measurements are not possible, by the technique of back-calculation. However, considerable care has to be taken, and results for important compounds must be obtained as the average of several determinations. In Table 4 is given a comparison of $\Sigma\beta^H_2$ with β^H_2, the latter obtained[26] from 1:1 complexation constants for hydrogen bonding. Nearly all ther 'activated' aromatics have $\Sigma\beta^H_2 > \beta^H_2$, no doubt because in solution the aromatic ring can also function as a basic site, as well as the functional group. Deactivated aromatics, however, such as nitrobenzene and benzonitrile seem to retain the same β^H_2 in bulk solution. Indeed such compounds are used as 'standard solutes' in setting up the regression equations for the RP-HPLC log k' values.

Table 1. Typical Reversed-phase HPLC Systems Used in the Analysis.

Number	Bonded phase	Mobile phase	Reference
1	Hypersil ODS	75% methanol	a
2		50% methanol	
3	Octadecyl	55% methanol	b
4	Octadecyl	90% acetonitrile	c
5		80% acetonitrile	
6		70% acetonitrile	
7		60% acetonitrile	
8	Hypersil ODS	90% methanol	d
9		75% methanol	
10		60% methanol	
11		45% methanol	
12		30% methanol	
13	Porous polymer gel	methanol pH 11	e
14		acetonitrile pH 11	
15		methanol pH 2	
16		acetonitrile pH 2	
17	Phospholipid-coated - silica gel	30% acetonitrile	f
18		20% acetonitrile	
19		10% acetonitrile	
20	Octadecyl	75% methanol	[illegible]
21		65% methanol	
22		60% methanol	
23		55% methanol	
24		50% methanol	
25		40% methanol	
26	Glyceryl-coated - glass beads	25% methanol	g
27		20% methanol	
28		15% methanol	
29		10% methanol	
30		5% methanol	
31	Octadecyl	30% acetonitrile	h
32		32.5% tetrahydrofuran	n
33		50% methanol	
34	LiChrosorb	Aqueous methanol	i
35	Octadecyl	80% acetonitrile	j
36		70% acetonitrile	
37		60% acetonitrile	
38		50% acetonitrile	
39	Octadecyl	Aqueous methanol	k
40	Octadecyl	75% methanol	l
41	Octadecyl	50% acetonitrile	m
42		30% acetonitrile	
43	Octadecyl	70% methanol	n
44		60% methanol	
45		50% methanol	
46		40% methanol	
47		60% acetonitrile	
48		50% acetonitrile	
49		30% acetonitrile	

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Table 2. Summary of Correlations Giving Data in Table 3.

										---- CONFIDENCE LEVEL % ---						
SET	c	d.δ2	s.π*2	a.α2	b.β2	m.Vx	r	n	s.d.	c	d	s	a	b	m	
1	-0.637	0.038	-0.453	-0.367	-1.461	1.384	0.9958	61	0.049	100	94.4	100	100	100	100	
2	-0.378	0.079	-0.572	-0.320	-2.128	2.229	0.9968	61	0.063	100	99.7	100	100	100	100	
3	-0.023	0.332	-0.769	-0.524	-1.993	1.862	0.9933	47	0.071	100	100	100	100	100	100	
4	-0.383	-0.096	-0.311	-0.283	-1.142	0.873	0.9981	81	0.025	100	100	100	100	100	100	
5	-0.248	-0.037	-0.396	-0.309	-1.374	1.025	0.9979	79	0.028	100	99.0	100	100	100	100	
6	-0.086	0.015	-0.471	-0.303	-1.572	1.143	0.9970	76	0.033	99.9	61.9	100	100	100	100	
7	0.082	0.060	-0.509	-0.301	-1.741	1.232	0.9953	68	0.036	98.5	99.7	100	100	100	100	
8	-0.825	-	-0.510	-0.374	-1.221	1.078	0.9967	30	0.038	100	-	100	100	100	100	
9	-0.580	-	-0.520	-0.366	-1.558	1.441	0.9974	30	0.041	100	-	100	100	100	100	
10	-0.368	-	-0.600	-0.370	-1.871	1.888	0.9983	30	0.041	100	-	100	100	100	100	
11	-0.237	-	-0.652	-0.334	-2.270	2.452	0.9985	30	0.047	100	-	100	100	100	100	
12	-0.245	-	-0.739	-0.278	-2.590	3.145	0.9975	30	0.074	99.6	-	100	100	100	100	
13	0.228	-	-0.326	-1.109	-1.441	1.599	0.9853	26	0.088	93.4	-	97.8	100	100	100	
14	0.783	-	-0.526	-1.115	-1.703	1.560	0.9757	26	0.127	100	-	98.8	100	100	100	
15	0.142	-	-0.438	-0.735	-1.645	1.872	0.9649	31	0.137	61.8	-	98.7	100	100	100	
16	0.447	-	-0.436	-0.780	-1.854	1.854	0.9824	31	0.098	99.9	-	99.9	100	100	100	
17	-1.079	-	-0.125	-0.106	-1.847	1.5[illegible]	0.9875	38	0.048	100	-	99.5	99.9	100	100	
18	-0.897	-	-0.112	0.118	-2.991	2.317	0.9864	45	0.081	100	-	91.7	98.9	100	100	
19	-0.892	-	-0.120	0.162	-3.063	2.567	0.9837	41	0.076	100	-	89.0	99.9	100	100	
20	-0.462	-	-0.046	-0.404	-1.086	0.657	0.9887	19	0.037	100	-	37.4	100	100	100	
21	-0.442	-	-0.124	-0.363	-1.571	1.060	0.9913	19	0.039	100	-	77.5	100	100	100	(a)
22	-0.453	-	-0.009	-0.366	-1.676	1.163	0.9876	19	0.049	100	-	5.6	100	100	100	(a)
23	-0.439	-	-0.166	-0.347	-2.004	1.482	0.9954	19	0.034	100	-	92.8	100	100	100	
24	-0.491	-	0.023	-0.404	-2.158	1.598	0.9935	19	0.044	100	-	15.8	100	100	100	
25	-0.539	-	-0.125	-0.378	-2.357	2.220	0.9924	19	0.057	100	-	60.4	100	100	100	
26	-0.177	-	-0.198	-0.660	-2.031	2.027	0.9920	65	0.051	99.2	-	99.8	100	100	100	
27	0.109	-	0.188	-0.270	-1.976	1.240	0.9700	62	0.085	67.9	-	92.0	100	100	100	
28	-0.309	-	-0.525	-0.453	-2.005	2.181	0.9983	79	0.052	100.0	-	100	100	100	100	
29	-1.721	-	-0.206	-0.205	-3.847	3.507	0.9923	24	0.113	100	-	82.5	80.7	100	100	
30	-0.819	-0.663	0.502	0.034	-2.641	0.998	0.9973	50	0.047	100	100	100	49.1	100	100	(b)
31	-0.595	-0.729	0.536	-0.092	-2.448	1.063	0.9954	48	0.057	100	100	100	85.5	100	100	(b)
32	-0.473	-0.637	0.359	-0.057	-2.543	1.224	0.9973	48	0.046	100	100	100	73.4	100	100	(b)
33	-0.311	-0.647	0.308	-0.082	-2.599	1.407	0.9981	48	0.042	100	100	100	91.9	100	100	(b)
34	0.523	-	-0.635	-0.171	-3.617	3.695	0.9902	57	0.118	99.9	-	100	99.4	100	100	
35	-0.342	-	-0.417	-0.371	-1.085	1.043	0.9913	47	0.042	100	-	100	100	100	100	
36	-0.165	0.179	0.025	0.330	-1.992	1.457	0.9992	14	0.019	92.7	99.9	14.7	97.1	100	100	
37	-0.527	0.325	0.533	0.102	-3.695	2.541	0.9989	13	0.034	97.7	99.9	91.0	31.7	100	100	
38	-0.287	-	-0.602	-0.502	-1.655	1.737	0.9963	23	0.040	99.9	-	100	100	100	100	
39	-0.131	-	-0.668	-0.551	-1.890	2.063	0.9972	23	0.039	90.9	-	100	100	100	100	
40	0.052	-	-0.715	-0.587	-2.164	2.373	0.9970	23	0.045	45.5	-	100	100	100	100	
41	0.191	-	-0.682	-0.605	-2.322	2.586	0.9961	22	0.052	93.0	-	100	100	100	100	
42	0.111	-	-0.361	-0.553	-1.316	1.135	0.9962	23	0.033	90.4	-	100	100	100	100	
43	0.125	-	-0.385	-0.628	-1.633	1.485	0.9960	23	0.041	87.5	-	100	100	100	100	
44	0.139	-	-0.387	-0.716	-2.011	1.890	0.9936	23	0.062	75.1	-	100	100	100	100	
45	1.320	-	-1.291	-0.256	-2.841	1.015	0.9811	30	0.032	100	-	100	96.3	100	100	
46	1.485	-	-1.403	-0.268	-2.980	1.145	0.9732	30	0.042	100	-	100	91.1	100	100	
47	1.614	-	-1.560	-0.174	-3.213	1.339	0.9844	30	0.036	100	-	100	81.6	100	100	
48	1.711	-	-1.711	-0.056	-3.430	1.565	0.9857	30	0.037	100	-	100	32.0	100	100	
49	1.655	-	-1.747	0.104	-3.478	1.803	0.9881	30	0.038	100	-	100	56.4	100	100	

(a) Omit 3-nitro- and 4-nitroaniline (b) Omit phenol

Table 3. Some Backcalculated ΣβH2 Values From HPLC Data (Table 1).

General compounds	Average	SD	No	Taken
benzyl bromide	0.250	0.074	10	0.25
diphenylether	0.231	0.058	5	0.24
3-methylanisole	0.352	0.009	2	0.35
1,2-dimethoxybenzene	0.648	0.013	2	0.65
1,4-dimethoxybenzene	0.578	0.014	8	0.58
phthalaldehyde	0.653	0.098	2	0.65
4-methoxybenzaldehyde	0.614	0.018	8	0.61
benzophenone	0.538	0.033	16	0.54
bromomethylphenylketone	0.552	0.018	2	0.55
methyl benzoate	0.475	0.038	28	0.47
ethyl benzoate	0.461	0.026	13	0.47
propyl benzoate	0.477	0.026	2	0.47
phenyl benzoate	0.455	0.013	3	0.47
dimethylphthalate	0.986	0.013	2	1.05
diethylphthalate	1.068	0.038	8	1.05
1-nitropropane	0.250	0.005	12	0.25
4-bromomethylnitrobenzene	0.406	0.085	9	0.41
1,3-dinitrobenzene	0.539	0.028	2	0.54
1,4-dinitrobenzene	0.548	0.013	7	0.55
1-MeO-4-nitrobenzene	0.416	0.044	3	0.42
2,4-dinitrotoluene	0.549	0.021	7	0.55
phenylacetonitrile	0.442	0.024	9	0.44

Anilines	Average	SD	No	Taken
aniline	0.544	0.021	17	0.53
diphenylamine	0.351	0.030	2	0.35
2-methylaniline	0.566	0.008	2	0.57
3-methylaniline	0.558	0.019	3	0.55
4-methylaniline	0.565	0.013	12	0.57
N-methylaniline	0.467	0.015	4	0.47
N,N-dimethylaniline	0.380	0.031	2	0.38
3-cyanoaniline	0.668	0.056	2	0.67
4-cyanoaniline	0.703	0.060	2	0.70
3-fluoroaniline	0.462	0.054	2	0.40
4-fluoroaniline	0.532	0.023	2	0.51
2-chloroaniline	0.438	0.004	2	0.44
3-chloroaniline	0.401	0.036	4	0.40
4-chloroaniline	0.462	0.032	11	0.45
3-bromoaniline	0.394	0.047	2	0.39
4-bromoaniline	0.419	0.036	2	0.44
3-iodoaniline	0.391	0.040	2	0.39
4-iodoaniline	0.402	0.033	2	0.42
3-methoxyaniline	0.760	0.010	4	0.76
4-methoxyaniline	0.831	0.002	3	0.83
methyl 4-aminobenzoate	0.775	0.040	6	0.78
3-nitroaniline	0.550	0.049	2	0.55
4-nitroaniline	0.599	0.035	11	0.60
3-aminoacetophenone	0.920	0.031	2	0.92
4-aminoacetophenone	0.946	0.068	3	0.95
acetanilide	0.689	0.012	3	0.69
benzamide	0.681	0.025	4	0.68

Pyridines, etc.	Average	SD	No	Taken
pyridine	0.63	0.01	4	0.62
3-methylpyridine	0.63	0.01	2	0.62
4-methylpyridine	0.63	0.01	2	0.65
2-chloropyridine	0.49	0.07	3	0.49
3-chloropyridine	0.49	0.01	4	0.49
4-chloropyridine	0.52	0.01	2	0.53
3-bromopyridine	0.50	0.01	4	0.50
4-bromopyridine	0.53	0.01	2	0.53
3-acetylpyridine	0.94	0.01	2	0.94
4-acetylpyridine	0.95	0.01	2	0.95
3-cyanopyridine	0.79	0.01	2	0.79
4-cyanopyridine	0.82	0.01	2	0.82
2-aminopyridine	0.61	0.02	3	0.61
3-aminopyridine	0.78	0.02	3	0.78
quinoline	0.63	0.01	2	0.63
isoquinoline	0.60	0.01	2	0.60
acridine	0.52	0.02	2	0.52

Table 3 (cont). Some Backcalculated ΣβH2 Values From HPLC Data.

Carboxylic acids	Average	SD	No	Taken
2-methylpropanoic acid	0.420	0.003	2	0.42
3-methylbutanoic acid	0.423	0.003	2	0.41
hexanoic acid	0.383	0.001	2	0.39
octanoic acid	0.357	0.009	2	0.36
decanoic acid	0.332	0.011	2	0.33
benzoic acid	0.424	0.023	24	0.42
3-fluorobenzoic acid	0.363	0.012	2	0.36
2-chlorobenzoic acid	0.387	0.010	9	0.39
3-chlorobenzoic acid	0.305	0.019	8	0.29
4-chlorobenzoic acid	0.309	0.018	24	0.31
2,4-dichlorobenzoic acid	0.206	0.005	5	0.21
2,5-dichlorobenzoic acid	0.229	0.017	5	0.23
2,6-dichlorobenzoic acid	0.340	0.020	5	0.34
3,4-dichlorobenzoic acid	0.103	0.003	5	0.10
3,5-dichlorobenzoic acid	0.102	0.006	5	0.10
2-bromobenzoic acid	0.362	0.008	4	0.36
3-bromobenzoic acid	0.274	0.014	7	0.29
4-bromobenzoic acid	0.294	0.013	16	0.31
4-fluorobenzoic acid	0.380	0.002	2	0.38
3-iodobenzoic acid	0.292	0.011	8	0.29
4-iodobenzoic acid	0.303	0.037	5	0.30
2-methylbenzoic acid	0.448	0.002	4	0.45
3-methylbenzoic acid	0.436	0.012	7	0.43
4-methylbenzoic acid	0.427	0.020	23	0.43
2,4-dimethylbenzoic acid	0.457	0.004	4	0.46
2,5-dimethylbenzoic acid	0.462	0.002	4	0.46
2,6-dimethylbenzoic acid	0.582	0.014	5	0.58
3,4-dimethylbenzoic acid	0.458	0.019	8	0.46
3,5-dimethylbenzoic acid	0.452	0.003	4	0.45
2,4,6-trimethylbenzoic acid	0.588	0.010	5	0.59
4-ethylbenzoic acid	0.447	0.016	8	0.45
4-isopropylbenzoic acid	0.408	0.007	3	0.41
4-t-butylbenzoic acid	0.411	0.146	2	0.41
4-phenylbenzoic acid	0.429	0.002	2	0.43
3-nitrobenzoic acid	0.609	0.004	2	0.61
4-nitrobenzoic acid	0.544	0.028	11	0.54
3-cyanobenzoic acid	0.636	0.035	2	0.64
4-cyanobenzoic acid	0.640	0.001	2	0.64
phenylacetic acid	0.552	0.005	5	0.55
2-methylphenylacetic acid	0.565	0.008	5	0.56
3-methylphenylacetic acid	0.552	0.012	5	0.55
2-chlorophenylacetic acid	0.473	0.004	5	0.47
4-chlorophenylacetic acid	0.424	0.005	5	0.42
3-phenylpropionic acid	0.549	0.005	5	0.55
4-phenylbutyric acid	0.556	0.005	5	0.56
t-cinnamic acid	0.459	0.004	5	0.46
t-4-methylcinnamic acid	0.447	0.004	5	0.45

Phenols	Average	SD	No	Taken
phenol	0.363	0.020	31	0.36
2-methylphenol	0.371	0.022	9	0.37
3-methylphenol	0.388	0.010	3	0.39
4-methylphenol	0.383	0.016	25	0.40
2,3-dimethylphenol	0.384	0.012	7	0.38
2,4-dimethylphenol	0.390	0.007	8	0.39
2,5-dimethylphenol	0.387	0.004	9	0.39
2,6-dimethylphenol	0.387	0.004	8	0.39
3,4-dimethylphenol	0.434	0.017	11	0.43
3,5-dimethylphenol	0.426	0.019	8	0.43
2,3,5-trimethylphenol	0.415	0.019	8	0.41
2,3,6-trimethylphenol	0.410	0.026	8	0.41
2,4,6-trimethylphenol	0.406	0.017	8	0.41
2-ethylphenol	0.396	0.014	8	0.40
3-ethylphenol	0.409	0.015	9	0.39
4-ethylphenol	0.414	0.017	11	0.40
2,3,5,6-tetramethylphenol	0.457	0.017	9	0.46
4-t-butylphenol	0.408	0.008	3	0.41
2,6-di-t-butylphenol	0.595	0.015	2	0.60
3-fluorophenol	0.246	0.024	2	0.24
4-fluorophenol	0.322	0.013	2	0.32
2-chlorophenol	0.291	0.025	12	0.29

Table 3 (cont). Some Backcalculated ΣβH2 Values From HPLC Data.

Phenols (cont).	Average	SD	No	Taken
3-iodophenol	0.210	0.014	2	0.23
3-chlorophenol	0.229	0.025	14	0.23
4-iodophenol	0.226	0.009	5	0.24
2,3-dichlorophenol	0.228	0.025	8	0.23
4-chlorophenol	0.261	0.025	26	0.25
3-bromophenol	0.234	0.015	9	0.23
4-bromophenol	0.244	0.027	19	0.25
2,6-dichlorophenol	0.281	0.017	11	0.28
2,5-dichlorophenol	0.205	0.002	8	0.21
3,4-dichlorophenol	0.188	0.018	8	0.19
3,5-dichlorophenol	0.128	0.011	8	0.13
2,4-dichlorophenol	0.195	0.013	8	0.20
2,4,5-trichlorophenol	0.138	0.007	8	0.14
3,4,5-trichlorophenol	0.113	0.010	8	0.11
2,3,4-trichlorophenol	0.171	0.011	8	0.17
2,3,5-trichlorophenol	0.167	0.043	8	0.17
2,3,6-trichlorophenol	0.239	0.011	8	0.24
2,4,6-trichlorophenol	0.192	0.013	7	0.19
2,3,4,5-tetrachlorophenol	0.106	0.028	8	0.11
2,3,5,6-tetrachlorophenol	0.188	0.030	8	0.19
pentachlorophenol	0.145	0.030	10	0.15
2-chloro-5-methylphenol	0.308	0.004	4	0.31
4-chloro-2-methylphenol	0.298	0.003	4	0.30
4-chloro-3-methylphenol	0.327	0.013	7	0.33
2,4-dibromophenol	0.189	0.006	8	0.19
2,6-dibromophenol	0.276	0.008	4	0.28
3-methoxyphenol	0.560	0.029	3	0.56
4-methoxyphenol	0.626	0.029	4	0.63
4-hydroxybenzaldehyde	0.538	0.013	7	0.54
3-acetylphenol	0.667	0.017	2	0.67
4-acetylphenol	0.708	0.023	2	0.71
3-CO2Me-phenol	0.630	0.005	2	0.63
4-CO2Me-phenol	0.631	0.012	9	0.63
2-nitrophenol	0.269	0.016	7	0.27
3-nitrophenol	0.310	0.028	6	0.31
4-nitrophenol	0.330	0.006	22	0.33
2,4-dinitrophenol	0.341	0.023	3	0.34
2-methyl-4,6-dinitrophenol	0.331	0.004	3	0.33
3-cyanophenol	0.400	0.029	2	0.40
4-cyanophenol	0.422	0.043	8	0.42

Benzyl alcohols	Average	SD	No	Taken
benzyl alcohol	0.498	0.044	15	0.50
2-chlorobenzyl alcohol	0.456	0.007	3	0.46
2,6-dichlorobenzyl alcohol	0.480	0.023	3	0.48
2-phenyl ethanol	0.534	0.043	2	0.53
4-phenylbenzyl alcohol	0.541	0.036	3	0.54
4-methylbenzyl alcohol	0.551	0.018	5	0.55
3,4-dimethylbenzyl alcohol	0.567	0.018	3	0.57
4-chlorobenzyl alcohol	0.453	0.007	5	0.45
3,5-dichlorobenzyl alcohol	0.341	0.008	6	0.34
3-iodobenzyl alcohol	0.427	0.025	6	0.42
4-methoxybenzyl alcohol	0.722	0.032	7	0.72

Sulphur compounds	Average	SD	No	Taken
PhSO2Me	0.786	0.002	2	0.79
PhSO2Et	0.855	0.012	2	0.85
PhSO2NH2	0.739	0.011	2	0.74
PhSO2NHMe	0.767	0.006	2	0.77

Table 4. Comparison of $\Sigma\beta^{H}_{2}$ Back-Calculated from RP-HPLC Data[47], and β^{H}_{2} Values

Compound Name	$\Sigma\beta^{H}_{2}$	β^{H}_{2}
Acetic Acid	0.41	-
Butanoic Acid	0.43	-
4-Methoxybenzaldehyde	0.61	0.47
1,4-Benzoquinone	0.59	0.34
Phenyl benzoate	0.47	0.39
Aniline	0.53	0.38
2-Methylaniline	0.57	0.38
3-Methylaniline	0.55	0.40
4-Methylaniline	0.57	0.42
4-Ethylaniline	0.57	0.42
4-Fluoroaniline	0.51	0.36
2-Chloroaniline	0.44	0.33
3-Chloroaniline	0.40	0.29
4-Chloroaniline	0.45	0.34
3-Bromoaniline	0.39	0.27
4-Iodoaniline	0.42	0.31
3-Methoxyaniline	0.76	0.40
4-Methoxyaniline	0.83	0.45
N,N-Dimethylaniline	0.38	0.35
4-Fluorophenol	0.32	0.21
2-Phenylethanol	0.53	0.45
Methylphenylsulphoxide	0.79	0.70
3-Cyanopyridine	0.79	0.44
4-Cyanopyridine	0.82	0.47

(ii) Calculation of a New Solute Parameter π^H_2

Having examined the extensive GLC data of McReynolds[44], and Laffort[45], this data, along with other extensive chromatographic data, could then be used to back-calculate a large number of solvation parameters for a huge set of solutes. Recommended values for solvation parameters will be presented in a summary table later, (see Table 8). Additionally, the opportunity arises to set up a coherent scale for the π^*_2 parameter, which had hitherto been a problem. Values of R_2, α^H_2, β^H_2, and log L^{16} can be obtained through various approximations and estimations, all based on the original experimentally determined values. There are, however, difficulties over the solute parameter π^*_2. Originally[41,48] π^*_2 was taken as identical to the Kamlet-Taft solvatochromic solvent parameter π^*_1 for non-associated liquids only. Since π^*_1 is experimentally accessible only for compounds that are liquid at 298K, values of π^*_2 had then to be estimated, not only for all associated compounds (including acids, alcohols, phenols, amides, *etc.*) but also for all compounds that are solid (or gaseous) at 298K. In addition, there is present the inherent assumption that π^*_1 is identical to π^*_2 for non-associated liquids. The Kamlet-Taft solvatochromic solvent basicity parameter β_1 is not exactly equivalent to the solute parameter β^H_2 even for non-associated liquids[49], and it is possible that whilst π^*_2 can be taken as equal to π^*_1 for non-associated liquids as a generality, there may be a number of exceptions to this rule.

It seems necessary to set up a scale of solute dipolarity/polarisability based on some experimental procedure that will include, at least in principle, all types of solute molecule. The data of McReynolds[44] and of Laffort[45] can be used to construct a new solute dipolarity/polarisability scale π^H_2 for use in our solvation equations. Since this work was started, Carr *et al.*[50] have also concluded that the π^*_2 scale derived from π^*_1 is not very suitable for use in solvation equations, and have constructed an alternative π^C_2 scale of solute dipolarity. This scale will be discussed later.

McReynolds[44] determined V_G^0 values for up to 376 solutes on up to 77 stationary phases. Nearly all the phases were examined at a common temperature of 120°C. Of these 77 phases, 75 were found[51] to have no hydrogen bond acidity at all, hence the $b.\beta^H_2$ term in general solvation equation 9 drops out, and the log V_G^o values can be correlated by equation 12.

$$\log V_G^0 = c + r.R_2 + s.\pi^*_2 + a.\alpha^H_2 + l.\log L^{16} \qquad [12]$$

It is possible to set up a series of equations (n = 1 to n = 75), one for each stationary phase, where the constants *c, r, s, a,* and *l* have been determined by MLRA, using known values of the solute parameters R_2, π^*_2, α^H_2, and log L^{16} for as many solutes as possible. Typically, around 150 solutes were included in each regression equation 12, generalised as equation 13.

$$\log V_{G(n)}{}^{0} = c_n + r_n.R_2 + s_n.\pi^*_2 + a_n.\alpha^H_2 + l_n.\log L^{16} \qquad [13]$$

It is convenient to subsume the constant c_n into the dependent variable to give 75 equations,

$$\begin{array}{ll} V_{n=1} = r_{n=1}.R_2 + s_{n=1}.\pi^*_2 + a_{n=1}.\alpha^H_2 + l_{n=1}.\log L^{16} & \\ \cdot & \\ \cdot & \\ \cdot & \\ \cdot & [14] \\ \cdot & \\ \cdot & \\ \cdot & \\ V_{n=75} = r_{n=75}.R_2 + s_{n=75}.\ \pi^*_2 + a_{n=75}.\alpha^H_2 + l_{n=75}.\log L^{16} & \end{array}$$

where $V_n = \log V_{G(n)}{}^{0} - c_n$ [15]

The matrix defined by equation 14 can be used in a vertical format, by regarding V_n for a given solute as the dependent variable, and the constants r_n, s_n, a_n and l_n as four explanatory variables. In this new (vertical) MLR equation, R_2, π^*_2, α^H_2, and $\log L^{16}$ for the particular solute now become the unknown coefficients to be evaluated by MLRA. Since all the input data is now related purely to properties of the solute, π^*_2 can be replaced by an experimentally determined parameter, π^H_2:

$$V(\text{solute}) = V_n = R_2.r_n + \pi^H_2.s_n + \alpha^H_2.a_n + \log L^{16}.l_n \qquad [16]$$

A thorough analysis was carried out using equation 16, where the regression equation was forced through the origin, (purely because the constant should be equal to zero), and obtained reasonable values of R_2, π^H_2, α^H_2, and $\log L^{16}$ for the various solutes studied. However, since R_2 is either known or can very easily be calculated for any solute, the number of explanatory variables can be reduced by incorporating R_2 into the dependent variable,

$$\left[\log V_{G(n)}{}^{0} - c_n - r_n.R_2\right] = V' = \pi^H_2.s_n + \alpha^H_2.a_n + \log L^{16}.l_n \qquad [17]$$

Again, the regression equation 17 is constrained to pass through the origin: results were found to be much more self-consistent than when a constant term was allowed to float. Results obtained using the preferred equation 17 can be checked by comparison of calculated solute parameters with known values, where available. Some typical results are given in Table 5 together with the standard deviation (S.D.) of the parameter, the number of stationary phases in the set (always less than 75, because not all solutes were examined on all phases by McReynolds), and the overall S.D. in the dependent variable V'. Correlation coefficients are not listed, because these have little meaning for a regression equation forced through the origin.

Table 5. Some Calculated Parameters Using equation 17.

Solute	π^H_2	α^H_2	log L^{16}	n	S.D.
Pent-l-ene	0.09 ± 0.004	0.00 ± 0.007	2.040 ± 0.007	36	0.014
	[a]0.08	0.00	2.013		
Toluene	0.47 ± 0.004	-0.01 ± 0.007	3.327 ± 0.008	73	0.017
	[a]0.55	0.00	3.344		
Diethyl ether	0.27 ± 0.004	-0.02 ± 0.007	1.975 ± 0.008	71	0.017
	[a]0.27	0.00	2.061		
Butanone	0.69 ± 0.004	0.00 ± 0.007	2.282 ± 0.007	71	0.016
	[a]0.67	0.00	2.287		
n-Propyl acetate	0.61 ± 0.004	0.00 ± 0.007	2.847 ± 0.007	73	0.016
	[a]0.55	0.00	2.878		
Propan-l-ol	0.41 ± 0.009	0.37 ± 0.006	2.060 ± 0.006	72	0.016
	[a]0.40	0.33	2.097		

[a] Previous values, see ref. 46.

There are a number of deficiencies in McReynolds' experimentation [51], and it is quite possible that for certain combinations of solute and stationary phase, the retention data are inexact due to sorption at the liquid interface. Note though, that the vertical or "inverse" MLRA procedure yields solvation parameters that are effectively averages for a given solute over some 30-70 stationary phases, see Table 5. In the event, hydrocarbons such as alkanes and alkenes behave quite normally in the inverse MLRA, see Table 6.

Listed in Table 6 are the π^H_2 values obtained through equation 17. The π^H_2 values in Table 6 are effective or 'summation' π^H_2 values for a situation in which a solute molecule is surrounded by an excess of solvent molecules, and so in a similar manner to $\Sigma\beta^H_2$, may be more correctly denoted as $\Sigma\pi^H_2$. Before discussing these $\Sigma\pi^H_2$ values from the McReynolds' data[44], the extensive GLC data of Laffort[45] can also be analysed, and many parameters back-calculated. The methodology of this follows after listing the $\Sigma\pi^H_2$ values in Table 6.

TABLE 6. CALCULATED VALUES OF π_2^H

		π_2^H	
Equation :	17	26	18
Alkanes			
Ethane		0.03	0.11
Propane		0.03	0.08
Butane		0.03	0.05
2-Methylpropane		0.07	0.07
Pentane		0.03	0.03
Hexane	0.02	0.03	0.02
2,3-Dimethylbutane	-0.01		
Heptane		0.03	0.01
2,4-Dimethylpentane		-0.04	-0.02
Octane	0.01	0.03	0.00
2-Methylheptane		0.08	0.01
3-Methylheptane		0.07	0.03
Nonane		0.03	0.00
2,2,5-Trimethylhexane		0.16	
Decane	0.03	0.03	-0.01
Undecane		0.03	-0.02
Dodecane	0.03	0.03	0.03
Tridecane		0.03	-0.04
Tetradecane	0.05	0.03	-0.03
Hexadecane	0.07		
Octadecane	0.05		
Cyclohexane		0.08	0.14
Hydrindane		0.19	0.22
Decalin		0.23	0.27
Alkenes			
Ethene		-0.13	0.32
Propene		-0.09	0.25
But-1-ene		-0.05	0.21
Pent-1-ene	0.09	-0.05	0.19
Hex-1-ene		0.00	0.11
Hept-1-ene		0.06	0.11
Oct-1-ene		0.08	0.09
cis-Oct-2-ene		0.11	0.12
2-Ethylhex-1-ene		0.16	0.13
α-Pinene		0.30	0.18
Alkynes			
But-2-yne		0.17	0.37
Oct-1-yne		0.19	0.23
Oct-2-yne		0.16	0.31
Haloaliphatics			
1-Fluoro-octane		0.30	
Dichloromethane	0.66		
Trichloromethane	0.65	0.25	0.36
Tetrachloromethane	0.35	0.28	0.35
1,2-Dichloroethane	0.74	0.35	0.55
1,1,2,2-Tetrachloroethane		0.32	0.65
1-Chlorohexane		0.27	0.36
Trichloroethene		0.34	0.33
Hexachlorobutadiene		0.62	
Bromoethane		0.30	0.42
1-Bromopentane		0.30	0.39
2-Bromo-octane		0.33	0.28
Iodomethane		0.35	0.44
1-Iodobutane		0.38	0.39
2-Iodobutane		0.40	0.39
1,1-Difluorotetrachloroethane		0.41	
1,2-Difluorotetrachloroethane		0.41	0.33
Aromatic hydrocarbons			
Benzene	0.48	0.53	0.47
Toluene	0.47	0.57	0.46
Ethylbenzene	0.47	0.56	0.46
o-Xylene	0.50	0.63	0.43
m-Xylene	0.47	0.60	0.46
p-Xylene	0.46	0.61	0.46
1,3,5-Trimethylbenzene		0.64	0.46
1,2-Diethylbenzene	0.50		
1,3-Diethylbenzene	0.48		
1,4-Diethylbenzene	0.47		

TABLE 6. CALCULATED VALUES OF π_2^H

		π_2^H	
Equation :	17	26	18
<u>Aromatic hydrocarbons (continued)</u>			
Styrene		0.70	0.55
Phenylethyne		0.55	0.68
<u>Haloaromatics</u>			
1,2-Dichlorobenzene		0.65	0.70
Benzyl chloride		0.69	0.78
<u>Ethers</u>			
Dimethyl ether	0.36		
Diethyl ether	0.27	0.19	0.27
Dipropyl ether	0.23		
Di-isopropyl ether	0.16		
Dibutyl ether	0.24	0.16	0.18
Dipentyl ether	0.27		
Di-isopentyl ether	0.21		
Dihexyl ether	0.27		
Di-2-ethyl-1-butyl ether	0.17		
Methyl propyl ether	0.30		
Methyl butyl ether	0.30		
Methyl isobutyl ether	0.25		
Methyl t-butyl ether	0.29		
Ethyl butyl ether	0.26		
Ethyl t-butyl ether	0.20		
Propyl isopropyl ether	0.19		
Isopropyl t-butyl ether	0.16		
Bis(2-ethoxyethyl)ether	0.79		
Ethyl vinyl ether	0.37		
Butyl vinyl ether	0.34		
Isobutyl vinyl ether	0.29		
2 Ethyl-1-hexyl vinyl ether	0.32		
2-Methoxyethyl vinyl ether	0.68		
Diallyl ether	0.38		
Ethylene oxide	0.59		
1,2-Propylene oxide	0.57		
1,2-Butylene oxide	0.55		
2-Methyl-1,2-Propylene oxide	0.52		
trans-2,3-Butylene oxide	0.52		
cis-2,3-Butylene oxide	0.55		
1,3-Propylene oxide	0.61		
1,3-Butylene oxide	0.52		
Furan	0.54	0.39	0.51
2-Methylfuran	0.50		
2-Acetyl-3-methylfuran		1.17	
2-Acetyl-5-methylfuran		1.19	
2-Propanoyl-3-methylfuran		0.91	
Tetrahydrofuran	0.55		
2-Methyltetrahydrofuran	0.47		
2,5-Dimethyltetrahydrofuran	0.38		
Dioxan	0.75	0.69	0.74
Tetrahydropyran	0.49		
3,4-Dihydropyran	0.51		
Trioxane	1.02		
Trimethyltrioxane (paraldehyde)	0.68		
2-Methyl-2-ethyl-1,3-dioxolane	0.58		
Anethole		1.02	
Dimethoxymethane	0.52		
Methoxyethoxymethane	0.49		
Methoxyisopropoxymethane	0.45		
Diethoxymethane	0.45		
Ethoxypropoxymethane	0.44		
Ethoxyisopropoxymethane	0.41		
Ethoxy-s-butyloxymethane	0.41		
Dipropyloxymethane	0.42		
Propoxy-s-butyloxymethane	0.40		
Di-isopropoxymethane	0.37		
Dibutyloxymethane	0.43		
Di-isobutyloxymethane	0.37		
Di-s-butyloxymethane	0.37		
1,1-Dimethoxyethane	0.49		
1,1-Diethoxyethane	0.41		
1,1-Dipropoxyethane	0.37		
1,1-Di-isobutyloxyethane	0.26		

TABLE 6. CALCULATED VALUES OF π_2^H

	π_2^H		
Equation :	17	26	18
<u>Ethers (continued)</u>			
1,1-Dimethoxypropane	0.46		
1,1-Diethoxypropane	0.38		
1,1-Dimethoxybutane	0.47		
1,1-Dimethoxy-2-methylpropane	0.42		
2,2-Dimethoxypropane	0.43		
2,2-Diethoxypropane	0.32		
1,1,3-Trimethoxybutane	0.69		
Methylphenylether		0.73	0.70
1,8-Cineole		0.47	
<u>Aldehydes</u>			
Formaldehyde	0.73		
Acetaldehyde	0.70	0.63	0.65
Propanal	0.65	0.59	0.62
Butanal	0.63	0.61	0.61
2-Methylpropanal	0.58	0.59	0.59
Pentanal	0 63		
2-Methylbutanal	0.58		
3-Methylbutanal	0.60	0.62	0.58
2,2-Dimethylpropanal	0.49		
Hexanal	0.64	0.59	0.59
Heptanal	0.65	0.58	0.59
Octanal		0.57	0.57
2-Ethylhexanal	0.56		
Prop-2-ene-1-al (acrolein)	0.74	0.68	0.58
trans-But-2-ene-1-al	0.81	0.85	0.75
2-Methylprop-2-ene-1-al (methacrolein)	0.62		
trans-Hex-2-ene-1-al		0.88	0.85
2-Ethylbut-2-ene-1-al	0.68		
trans-Hept-2-ene-1-al		0.85	0.84
trans-Oct-2-ene-1-al		0.55	
2-Ethylhex-2-ene-1-al	0.62		
Hexa-2,4-dienal	0.90		
Furfural		0.97	1.05
Benzaldehyde		0.99	0.94
3-Methoxybutanal	0.85		
<u>Ketones</u>			
Propanone	0.73	0.77	0.66
Butanone	0.69	0.72	0 66
Pentan-2-one	0.66	0.70	0.66
Pentan-3-one	0.64		
3-Methylbutan-2-one	0.63		
Hexan-2-one	0.67	0.71	0.65
Hexan-3-one	0.62	0.65	0.58
3-Methylpentan-2-one	0.62		
4-Methylpentan-2-one	0.62		
3,3-Dimethylbutan-2-one	0.58		
Heptan-2-one	0 67	0.69	0 64
Heptan-3-one	0.62		
Heptan-4-one	0.61		
4,4-Dimethylpentan-2-one	0.57		
2,4-Dimethylpentan-3-one	0.52		
Octan-2-one	0.68	0.68	0.65
Nonan-2-one	0.68	0.69	0.64
Nonan-5-one	0.61		
Decan-2-one		0.67	0.65
Undecan-2-one		0.67	0.64
Dodecan-2-one		0.67	0.64
Cyclopentanone	0.84	0.83	0.86
Cyclohexanone	0.84	0.87	0.87
Cycloheptanone		0.84	0.86
Cyclo-octanone		0.83	0.85
Cyclononanone		0.83	0.84
Cyclodecanone		0.83	0.84
Cycloundecanone		0.83	0.83
Cyclododecanone		0.83	0.83
Cyclotridecanone		0.82	0 82
Cyclotetradecanone		0.82	0.82
Carvone		0.86	0.98
But-3-ene-2-one	0.76		
3-Methylbut-3-ene-2-one	0.68		

TABLE 6. CALCULATED VALUES OF π_2^H

	π_2^H		
Equation :	17	26	18
Ketones (continued)			
Hex-5-ene-2-one	0.75		
4-Methylpent-3-ene-2-one	0.70		
Butan-2,3-dione	0.52	0.71	0.74
Pentan-2,3-dione	0.47		
Pentan-2,4-dione	0.56		
Acetophenone		1.09	0.99
Esters			
Methyl formate	0.72		
Ethyl formate	0.67		
Propyl formate	0.65	0.56	0.60
Isopropyl formate	0.62		
Butyl formate	0.66		
Isobutyl formate	0.62		
sec-Butyl formate	0.61		
Pentyl formate	0.66		
2-Pentyl formate	0.60		
3-Pentyl formate	0.60		
Hexyl formate	0.67		
Methyl acetate	0.67	0.63	0.61
Ethyl acetate	0.62	0.60	0.59
Propyl acetate	0.61	0.60	0.57
Isopropyl acetate	0.57		
Butyl acetate	0.61	0.59	0.58
Isobutyl acetate	0.58		
sec-Butyl acetate	0.56		
tert-Butyl acetate	0.50		
Pentyl acetate	0.62	0.58	0.59
Isopentyl acetate	0.60	0.59	0.53
2-Pentyl acetate	0.56		
3-Pentyl acetate	0.56		
2-Methyl-2-butyl acetate	0.51		
Hexyl acetate	0.63		
4-Methyl-2-pentyl acetate	0.55		
2-Ethyl-1-butyl acetate	0.60		
Heptyl acetate	0.63		
2-Ethyl-1-hexyl acetate	0.60		
Cyclohexyl acetate	0.69		
Methyl propanoate	0.62	0.56	0.58
Ethyl propanoate	0.58		
Propyl propanoate	0.57		
Isopropyl propanoate	0.52		
Butyl propanoate	0.57		
Isobutyl propanoate	0.54		
Pentyl propanoate	0.58		
Isopentyl propanoate	0.56		
2-Pentyl propanoate	0.52		
2-Ethyl-1-hexylpropanoate	0.55		
Methyl butanoate	0.61		
Ethyl butanoate	0.56		
Propyl butanoate	0.56	0.54	0.51
Isopropyl butanoate	0.51		
Butyl butanoate	0.56		
Isobutyl butanoate	0.54		
Pentyl butanoate	0.57		
Isopentyl butanoate	0.55		
2-Pentyl butanoate	0.51		
2-Ethyl-1-hexyl butanoate	0.57		
Methyl isobutanoate	0.56		
Butyl isobutanoate	0.51		
Isobutyl isobutanoate	0.49	0.56	0.46
Isopentyl isopentanoate		0.55	0.55
Allyl formate	0.76		
Allyl acetate	0.72		
Allyl propanoate	0.67		
Vinyl acetate	0.66		
Vinyl butanoate	0.56		
1-Propenyl acetate	0.67		
Isopropenyl acetate	0.68		
Methyl acrylate	0.68		
Ethyl acrylate	0.64		
2-Ethyl-1-hexyl acrylate	0.61		

TABLE 6. CALCULATED VALUES OF π_2^H

Equation :	π_2^H 17	π_2^H 26	π_2^H 18
Esters (continued)			
Propyl acrylate	0.62		
Butyl acrylate	0.62		
Methyl methacrylate	0.62		
Allyl acrylate	0.72		
2-Methoxyethyl acetate	0.93		
2-Ethoxyethyl acetate	0.87	0.68	0.79
3-Methoxy-1-butyl acetate	0.83		
3-Methoxy-1-butyl acrylate	0.83		
Methylene diacetate	1.16		
Ethylene diacetate	1.20		
Ethylene dipropanoate	1.05		
Propylene diacrylate	1.10		
Benzyl acetate		1.19	0.95
Methyl benzoate		0.77	1.11
Methyl salicylate		0.82	
Nitrocompounds			
Nitromethane		0.73	0.86
Nitroethane		0.74	0.87
1-Nitropropane		0.71	0.86
2 Methyl-2-nitropropane		0.82	0.82
3-Nitrotoluene		1.08	1.05
Nitriles			
Acetonitrile		0.80	0.85
1-Cyanopropane		0.78	0.84
1-Cyanobutane		0.80	0.83
Benzonitrile		1.05	1.04
Amines			
s-Butylamine		0.21	0.47
Allylamine		0.29	
Trimethylamine		0.47	
Heterocyclics			
Pyridine		0.80	0.80
2,3,6-Trimethylpyridine		0.71	
Pyrrole		0.61	0.65
Trimethylpyrazine		0.77	
2-Methyl-3-ethylpyrazine		0.73	
2-Methoxy-3-isobutylpyrazine		0.56	
2,4,5-Trimethyloxazole		0.68	
Carboxylic acids			
Acetic acid		0.68	
Propanoic acid		0.60	
Butanoic acid		0.56	
2-Methylpropanoic acid		0.58	
Pentanoic acid		0.58	
2-Methylbutanoic acid		0.55	
3-Methylbutanoic acid		0.56	
Hexanoic acid		0.62	
2-Methylpentanoic acid		0.68	
Heptanoic acid		0.58	
Octanoic acid		0.56	
Nonanoic acid		0.53	
Decanoic acid		0.50	
Undecanoic acid		0.46	
Dodecanoic acid		0.43	
3-Butenoic acid		0.62	
Phenols			
2-Chlorophenol		0.66	
Salicylaldehyde		0.98	
Hydroxylic compounds			
Water	0.40		
Methanol	0.39	0.46	
Ethanol	0.40	0.41	
Propan-1-ol	0.41	0.42	
Butan-1-ol	0.42	0.41	
2-Methylpropan-1-ol	0.38	0.42	

TABLE 6. CALCULATED VALUES OF π_2^H

	π_2^H		
Equation :	17	26	18
Hydroxylic compounds (continued)			
Pentan-1-ol		0.41	
2-Methylbutan-1-ol	0.39	0.41	
3-Methylbutan-1-ol	0.39	0.42	
2,2-Dimethylpropan-1-ol	0.33		
Hexan-1-ol	0.42	0.40	
2-Methylpentan-1-ol	0.40		
3-Methylpentan-1-ol	0.44		
4-Methylpentan-1-ol	0.43		
2-Ethylbutan-1-ol	0.40		
2,2-Dimethylbutan-1-ol	0.37		
Heptan-1-ol	0.43	0.39	
2,2-Dimethylpentan-1-ol	0.37		
Octan-1-ol	0.43	0.39	
2-Ethylhexan-1-ol	0.41		
2-Ethyl-4-methylpentan-1-ol	0.39		
Nonan-1-ol	0.39	0.39	
Decan-1-ol		0.39	
Undecan-1-ol		0.39	
Dodecan-1-ol		0.38	
Propan-2-ol	0.39	0.42	
Butan-2-ol	0.41	0.44	
Pentan-2-ol	0.40		
Pentan-3-ol	0.40		
3-Methylbutan-2-ol	0.39		
Hexan-2-ol	0.40	0.44	
Hexan-3-ol	0.39	0.41	
3-Methylpentan-2-ol	0.40		
4-Methylpentan-2-ol	0.38		
2-Methylpentan-3-ol	0.39		
2,3-Dimethylbutan-2-ol	0.41		
3,3-Dimethylbutan-2-ol	0.37		
Heptan-2-ol	0.40		
Heptan-3-ol	0.40		
Heptan-4-ol	0.39		
2,4-Dimethylpentan-3-ol	0.40		
Octan-2-ol	0.41		
2-Methylpropan-2-ol	0.38	0.50	
2-Methylbutan-2-ol	0.41	0.47	
2-Methylpentan-2-ol	0.40	0.48	
3-Methylpentan-3-ol	0.45	0.47	
2-Methylheptan-2-ol		0.47	
3-Methylheptan-3-ol		0.46	
3-Ethylpentan-3-ol	0.47		
Cyclopropylcarbinol	0.57		
Cyclopentanol	0.55	0.47	
Cyclohexanol	0.57		
2-Methylcyclohexanol	0.52		
cis,cis-2,6-Dimethylcyclohexanol		0.43	
cis,trans-2,6-Dimethylcyclohexanol		0.45	
trans,trans-2,6-Dimethylcyclohexanol		0.51	
dl-α-Terpineol		0.57	
exo-Ethylfenchol		0.52	
1,2-Ethane diol	0.50		
1,2-Propane diol	0.49		
1,2-Butane diol	0.63		
2-Methyl-1,2-propane diol	0.60		
dl-2,3-Butane diol	0.62		
meso-2,3-Butane diol	0.65		
1,3-Propane diol	0.46		
1,3-Butane diol	0.68		
1,4-Butane diol	0.46		
Prop-2-ene-1-ol (allyl alcohol)	0.44	0.46	
But-2-ene-1-ol	0.49		
But-3-ene-1-ol	0.47		
But-3-ene-2-ol	0.43		
2-Methylprop-2-ene-1-ol	0.45		
Pent-3-ene-1-ol	0.50		
Pent-4-ene-1-ol	0.46		
Pent-1-ene-3-ol	0.43		
2-Methylbut-3-ene-2-ol	0.41		
trans-Hex-2-ene-1-ol		0.43	
trans-Hept-2-ene-1-ol		0.40	

TABLE 6. CALCULATED VALUES OF π_2^H

Equation :	π_2^H 17	π_2^H 26	π_2^H 18
<u>Hydroxylic compounds (continued)</u>			
trans-Oct-2-ene-1-ol		0.41	
Prop-2-yne-1-ol	0.46		
2-Methylbut-3-yne-2-ol	0.47		
2-Chloroethanol	0.54		
2-Methoxyethanol	0.59		
2-Ethoxyethanol	0.56		
2-Butoxyethanol	0.57		
2-Allyloxyethanol	0.64		
2-Methoxypropan-1-ol	0.58		
2-Ethoxypropan-1-ol	0.56		
3-Ethoxypropan-1-ol	0.57		
1-Methoxypropan-2-ol	0.61		
1-Propoxypropan-2-ol	0.57		
3-Methoxybutan-1-ol	0.66		
1-Ethoxypentan-3-ol	0.60		
4-Methyl-4-methoxypentan-2-ol	0.65		
3-Hydroxybutan-2-one	0.78		
4-Hydroxybutan-2-one	0.85		
3-Methyl-4-hydroxybutan-2-one	0.81		
3-Methyl-3-hydroxybutan-2-one	0.75		
4-Methyl-4-hydroxypentan-2-one	0.83		
<u>Thiols</u>			
Ethylthiol		0.26	0.34
Propylthiol		0.25	0.34
Isopropylthiol		0.30	0.32
Butylthiol		0.28	0.33
Isobutylthiol		0.30	0.37
t-Butylthiol		0.28	0.29
Pentylthiol		0.27	0.34
Isopentylthiol		0.27	0.18
Hexylthiol		0.26	0.35
Heptylthiol		0.27	0.33
Octylthiol		0.26	0.33
Nonylthiol		0.26	0.33
Decylthiol		0.25	0.33
Thiophenol		0.70	0.84
1,2-Ethanedithiol		0.43	
Benzylthiol		0.71	
Allylthiol		0.35	0.44
<u>Sulphides</u>			
Dithiapentane		0.68	
Dimethyl sulphide		0.40	0.37
Diethyl sulphide		0.37	0.34
Dipropyl sulphide		0.36	0.31
Methylethyl sulphide		0.28	
Methylpropyl sulphide		0.38	0.34
Diisopentyl sulphide		0.44	0.28
Dibutyl sulphide		0.38	0.33
Diallyl sulphide		0.49	
Propylene sulphide		0.39	
Tetrahydrothiophene		0.47	0.50
Thiophene		0.50	0.50
2-Methylthiophene		0.55	0.53
2,5-Dimethylthiophene		0.60	0.49
Dimethyl disulphide		0.47	0.41
Diethyl disulphide		0.49	0.44
Dimethyl trisulphide		0.53	
Methylthioacetate		0.65	
Methylthiopropanoate		0.61	
Methylthiobutanoate		0.59	
Methylthiopentanoate		0.61	
<u>Thiocyanates and isothiocyanates</u>			
Phenyl isothiocyanate		1.00	
Allyl isothiocyanate		0.60	
Ethyl isothiocyanate		0.61	
Methyl thiocyanate		0.76	

Laffort obtained retention data for 240 solutes on five stationary phases. All these phases are nonacidic, and so five regression equations can be obtained[46] of the following type, one for each phase:

$$\log L' = c + r.R_2 + s.\pi^*_2 + a.\alpha^H_2 + l.\log L^{16} \qquad [18]$$

In equation 18, log L' = log L - log L(decane), but this affects only the constant in the regression equations. The "reverse" MLRA cannot be applied as used for the McReynolds data set, because there would be only five data points in each regression, and no less than four explanatory variables. In principle, since there are five equations and (for each solute) four unknowns, *viz.* R_2, π^*_2, α^H_2, and $\log L^{16}$, these unknowns could be determined through a set of simultaneous equations. This procedure proved to be quite useless, probably because there is not a wide enough range of constants in the five equations of type equation 18. However, Laffort[45] did manage to analyse the 240 x 5 data matrix to yield five characteristic solute parameters denoted as α, w, ϵ, π, and ß. In order to avoid confusion with our own parameters, the Laffort set is referred to as αL, wL, εL, πL, and ßL. Each of these parameters for the 240 solute set can be examined via general solvation equation 9, where log SP = αL, wL, etc. αL was found to be mainly a size factor and ßL was a general combination of factors. For the other three Laffort solute parameters the following regressions were obtained,

$$\pi L = -0.040 + 0.342R_2 - 0.265\pi^*_2 + 2.540\alpha^H_2 \qquad [19]$$

$$\epsilon L = 0.165 + 2.796R_2 - 0.602\pi^*_2 - 1.426\alpha^H_2 \qquad [20]$$

$$wL = -0.081 - 1.700R_2 + 2.490\pi^*_2 + 0.561\alpha^H_2 \qquad [21]$$

These equation (19-21) can be re-arranged to yield,

$$\alpha^H_2 = 0.0218 + 0.0335wL - 0.0251\epsilon L + 0.3722\pi L \qquad [22]$$

$$\pi^*_2(\pi^H_2) = -0.0060 + 0.4755wL + 0.2826\epsilon L + 0.0536\pi L \qquad [23]$$

$$R_2 = 0.0492 + 0.1195wL + 0.4057\epsilon L + 0.2014\pi L \qquad [24]$$

If R_2 is known, as it usually is, then any two equations out of equation (22-24) will yield α^H_2 and π^*_2. But the best pair of equations to use is clearly equation 22 and equation 24 which yield,

$$\alpha^H_2 = 0.0187 - 0.0620R_2 + 0.0409wL + 0.3847\pi L \qquad [25]$$

$$\pi^*_2(\pi^H_2) = 0.0287 + 0.6954R_2 + 0.3932wL - 0.0789\pi L \qquad [26]$$

Values of π^H_2 calculated via equation 81 are listed in Table 6. Also, it is possible to simply take the set of five equations, equation 17, and, knowing R_2, $\log L^{16}$, and where necessary α_2, back-calculate values of π_2. For each solute the five back-calculated π^H_2 values can be averaged, and this average is also given in Table 6. The error in π^H_2 as between the five equations is around 0.03 units. There are a few omissions in this set of π^H_2 values: these arise through lack of one or another of the remaining solute parameters.

Although the combination of solutes in the McReynolds and Laffort sets numbers several hundred, there are some notable omissions. Firstly, the great majority of solutes are aliphatic, so that some of the simplest functionally substituted aromatic solutes are missing. Secondly, many of the polyhalogenated aliphatic solutes are either missing, or have π^H_2 values that are discordant when calculated from the McReynolds or Laffort set. And finally, a number of important solutes such as nitroalkanes and nitriles need to be further studied.

Fellous *et al*[52] have listed GLC data for 17 aromatic solutes on a number of stationary phases. In order to back-calculate π^H_2 using the general solvation equation 9, it is essential that the *s*-coefficient be as large as possible, *i.e.* that the stationary phase be quite polar. Results from the seven most polar phases used by Fellous are in Table 7. There is generally good agreement with values listed in Table 6.

Table 7. Values Of π^H_2 For Some Aromatic Compounds Calculated From Results Of Fellous *et al.*[52].

X in PhX	π_2^H	S.D.[a]	π_2^H (Table 6)		
H	0.53	0.02	0.48	0.47	
CF_3	0.45	0.02			
Me	0.52	0.01	0.47	0.57	0.46
OMe	0.73	0.02		0.73	0.70
F	0.57	0.02			
Cl	0.67	0.01			
Br	0.73	0.01			
I	0.79	0.01			
CHO	0.99	0.01		0.99	0.94
SH	0.78	0.01		0.70	0.84
CO_2Me	0.85	0.01		0.77	1.11
CN	1.07	0.01		1.05	1.04
COMe	0.98	0.01		1.09	0.99
NH_2	0.96	0.02			
NO_2	1.10	0.01		1.08[b]	1.05[b]
CH_2OH	0.85	0.01			
OH	0.88	0.01			

[a] Average deviation from 7 results. [b] For 3-nitrotoluene

Several workers have examined sets of halogenated or polyhalogenated solutes on various stationary phases[53-56]. In Table 8 are given π^H_2 values back-calculated from the general solvation regression equation, equation 9, as well as from results obtained on a variety of polar stationary phases.

McReynolds[44] did not examine any aliphatic nitro compounds or nitriles, but in Table 6 are given values of π^H_2 for a few such compounds, obtained from the Laffort data set. Both series of solutes on a number of stationary phases have been carefully examined, and it is apparent that π^H_2 is even larger than the values given in Table 6. These results suggest that for 1-nitroalkanes π^H_2 is 0.95 and that for n-alkyl cyanides π^H_2 is around 0.90 units, see Table 8.

The α^H_2 (or more correctly $\Sigma\alpha^H_2$) values calculated from equation 17 or equation 25 have not been detailed because these follow quite closely the original hydrogen bond α^H_2 values as described before[57]. Only in the case of the carboxylic acids do the new effective or $\Sigma\alpha^H_2$ values (0.60 units) differ markedly from α^H_2 (0.54 units). In Table 8 are collected all the $\Sigma\alpha^H_2$ values that correspond to the $\Sigma\pi^H_2$ values out.

The "inverse matrix" method used to analyse the data of McReynolds is a quite novel approach to the extraction of solvation parameters from data on a large number of stationary phases. The method works very well indeed, but is limited in scope to results for a given set of solutes on at least 15 phases. Back-calculation of parameters from regression equations based on Laffort's data set, equation 18, is likely to be the most common procedure. In principle, as pointed out above, if three solvation parameters are unknown (*e.g.* π^H_2, α^H_2 and $\log L^{16}$ in equation 9), it is possible to calculate all three using three simultaneous equations derived from retention data on three phases. In practice, this method can hardly ever be used unless the three phases are specifically chosen to give rise to solvation equations with very different coefficients. In the event, all of the new π^H_2 values have been obtained by either the inverse matrix method or simple back-calculation and averaging. By and large, the π^H_2 values listed in Table 8 are good to about 0.02 units, not more.

TABLE 8. RECOMMENDED SOLVATION PARAMETERS[a] FOR USE IN EQUATION 9[b]

Solute	$\Sigma\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$
Rare gas	0.00	0.00	0.00
Hydrogen	0.00	0.00	0.00
Oxygen	0.00	0.00	0.00
Nitrogen	0.00	0.00	0.00
Nitrous Oxide	0.35	0.00	0.10
Carbon Monoxide	0.00	0.00	0.04
Carbon Dioxide	0.42	0.00	0.10
Alkane	0.00	0.00	0.00
Cycloalkane	0.10	0.00	0.00
Decalin	0.25	0.00	0.00
Hydrindane	0.20	0.00	0.00
Ethene	0.10	0.00	0.07
Other alkene	0.08	0.00	0.07
Cycloalkene	0.20	0.00	0.10
α-Pinene	0.24	0.00	0.10
Diene	0.23	0.00	0.10
Ethyne	0.25	0.15	0.15
Propyne	0.25	0.13	0.15
But-1-yne	0.25	0.13	0.15
Other alk-1-yne	0.23	0.13	0.10
Alk-2-yne	0.30	0.00	0.10
Benzene	0.52	0.00	0.14
Toluene	0.52	0.00	0.14
o-Xylene	0.54	0.00	0.17
m-Xylene	0.52	0.00	0.17
p-Xylene	0.52	0.00	0.17
Ethylbenzene	0.52	0.00	0.15
n-Propylbenzene	0.52	0.00	0.15
Isopropylbenzene	(0.51)	0.00	0.15
1,2,3-Trimethylbenzne	0.54	0.00	0.20
1,2,4-Trimethylbenzene	0.52	0.00	0.20
1,3,5-Trimethylbenzene	0.52	0.00	0.20
n-Alkylbenzene	0.52	0.00	0.15
Styrene	0.63	0.00	0.18
Phenylethyne	0.58	0.12	0.21
Naphthalene	0.90	0.00	0.21
Fluoroalkane	0.35	0.00	0.10
Chloromethane	0.43 [c]	0.00	0.08
Chloroalkane	0.40	0.00	0.10
Bromomethane	0.43 [c]	0.00	0.10
Bromoalkane	0.40	0.00	0.12
Iodomethane	0.43 [c]	0.00	0.13
Iodoalkane	0.40	0.00	0.15
s-Chloroalkane	0.35 [c]	0.00	0.12
s-Bromoalkane	0.35 [c]	0.00	0.14
s-Iodoalkane	0.35 [c]	0.00	0.17
t-Chloroalkane	0.25 [c]	0.00	0.12
t-Bromoalkane	0.25 [c]	0.00	0.12
t-Iodoalkane	0.25 [c]	0.00	0.10
Dichloromethane	0.57 [c]	0.10	0.05
Trichloromethane	0.49	0.15	0.02
Tetrachloromethane	0.38	0.00	0.00
1,1-Dichloroethane	0.49	0.10	0.10
1,2-Dichloroethane	0.64	0.10	0.11
1,1,1-Trichloroethane	0.41	0.00	0.09
1,1,2-Trichloroethane	0.68	0.13	0.08
1,1,1,2-Tetrachloroethane	0.63	0.10	0.08
1,1,2,2-Tetrachloroethane	0.76	0.16	0.12
Dibromomethane	0.67	0.10	0.10
Tribromomethane	0.68	0.15	0.09
Fluorobenzene	0.57	0.00	0.10
Chlorobenzene	0.67	0.00	0.09
1,2-Dichlorobenzene	0.79	0.00	0.03
1,3-Dichlorobenzene	0.74	0.00	0.03
1,4-Dichlorobenzene	0.69	0.00	0.03
2-Chlorotoluene	0.66	0.00	0.09
3-Chlorotoluene	0.67	0.00	0.09

TABLE 8. RECOMMENDED SOLVATION PARAMETERS[a] FOR USE IN EQUATION 9[b]:

Solute	$\Sigma\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$
4-Chlorotoluene	0.67	0.00	0.09
2,4-Dichlorotoluene	0.73	0.00	0.03
2,6-Dichlorotoluene	0.73	0.00	0.03
3,4-Dichlorotoluene	0.79	0.00	0.03
Bromobenzene	0.73	0.00	0.09
1,2-Dibromobenzene	0.89	0.00	0.03
1,3-Dibromobenzene	0.84	0.00	0.03
1,4-Dibromobenzene	0.79	0.00	0.03
Iodobenzene	0.79	0.00	0.09
Dimethylether	0.27	0.00	0.41
Di-n-alkylether	0.25 [c]	0.00	0.45
Furan	0.53	0.00	0.15
2-Methylfuran	0.50	0.00	(0.15)
Tetrahydrofuran	0.52	0.00	0.48
2-Methyltetrahydrofuran	0.48	0.00	0.55
3,5-Dimethyltetrahydrofuran	0.38	0.00	0.55
Tetrahydropyran	0.47	0.00	0.55
1,4-Dioxane	0.75	0.00	0.64
Paraldehyde	0.68	0.00	
Methylphenylether	0.73	0.00	(0.33)
Ethylphenylether	0.72	0.00	(0.33)
Benzodioxane	1.01	0.00	
Formaldehyde	0.70	0.00	(0.33)
Acetaldehyde	0.67	0.00	0.45
n-Alkanal	0.65 [c]	0.00	0.45
Prop-2-en-1-al	0.74	0.00	0.45
trans-Alk-2-en-1-al	0.80	0.00	0.45
Benzaldehyde	0.99	0.00	(0.42)
2-, 3-, or 4-Methylbenzaldehyde	0.95	0.00	(0.44)
Propanone	0.70	0.04	0.51
Butanone	0.70	0.00	0.51
Alkan-2-one	0.68 [c]	0.00	0.51
Alkan-(3,4,5)-one	0.66 [c]	0.00	0.51
Cycloalkanone	0.86 [c]	0.00	0.52
Acetophenone	0.98	0.00	(0.51)
Methyl formate	0.68	0.00	0.38
Ethyl formate	0.66	0.00	0.38
n-Alkyl formate	0.63 [c]	0.00	0.38
Methyl acetate	0.64	0.00	0.45
Ethyl acteate	0.62	0.00	0.45
n-Alkyl acetate	0.60 [c]	0.00	0.45
Methyl propanaote	0.60	0.00	0.45
Ethyl propanoate	0.58	0.00	0.45
n-Alkyl propanoate	0.56 [c]	0.00	0.45
Vinyl acetate	0.64	0.00	0.42
Methyl acrylate	0.66	0.00	0.42
Ethyl acrylate	0.64	0.00	0.42
n-Alkyl acrylate	0.62 [c]	0.00	0.42
Methyl benzoate	0.85	0.00	0.50
n-Aikyl benzoates	0.80	0.00	0.50
Nitromethane	0.95	0.12	0.27
Nitroethane	0.95	0.05	0.27
1-Nitropropane	0.95	0.02	0.27
1-Nitroalkane	0.95 [c]	0.00	0.27
Nitrobenzene	1.10	0.00	0.27
2-, 3- or 4-Nitrotoluene	1.10	0.00	0.27
Acetonitrile	0.90	0.09	0.30
Propionitrile	0.90	0.02	0.35
n-Alkyl cyanide	0.90	0.00	0.36
Benzonitrile	1.07 [c]	0.00	(0.30)

TABLE 8. RECOMMENDED SOLVATION PARAMETERS[a] FOR USE IN EQUATION 9[b]

Solute	$\Sigma\pi^H_2$	$\Sigma\alpha^H_2$	$\Sigma\beta^H_2$
Ammonia	0.35 [d]	0.10	0.62
Primary n-alkylamines	0.35 [d]	0.10	0.64
Dimethylamine	0.30 [d]	0.08	0.67
Sec di-alkylamines	0.30 [d]	0.08	0.70
Triethylamine	0.15 [d]	0.00	0.81
Aniline	0.96	0.26	(0.53)
o-Toluidine	0.94	0.23	(0.57)
m-Toluidine	0.94	0.23	(0.55)
p-Toluidine	0.94	0.23	(0.57)
2,6-Dimethylaniline	0.93	0.20	(0.60)
N-Methylaniline	0.94	0.17	(0.47)
N,N-Dimethylaniline	0.82	0.00	(0.48)
Pyridine	0.82	0.00	
2-Methylpyridine	0.80	0.00	
3-Methylpyridine	0.80	0.00	
4-Methylpyridine	0.80	0.00	
2,4,6-Trimethylpyridine	0.72	0.00	
Acetic acid	0.65	0.61	0.41
Propanoic acid	0.65	0.60	0.43
Butanoic Acid	0.62	0.60	0.43
n-Alkanoic Acids	0.60 [c]	0.60	0.43
Water	0.45	0.82	0.35
Methanol	0.44	0.43	0.47
Ethanol	0.42	0.37	0.48
Primary Alcohols	0.42 [c]	0.37	0.48
Secondary Alcohols	0.36 [c]	0.33	0.56
Tertiary Alcohols	0.30 [c]	0.31	0.60
Trifluoroethanol	0.60	0.57	(0.15)
Hexafluoropropan-2-ol	0.55	0.77	(0.03)
Decafluoroheptan-1-ol	0.55	0.60	0.22
Phenol	0.88	0.60	
o-Cresol	0.86	0.52	
m-Cresol	0.87	0.57	
p-Cresol	0.87	0.57	
2,3-Dimethylphenol	0.82	0.53	
2,4-Dimethylphenol	0.82	0.53	
2,5-Dimethylphenol	0.82	0.54	
2,6-Dimethylphenol	0.82	0.39	
3,4-Dimethylphenol	0.87	0.56	
3,5-Dimethylphenol	0.87	0.57	
2,4,6-Trimethylphenol	0.83	0.37	
Benzyl alcohol	0.85	0.39	
Carbon disulphide	0.21	0.00	0.07
Methanethiol	(0.35)	0.00	
n-Alkylthiol	0.35 [c]	0.00	0.24
Isopentylthiol	0.18 [e]	0.00	
Thiophenol	0.78	0.12	(0.15)
Di-n-alkylsulphide	0.38 [c]	0.00	0.32
Tetra-alkyltin	0.00	0.00	0.00

[a] Values of $\Sigma\pi^H_2$ (this work) derived from those in Table 6 and 7, plus other calculated values. Values of $\Sigma\alpha^H_2$ and $\Sigma\beta^H_2$ are based on those given in references 57 and 61, and back-calculated where necessary or feasible. Note $\Sigma\beta^H_2$ may not necessarily be identical to values presented previously in Table 3, pages 20-22. Subsequent back-calculation of $\Sigma\beta^H_2$ using improved solvation parameters such as $\Sigma\pi^H_2$, and averaging of $\Sigma\beta^H_2$ for a wide range of systems may have altered the provisional values in Table 3.

[b] General solvation equation 9, $\log SP = c + r.R_2 + s.\pi^*_2 + a.\alpha^H_2 + b.\beta^H_2 + l.\log L^{16}$.

[c] Subtract 0.03 from $\Sigma\pi^H_2$ for each additional branch.

[d] Provisional values

[e] See text.

As can be seen from the data collected in Table 6, there is a compelling need to correlate and to interpret π^H_2 values in order to codify existing data and to help in the estimation of further values. An analysis of all these results has led to two very simple rules governing π^H_2 values for aliphatic solutes:

Rule 1: In any homologous series of functionally substituted aliphatic compounds, π^H_2 is constant except for the first one or two members of the series.

Rule 2: In any given series of functionally substituted aliphatic compounds, π^H_2 decreases by 0.03 units for each branch in a carbon chain.

Rule 1 would be extremely valuable in the estimation of π^H_2 values, since if π^H_2 was known for a few members of an homologous series, then the same value could be applied to all other members. Unfortunately, Carr[49] apparently finds that his own π^C_2 parameter varies quite markedly along homologous series. Thus along the homologous series of n-alkyl carboxylic acids, π^C_2 increases from 0.50 (acetic acid) to 0.72 (nonanoic acid), see Table 9, whereas π^H_2 is set constant at 0.62 units after the first few members of the series. Note that π^C_2 and π^H_2 are "scaled" differently, so that for the present discussion only trends in these parameters are important. How the two sets of π_2 values in Table 9 both result in good fits to experimental data can be seen by inspection of the corresponding $\Sigma\alpha^H_2$ values, also in Table 9. A constant π^H_2 value is accompanied by a constant $\Sigma\alpha^H_2$ value, whereas Carr's increase in π^C_2 is counteracted by a decrease in $\Sigma\alpha^H_2$, so that both combinations of $\pi_2/\Sigma\alpha^H_2$ fit experimental data with respect to the solvation equation 9. However, other experimental evidence supports the constancy of π^H_2 and $\Sigma\alpha^H_2$. Thus the dipole moment of the n-alkyl carboxylic acids (except for formic acid) remains constant[58], the gas phase proton transfer acidity of acetic acid, propanoic acid, and butanoic acid is almost the same (if anything, there is a slight increase in acidity along this series)[59], and the gas phase hydrogen bond acidity of propanoic acid is slightly less than that of acetic acid[60], not larger. Since retention data can as well be accommodated by the constant π^H_2 and $\Sigma\alpha^H_2$ values as by the variable parameters of Carr, Rule 1 is here operative.

Table 9. Comparison Of π^H_2 With π^C_2 For Carboxylic Acids

	- This work -		- Carr[50] -	
R in ROC_2H	π_2^H	α_2^H	π_2^C	α_2^H
Me	0.65	0.61	0.50	0.72
Et	0.65	0.60	0.61	0.67
n-Pr	0.62	0.60	0.57	0.62
n-Bu	0.60	0.60	0.56	0.62
n-Pe	0.60	0.60	0.60	0.52
n-Hex	0.60	0.60	0.64	0.47
n-Hept	0.60	0.60	0.68	0.41
n-Oct	0.60	0.60	0.72	0.35

There are other homologous series for which Carr finds π_2 as a variable quantity, but for which $\Sigma\alpha^H_2 = 0$, for example the alkan-2-ones or the cycloalkanones where π^C_2 increases quite sharply along the series. In some other series, however, π^C_2 decreases slightly (the alk-l-ene series), or remains approximately constant (the alkanal series or the alkylbenzene series). For the cycloalkanone series, as an example, the difference between Carr's result and the findings here is not fundamental at all, but is probably due to small but systematic differences in the log L^{16} values. Since the sign of the $s.\pi_2$ and $l.$log L^{16} coefficients is always positive, a systematic trend in π^C_2 increasing, together with a trend in log L^{16} becoming slightly smaller than expected, would tend to cancel out. This can be seen by comparison of the figures in Table 10.

Table 10. Comparison Of π^H_2 With π^C_2 For Cycloalkanones

	- This work -		- Carr[50] -	
n in $(CH_2)_nCO$	π_2^H	log L^{16}	π_2^C	log L^{16}
4	0.86	3.221	0.58	3.120
5	0.86	3.792	0.59	3.616
6	0.86	4.376	0.66	4.110
7	0.86	4.981	0.69	4.610
8	0.86	5.537	0.72	5.110
9	0.86	6.063	0.75	5.610
10	0.86	6.621	0.78	6.110
11	0.86	7.226	0.81	6.600

Just as for the carboxylic acid results, the combination of π^C_2 with Carr's calculated log L^{16} values will lead to very nearly the same goodness-of-fit as the combination of π^H_2 and log L^{16}. Since it is always found that solute dipolarity, as the dipole moment, is constant along any homologous series, it is felt that Rule 1 applies to the various homologous series considered.

Rule 2 is not so well founded, and it quite possible that there will be exceptions or amendments to the rule. But at the moment, application of Rule 2 does allow a very large number of π^H_2 values to be estimated for aliphatic compounds. Note that the starting point for application of the rule is not always the simplest member of any series.

According to the results in Table 6, the alkanols are a significant exception to Rule 2, since π^H_2 seems roughly constant over nonbranched and branched members. However, because the coefficients of π^H_2 and α^H_2 are both positive, and, indeed, follow each other for most stationary phases, there will be various combinations of π^H_2 and α^H_2 that give rise to the same (or very similar) goodness-of-fit in any given solvation equation. As a check, if π^H_2 values for alkanols calculated using Rules 1 and 2, are used together with the α^H_2 values listed in Table 8, regression equations are yielded that are just as good as if π_2 and α_2 are allowed to "float". In summary Table 8, are suggested π_2 and α^H_2 values for alkanols, with deliberate amendments to the first-calculated values in Table 6.

There are also a few minor anomalies with respect to Rule 2. Thus π^H_2 for isopentylthiol is 0.18 (using the Laffort set) rather than 0.32 as calculated by Rule 2. Whether or not this is the result of a systematic experimental error, or even of an incorrectly named compound is not clear. Interestingly, Carr[50] also finds an anomalously low π^C_2 value for isopentylthiol.

Finally, the new π^H_2 scale, as summarised in Table 8, can be compared with the π^C_2 scale of Carr. As Carr obviously agrees, there is a need for a new π_2 scale in place of π^*_2. Apart from the difference in treatment of homologous series, the two scales are in approximate agreement. For 198 out of the 203 compounds listed by Carr[50], there are π^H_2 values, and a correlation equation yields the relationship,

$$\pi^C_2 = -0.103 + 0.845\,\pi^H_2 \qquad [27]$$

with $r = 0.944$ and S.D. = 0.083 units. The intercept of -0.103 arises because Carr takes cyclohexane as the zero ($\pi^C_2 = 0.00$), but the π^H_2 scale is originated with alkanes taken as zero. On the π^H_2 scale, cyclohexane has $\pi^H_2 = 0.10$ units. Carr records π^C_2 for a few compounds not included in Table 28, and as a first approximation equation 27 can be used to estimate π^H_2 values for dimethylformamide and dimethylacetamide (approx. 1.10 in each case) and also for DMSO (approx. 1.30 units).

Included in summary Table 8, are a provisional set of $\Sigma\beta^H_2$ values to use with the new π^H_2 and $\Sigma\alpha^H_2$ scale. It is most important that these three scales are constructed more-or-less simultaneously in order that they all be compatible. As has been said previously, HPLC data affords the opportunity to calculate new $\Sigma\beta^H_2$ values, and/or review old values of β^H_2. Reliable GLC data for basic compounds on acidic phases is rare, and crucial compounds (such as phenols) prove to be remarkably difficult to elute. HPLC data analysed by an iterative MLRA process may well prove to be one of the only suitable methods to obtain 'effective' β^H_2 values. Note, $\Sigma\beta^H_2$ values listed in Table 8 may not be identical to values of $\Sigma\beta^H_2$ set out in Table 3, pages 20-22. Subsequent back-calculation of $\Sigma\beta^H_2$ using improved solvation equations containing parameters R_2 and π^H_2 *etc.*, and averaging of $\Sigma\beta^H_2$ values over a wide range of systems studied may have altered the provisional values in Table 3.

How well the parameters listed in Table 8 deal with various processes remains to be seen, but at the moment, regressions of the Laffort data using the Table 8 values can be compared with original regression equations. Details are in Table 11, and show that the new equations are very much better than the old ones in terms of the correlation constant and standard deviation. However, the characteristic constants, *r, s, a* and *l* are almost unchanged. Similarly, regression equations using McReynolds data are much better than the original ones, whilst still giving very similar characteristic constants. Hence the analysis of the McReynolds phases into clusters or groups remains unchanged, and it is not necessary to repeat the 75 regressions. Given in Table 11 are a few comparisons to show exactly the connection between the old and the new equations.

The new $\pi^{H}{}_{2}$ scale is based only on solute properties. Since the dependent variable, log L' or log V_G, in the equations used to calculate $\pi^{H}{}_{2}$ is a free energy related term, then $\pi^{H}{}_{2}$ will also be related to Gibbs energy. The main terms in a new solvation equation, *viz.* $\pi^{H}{}_{2}$, $\Sigma\alpha^{H}{}_{2}$, $\Sigma\beta^{H}{}_{2}$, and log L^{16}, are all related to Gibbs energy and hence form a thermodynamically consistent set of explanatory variables. The new $\pi_2{}^{H}$ scale has an advantage in that the characteristic constants in all previous equations remain the same, within any reasonable experimental error, so that previous analyses and conclusions are unchanged.

Table 11. Comparison Of New And Old Regressions

Phase	*c*	*r*	*s*	*a*	*l*	S.D.	R	No.
A. The Laffort set								
Carbowax	-2.01	0.25	1.26	2.07	0.429	0.07	0.997	199
	-2.07	0.26	1.37	2.11	0.442	0.13	0.986	168
DEGS [b]	-1.77	0.35	1.58	1.84	0.383	0.07	0.997	199
	-1.83	0.35	1.70	1.92	0.396	0.15	0.981	168
PPE (6 rings) [b]	-2.51	0.14	0.89	0.67	0.547	0.06	0.997	199
	-2.55	0.19	0.98	0.59	0.552	0.11	0.991	168
TCEP [b]	-1.69	0.26	1.93	1.88	0.365	0.06	0.998	199
	-1.75	0.23	2.12	1.94	0.379	0.16	0.982	168
ZE7 [b]	-1.99	-0.41	1.46	0.77	0.432	0.07	0.995	199
	-2.07	-0.38	1.61	0.70	0.442	0.13	0.983	168
B. The McReynolds set at 120°C								
Apiezon J	-0.48	0.24	0.15	0.13	0.596	0.02	0.999	165
	-0.48	0.27	0.13	0.13	0.594	0.03	0.998	148
PPE (5 rings)	-0.69	0.14	0.92	0.61	0.560	0.02	0.999	168
	-0.70	0.21	0.88	0.54	0.564	0.06	0.994	155
Pluronic L72	-0.54	0.09	0.93	1.42	0.529	0.03	0.998	163
	-0.54	0.17	0.89	1.41	0.531	0.08	0.992	153
Carbowax 1540	-0.75	0.22	1.37	1.92	0.456	0.04	0.998	169
	-0.75	0.31	1.34	1.87	0.457	0.09	0.987	151
DEGS [b]	-0.97	0.26	1.76	1.80	0.375	0.05	0.995	158
	-0.99	0.43	1.74	1.68	0.379	0.11	0.975	145
ZE7 [b]	-0.76	-0.42	1.55	0.78	0.448	0.07	0.991	170
	-0.82	-0.28	1.63	0.69	0.449	0.07	0.990	150

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[a] The new constants in equation 9 are on the top lines, and the old constants are on the bottom lines; in all cases b = 0.

[b] These abbreviations are: DEGS, diethyleneglycol succinate; PPE, polyphenyl ether; TCEP, tricyanoethoxypropane; ZE7, Zonyl E-7.

(iii) The Log L^{16} Parameter

The characterisation of solvent phases using the general solvation equation 9 nearly always produces superior results to using a solute volume term, such as V_X, in place of log L^{16}, when processes involving gas ⇨ condensed phase transfer are considered.

$$\log SP = c + r.R_2 + s.\pi^*_2 + a.\alpha^H_2 + b.\beta^H_2 + l.\log L^{16} \qquad [9]$$

Equation 9 can be re-cast using the improved parameters discussed previously in section (ii),

$$\log SP = c + r.R_2 + s.\pi^H_2 + a.\Sigma\alpha^H_2 + b.\Sigma\beta^H_2 + l.\log L^{16} \qquad [28]$$

Use of equation 28 will give improved results over equation 9, but the various parameters are all interchangeable, and where a 'summation' or 'effective' value is not known , the corresponding monofunctional value can be used; additionally for many solutes, the 'summation' value and the monofunctional one are identical. Parameters R_2, π^*_2 ($\Sigma\pi^H_2$), α^H_2 ($\Sigma\alpha^H_2$), and β^H_2 ($\Sigma\beta^H_2$) are now known for many hundreds of solutes, and application of the solvation equations to processes requiring the use of log L^{16} would be severely limited if this term is not known for a great many solutes. Originally[7], solvation equations were restricted to those solutes for which log L^{16} values were experimentally available (240), and those for which values could be estimated, giving a total of not more than 300. At present, $\Sigma\pi^H_2$ values are available for 1008 compounds, $\Sigma\alpha^H_2$ for 2064, and $\Sigma\beta^H_2$ values for 1439. Clearly, the scope of application for the solvation equations will be severely limited if the number of log L^{16} values are not of the same order as other parameters.

To do this, a major aim during the course of this work was to obtain log L^{16} values to ensure a database as large as, or exceeding the other parameters. A secondary aim was to reference these values so their origin was known along with their accuracy. Log L^{16} values were also required for polyfunctional molecules, to enable the solvation equations to deal with the many important polyfunctional solutes (this stipulation applied to the other solvation parameters as well). Primary experimental values where possible are to be preferred, and these have been obtained on n-hexadecane at 298.15K by the gas-chromatographic method as has been described before[7]. Many compounds will either elute far too quickly (such as CFCs), or too slowly (*eg.* phenols and large and/or polyfunctional molecules generally) on n-hexadecane at 298.15K. Longer or shorter gas-chromatographic columns can be used to alleviate this problem to some extent, and the temperature can be raised or lowered to affect solute elution rate (and the obtained value later corrected to 298.15K). However n-hexadecane freezes at

18.17°C, and tends to 'bleed' off the column if temperatures exceed about 40°C. In light of these drawbacks, log L^{16} values for rare or difficult compounds have to be obtained by other means.

Secondary values (*i.e.* values not directly obtained on n-hexadecane at 298.15K) can also be obtained either experimentally, or from the literature. Using phases which are similar in nature to n-hexadecane, *i.e* non-polar hydrocarbon stationary phases, retention information can be correlated with log L^{16}, providing equations which can be used to back-calculate further log L^{16} values. Published or experimentally determined retention data can be in the form of log relative retention times (relative to a standard), retention indices (I), or log retention volumes *etc.* Typical forms of the correlations that can be used to back-calculate log L^{16} values are,

$$\log(\text{relative retention time, or volume}) = c + l.\log L^{16} \quad [29]$$
$$\log(\text{relative retention time, or volume}) = c + r.R_2 + l.\log L^{16} \quad [30]$$
$$I = c + l.\log L^{16} \quad [31]$$
$$I = c + r.R_2 + l.\log L^{16} \quad [32]$$

The values of log L^{16} obtained can be assumed to be fairly accurate if a number of conditions are met;-

(1) The correlation of log L^{16} and the published (or experimental) data must be good, $R > 0.99$, and the standard deviation must be low.

(2) Data must be obtained from a non-polar stationary phase, similar to n-hexadecane.

(3) Data must all be measured at the same temperature, and ideally be as near 298.15K as is possible. Frequently, published retention indices are presented with a $\delta I/\delta T$ factor, so they can be corrected to 298.15K.

It is useful to carry out a preliminary plot by hand of data against log L^{16}, to show outliers, or to show if separate correlation equations are necessary for different classes of compounds. For example, in the correlation of retention indices on Apiezon L at 403K provided from data of Kovats and Wehrli[62], two distinct correlation equations become apparent, one for aliphatic compounds and one for aromatic (the quality and form of these equations is fairly typical),

$$I/1000_{\text{ALIPHATIC}} = 0.071 + 0.202 \log L^{16} \quad [33]$$

$$R = 0.9977 \quad SD = 0.012 \quad N = 44$$

$$I/1000_{\text{AROMATIC}} = -0.22 + 0.246 \log L \qquad [34]$$

$$R = 0.9919 \quad SD = 0.019 \quad N = 20$$

Outliers observed from plots of retention data against log L^{16} were further examined as follows. For a homologous series, or a series of structurally related compounds, plots of log L^{16} against log P (solute vapour pressure at 298K), or of retention data against log P are always excellent straight lines. Use of log P plots can therefore determine whether log L^{16} values used to generate a regression or the published retention data are inaccurate. In all cases, these plots showed that published data was at fault, (very possibly due to misprints *etc*).

Correlations of log P against log L^{16} can also be used to obtain additional values, as can various other correlations (such as along homologous series). Many log L^{16} values were calculated from the data of McReynolds[44], using the novel 'inverse' MLRA technique. Additionally, some log L^{16} values are available directly from the literature.

As a result of this, the database on important log L^{16} values has now been raised to 936 compounds. Many more values have been assimilated, but have not been inputted into the database, because they are merely extensions along homologous series, or are not compounds in common use, isomers *etc*. Rather than detail here every method that has been used to obtain solute log L^{16} values, the entire set of log L^{16} values currently in the solute database are presented in Table 12, together with comprehensive footnote references, which exactly indicate their origin and/or method of calculation.

Table 12. Log L16 Values in the Solute Database

No	Compound Name	Log L16	Ref
1	Helium	-1.741	L4
2	Neon	-1.575	L5
3	Argon	-0.688	L5
4	Krypton	-0.211	L7
5	Xenon	0.378	L9
6	Radon	0.877	L9
11	Hydrogen	-1.200	L4
12	Deuterium	-1.200	L4
13	Oxygen	-0.723	L5
15	Nitrogen	-0.978	L10
16	Nitrous oxide	0.164	L10
21	Carbon monoxide	-0.836	L6
22	Carbon dioxide	0.057	L10
26	Sulphur dioxide	0.700	L22
101	Methane	-0.323	L23
102	Ethane	0.492	L13
103	Propane	1.050	L14
104	n-Butane	1.615	L15
105	2-Methylpropane	1.409	L12
106	n-Pentane	2.162	L3
107	2-Methylbutane	2.013	L16
108	2,2-Dimethylpropane	1.820	L3
109	n-Hexane	2.668	L3
110	2-Methylpentane	2.503	L62
111	3-Methylpentane	2.581	L62
112	2,2-Dimethylbutane	2.352	L62
113	2,3-Dimethylbutane	2.495	L18
114	n-Heptane	3.173	L3
115	2-Methylhexanee	3.001	L9
116	3-Methylhexane	3.044	L17
117	3-Ethylpentane	3.091	L9
118	2,2,-Dimethylpentane	2.791	L9
119	2,3-Dimethylpentane	3.016	L9
120	2,4-Dimethylpentane	2.809	L62
121	3,3-Dimethylpentane	2.946	L9
122	2,2,3-Trimethylbutane	2.844	L9
126	n-Octane	3.677	L3
127	2-Methylheptane	3.480	L18
128	3-Methylheptane	3.510	L18
129	4-Methylheptane	3.483	L62
130	2,2-Dimethylhexane	3.261	L62
131	2,3-Dimethylhexane	3.451	L62
132	2,4-Dimethylhexane	3.319	L62
133	2,5-Dimethylhexane	3.308	L62
134	3,3-Dimethylhexane	3.359	L62
135	3,4-Dimethylhexane	3.495	L62
136	3-Ethylhexane	3.519	L62
137	2-Methyl-3-ethylpentane	3.459	L62
138	3-Methyl-3-ethylpentane	3.502	L62
139	2,2,3-Trimethylpentane	3.325	L62
140	2,2,4-Trimethylpentane	3.106	L62
141	2,3,3-Trimethylpentane	3.428	L62
142	2,3,4-Trimethylpentane	3.403	L62
143	2,2,3,3-Tetramethylbutane	3.265	L62
145	n-Nonane	4.182	L18
146	2-Methyloctane	3.966	L62
147	3-Methyloctane	3.998	L62
148	4-Methyloctane	3.961	L62
149	3-Ethylheptane	3.992	L62
150	4-Ethylheptane	3.944	L62
151	2,2-Dimethylheptane	3.739	L62
152	2,3-Dimethylheptane	3.925	L62
153	2,4-Dimethylheptane	3.758	L62
154	2,5-Dimethylheptane	3.822	L62
155	2,6-Dimethylheptane	3.780	L18
156	3,3-Dimethylheptane	3.833	L62
157	3,4-Dimethylheptane	3.935	L62
158	3,5-Dimethylheptane	3.826	L62
159	4,4-Dimethylheptane	3.770	L18
160	2-Methyl-3-ethylhexane	3.850	L18
161	2-Methyl-4-ethylhexane	3.760	L18
162	3-Methyl-3-ethylhexane	3.890	L18
163	3-Methyl-4-ethylhexane	3.900	L18
164	2,2,3-Trimethylhexane	3.762	L62
165	2,2,4-Trimethylhexane	3.605	L62
166	2,2,5-Trimethylhexane	3.567	L62
167	2,3,3-Trimethylhexane	3.832	L62
168	2,3,4-Trimethylhexane	3.882	L62
169	2,3,5-Trimethylhexane	3.724	L62
170	2,4,4-Trimethylhexane	3.683	L62
171	3,3,4-Trimethylhexane	3.891	L62
172	3-Ethyl-2,2-dimethylpentane	3.740	L18
173	3-Ethyl-2,3-dimethylpentane	3.970	L18
174	3-Ethyl-2,4-dimethylpentane	3.828	L18
175	2,2,3,3-Tetramethylpentane	3.880	L18
176	2,2,3,4-Tetramethylpentane	3.738	L62
177	2,2,4,4-Tetramethylpentane	3.512	L62
178	2,3,3,4-Tetramethylpentane	3.910	L18
179	3,3-Diethylpentane	4.013	L62
180	n-Decane	4.686	L3
181	2-Methylnonane	4.453	L62
182	3-Methylnonane	4.486	L62
183	4-Methylnonane	4.441	L62
184	5-Methylnonane	4.432	L62
185	2,2-Dimethyloctane	4.225	L62
186	2,3-Dimethyloctane	4.401	L62
189	2,6-Dimethyloctane	4.304	L62
190	2,7-Dimethyloctane	4.282	L62
191	3,3-Dimethyloctane	4.307	L62
192	3,4-Dimethyloctane	4.324	L62
193	3,5-Dimethyloctane	4.259	L62
194	3,6-Dimethyloctane	4.331	L62
195	4,4-Dimethyloctane	4.236	L62
197	3-Ethyloctane	4.467	L62
198	4-Ethyloctane	4.409	L62
201	3-Ethyl-2-methylheptane	4.337	L62
203	3-Methyl-3-ethylheptane	4.368	L62
225	3,4,5-Trimethylheptane	4.361	L62

Table 12. Log L16 Values in the Solute Database

No	Compound Name	Log L16	Ref
262	4-Propylheptane	4.359	L62
265	n-Undecane	5.191	L20
266	n-Dodecane	5.696	L20
267	n-Tridecane	6.200	L20
268	n-Tetradecane	6.705	L20
269	n-Pentadecane	7.209	L20
270	n-Hexadecane	7.714	L20
271	n-Heptadecane	8.218	L20
272	n-Octadecane	8.722	L20
273	n-Nonadecane	9.226	L20
274	Eicosane C20H42	9.731	L20
275	Heneicosane C21H44	10.236	L20
276	Docosane C22H46	10.740	L20
286	Dotriacontane C32H66	15.785	L20
501	Cyclopropane	1.314	L9
601	Cyclopentane	2.515	L62
602	Methylcyclopentane	2.816	L53
603	1,1-Dimethylcyclopentane	3.029	L62
604	1,2-cis-Dimethylcyclopentane	3.273	L62
605	1,2-trans-Dimethylcyclopentane	3.099	L62
606	1,3-cis-Dimethylcyclopentane	3.065	L62
607	1,3-trans-Dimethylcyclopentane	3.075	L62
608	Ethylcyclopentane	3.324	L62
609	1-Methyl-1-ethylcyclopentane	3.612	L62
701	Cyclohexane	3.007	L55
702	Methylcyclohexane	3.278	L62
703	1,1-Dimethylcyclohexane	3.582	L62
704	1,2-cis-Dimethylcyclohexane	3.795	L62
705	1,2-trans-Dimethylcyclohexane	3.634	L62
706	1,3-cis-Dimethylcyclohexane	3.533	L62
707	1,3-trans-Dimethylcyclohexane	3.655	L62
708	1,4-cis-Dimethylcyclohexane	3.661	L62
709	1,4-trans-Dimethylcyclohexane	3.538	L62
710	Ethylcyclohexane	3.812	L62
711	n-Propylcyclohexane	3.930	L24
712	n-Butylcyclohexane	4.270	L18
800	Cycloheptane	3.706	L55
801	Methylcycloheptane	4.034	L53
820	Cyclooctane	4.314	L55
821	Cyclononane	4.862	L53
822	Cyclodecane	5.353	L53
823	Cycloundecane	5.791	L53
824	Cyclododecane	6.218	L53
830	Methylcyclo-octane	4.548	L53
900	trans-Hydrindane	4.450	L24
901	cis-Hydrindane	4.610	L24
902	Hydrindane	4.530	L25
903	Adamantane	4.768	L3
904	trans-Decalin	4.987	L53
905	cis-Decalin	5.167	L53
906	Decalin	5.077	L53
1001	Ethene	0.289	L16
1002	Propene	0.946	L6
1003	But-1-ene	1.491	L20
1004	Iso-butene	1.560	L19
1005	Pent-1-ene	2.047	L53
1006	cis-Pent-2-ene	2.211	L18
1007	trans-Pent-2-ene	2.180	L19
1008	2-Methylbut-1-ene	2.125	L53
1009	3-Methylbut-1-ene	1.910	L18
1010	2-Methylbut-2-ene	2.262	L18
1015	Hex-1-ene	2.572	L18
1016	2-Methylpent-1-ene	2.567	L18
1019	4-Methylpent-2-ene	2.485	L18
1030	Hept-1-ene	3.063	L26
1040	Oct-1-ene	3.568	L18
1041	cis-Oct-2-ene	3.683	L18
1048	2-Ethylhex-1-ene	3.510	L18
1051	2,4,4-Trimethylpent-2-ene	3.249	L18
1100	Non-1-ene	4.073	L18
1150	Buta-1,3-diene	1.543	L12
1152	2-Methylbuta-1,3-diene	2.101	L53
1153	2,3-Dimethylbuta-1,3-diene	2.690	L19
1180	cis-Penta-1,3-diene	2.280	L19
1181	Trans-penta-1,3-diene	2.250	L19
1300	Cyclopentene	2.402	L53
1301	1-Methylcyclpentene	2.864	L53
1340	Cyclohexene	3.021	L53
1341	1-Methylcyclohexene	3.483	L53
1350	Cycloheptene	3.626	L53
1351	1-Methylcycloheptene	3.957	L53
1360	Cyclooctene	4.119	L53
1361	1-Methylcyclo-octene	4.487	L53
1400	Cyclopentadiene	2.222	L3
1500	Limonene	4.500	L28
1501	a-Pinene	4.200	L29
1701	Ethyne	0.150	L30
1702	Propyne	1.025	L12
1703	But-1-yne	1.520	L20
1704	But-2-yne	1.856	L1
1705	Pent-1-yne	2.010	L31
1720	Hex-1-yne	2.510	L31
1740	Hept-1-yne	3.000	L31
1760	Oct-1-yne	3.480	L31
1761	Oct-2-yne	3.850	L32
1800	Non-1-yne	3.960	L31
1850	Dodec-1-yne	5.657	L32
2200	Tetrafluoromethane	-0.800	L34
2201	Perfluoroethane	-0.230	L20
2202	Perfluoropropane	0.100	L20
2203	Perfluoro-n-butane	0.380	L20
2205	Perfluoropentane	0.690	L33
2206	Perfluoro-n-hexane	0.924	L33
2207	Perfluoro-n-heptane	1.121	L33
2208	Perfluoro-n-octane	1.464	L33
2209	Perfluoro-n-nonane	1.771	L33
2500	Hydrogen chloride	0.277	L11
2501	Chloromethane	1.163	L20

Table 12. Log L16 Values in the Solute Database

No	Compound Name	Log L16	Ref
2502	Dichloromethane	2.019	L3
2503	Trichloromethane	2.480	L3
2504	Tetrachloromethane	2.823	L3
2505	Chloroethane	1.678	L20
2506	1,1-Dichloroethane	2.316	L51
2507	1,2-Dichloroethane	2.573	L3
2508	1,1,1-Trichloroethane	2.733	L51
2509	1,1,2-Trichloroethane	3.290	L35
2510	1,1,2,2-Tetrachloroethane	3.803	L3
2511	1,1,1,2-Tetrachlorethane	3.641	L50
2512	Pentachloroethane	4.267	L51
2513	Hexachloroethane	4.808	L51
2514	1-Chloropropane	2.202	L36
2515	2-Chloropropane	1.970	L3
2517	1,2-Dichloropropane	2.857	L37
2518	1,3-Dichloropropane	3.101	L37
2530	1-Chlorobutane	2.722	L3
2531	1-Chloro-2-methylpropane	2.566	L36
2532	2-Chlorobutane	2.540	L19
2533	2-Chloro-2-methylpropane	2.217	L3
2550	1-Chloropentane	3.223	L26
2552	1-Chloro-3-methylbutane	3.094	L50
2553	2-Chloro-2-methylbutane	2.858	L50
2555	1,5-Dichloropentane	4.632	L65
2560	1-Chlorohexane	3.710	L31
2570	1-Chloroheptane	4.210	L31
2719	Chlorocyclopentane	3.436	L53
2720	Chlorocyclohexane	3.988	L53
2721	Chlorocycloheptane	4.667	L53
2722	Chlorocyclo-octane	5.262	L53
2801	1,1-Dichloroethene	2.110	L3
2802	cis-1,2-Dichloroethene	2.439	L3
2803	trans-1,2,-Dichloroethene	2.278	L3
2804	Trichloroethene	2.997	L3
2805	Tetrachloroethene	3.584	L3
2806	1-Chloroprop-2-ene	2.109	L3
2807	2-Chloroprop-1-ene	1.729	L50
2901	1-Chloroprop-2-yne	2.080	L34
3001	Bromomethane	1.630	L60
3002	Dibromomethane	2.855	L51
3003	Tribromomethane	3.719	L51
3004	Tetrabromomethane	4.557	L51
3005	Bromoethane	2.120	L3
3007	1,2-Dibromoethane	3.382	L51
3014	1-Bromopropane	2.620	L38
3015	2-Bromopropane	2.390	L36
3030	1-Bromobutane	3.105	L3
3031	1-Bromo-2-methylpropane	2.960	L36
3032	2-Bromobutane	2.933	L36
3033	2-Bromo-2-methylpropane	2.616	L36
3050	1-Bromopentane	3.611	L1
3060	1-Bromohexane	4.130	L31
3070	1-Bromoheptane	4.600	L31
3080	1-Bromooctane	5.090	L31
3081	2-Bromooctane	5.110	L19
3090	1-Bromononane	5.560	L31
3219	Bromocyclopentane	3.841	L53
3220	Bromocyclohexane	4.401	L53
3221	Bromocycloheptane	5.021	L53
3222	Bromocyclo-octane	5.485	L53
3302	cis-1,2-Dibromoethene	3.227	L51
3303	trans-1,2-Dibromoethene	3.132	L51
3306	1-Bromoprop-2-ene	2.510	L3
3501	Iodomethane	2.106	L3
3502	Diiodomethane	3.857	L51
3505	Iodoethane	2.573	L3
3514	1-Iodopropane	3.130	L38
3515	2-Iodopropane	2.900	L34
3530	1-Iodobutane	3.628	L1
3532	2-Iodobutane	3.390	L19
3550	1-Iodopentane	4.130	L31
3560	1-Iodohexane	4.620	L31
3806	1-Iodoprop-2-ene	3.010	L40
4004	Bromochloromethane	2.445	L51
4005	Chloroiodomethane	2.947	L51
4040	Bromodichloromethane	2.891	L51
4042	Dibromochloromethane	3.304	L51
4050	Fluorotrichloromethane Freon 11	1.930	L34
4051	Difluorodichloromethane Freon 1	1.050	L34
4052	Irifluorochloromethane Freon 13	0.145	L34
4055	Tribromofluoromethane	3.206	L3
4059	Bromotrichloromethane	3.294	L51
4105	1-Chloro-2-bromoethane	2.982	L51
4258	Halothane CF3CHBrCl	2.177	L3
4260	CF3CHFBr teflurane	1.370	L33
4304	1,1,2-Trifluorotrichloroethane	2.123	L3
4306	1,2-Difluorotetrachloroethane	3.000	L34
4501	Dimethylether	1.285	L63
4502	Diethylether	2.015	L63
4503	Di-n-propylether	2.954	L63
4504	Di-isopropylether	2.482	L63
4505	Di-n-butylether	3.924	L53
4510	Di-n-pentylether	4.875	L53
4511	Di-isopentylether	4.538	L63
4520	Di-n-hexylether	5.938	L27
4553	Methyl-n-propyl ether	2.090	L42
4554	Methyl-n-butylether	2.630	L19
4555	Methyl-isobutyl ether	2.442	L63
4557	Methyl-t-butylether	2.378	L63
4582	Ethyl-n-butylether	2.989	L63
4585	Ethyl-t-butylether	2.611	L63
4601	Propyl-isopropyl ether	2.771	L62
4620	Isopropyl-t-butyl ether	2.896	L62
4703	Ethylvinyl ether	1.910	L42
4706	n-Butylvinyl ether	2.970	L42
4707	Isobutyl-vinyl ether	2.746	L63
4710	2-Ethyl-1-hexyl vinyl ether	4.682	L62
4722	Ethyl-allyl ether	2.417	L63

Table 12. Log L16 Values in the Solute Database

No	Compound Name	Log L16	Ref
4730	Di(2-ethoxyethyl) ether	4.592	L63
4735	2-Methoxyethyl vinyl ether	2.932	L63
4750	Dimethoxymethane	1.894	L63
4751	Methoxyethoxymethane	2.371	L63
4752	Diethoxymethane	2.789	L63
4754	Methoxyisopropoxymethane	2.697	L63
4759	Ethoxy-n-propoxymethane	3.280	L63
4760	Ethoxyisopropoxymethane	3.093	L63
4761	Di-n-propoxymethane	3.762	L63
4762	Di-isopropoxymethane	3.376	L63
4772	Ethoxy-s-butoxymethane	3.609	L63
4776	n-Propoxy-s-butoxymethane	4.037	L63
4782	Di-n-butoxymethane	4.726	L63
4783	Di-isobutoxymethane	4.331	L63
4784	Di-s-butoxymethane	4.380	L63
4800	1,1-Dimethoxyethane	2.334	L63
4801	1,1-Diethoxyethane	3.066	L63
4802	1,1-Di-n-propoxyethane	3.964	L63
4805	1,1-Di-isobutoxyethane	4.491	L63
4810	1,1-Dimethoxypropane	2.841	L63
4811	1,1,-Diethoxypropane	3.498	L63
4820	1,1-Dimethoxybutane	3.313	L63
4830	2,2-Dimethoxypropane	2.699	L63
4831	2,2-Diethoxypropane	3.304	L63
4851	1,2-Dimethoxyethane	2.565	L63
4855	1,2-Di-n-butoxyethane	5.176	L63
5001	Ethylene oxide	1.371	L63
5002	1,2-Propylene oxide	1.775	L42
5003	2-Methyl-1,2-propylene oxide	2.050	L42
5004	1,3-Propylene oxide	2.086	L63
5005	1,2-Butylene oxide	2.350	L42
5006	cis-2,3-Butylene oxide	2.290	L42
5007	trans-2,3-Butylene oxide	2.140	L42
5008	1,3-Butylene oxide	2.360	L42
5090	Methoxyflurane CHCl2CF2OCH3	2.864	L3
5091	Isoflurane CF3CHClOCF2H	1.576	L3
5092	Enflurane CHFClCF2OCF2H	1.653	L9
5094	Fluroxene CF3CH2OCH-CH2	1.400	L9
5100	[CH2]3 O	2.140	L42
5110	Tetrahydrofuran [CH2]4 O	2.636	L53
5111	2-Methyltetrahydrofuran	2.820	L42
5113	2,5-Dimethyltetrahydrofuran	2.980	L42
5160	Tetrahydropyren [CH2]5 O	3.057	L53
5165	Dihydropyran	2.910	L42
5200	Dioxan	2.892	L63
5301	Formaldehyde	0.730	L33
5302	Acetaldehyde	1.230	L3
5303	Propionaldehyde	1.815	L3
5304	Butyraldehyde	2.270	L3
5305	Iso-butyraldehyde	2.120	L63
5306	Pentanal	2.851	L63
5308	3-Methylbutanal	2.620	L19
5309	2,2-Dimethylpropanal	2.406	L62
5310	Hexanal	3.370	L20
5320	Heptanal	3.860	L20
5330	Octanal	4.380	L20
5335	2-Ethylhexanal	4.179	L62
5340	Nonanal	4.900	L20
5401	Propenal , acrolein	1.656	L63
5402	trans-But-2-ene-1-al (crotonalde	2.570	L29
5403	2-Methylpropenal (methacrolein)	2.180	L62
5415	2-Ethyl-2-butenal	3.436	L62
5435	2-Ethyl-2-hexenal	4.371	L62
5450	Hexa-2,4-dienal	3.800	L62
5501	Propanone	1.696	L63
5502	Butanone	2.287	L1
5503	Pentan-2-one	2.755	L1
5504	Pentan-3-one	2.811	L1
5505	3-Methylbutan-2-one	2.692	L53
5506	Hexan-2-one	3.262	L20
5507	Hexan-3-one	3.271	L53
5508	3-Methylpentan-2-one	3.163	L62
5509	4-Methylpentan-2-one	3.089	L53
5511	3,3-Dimethylbutan-2-one	2.928	L53
5512	Heptan-2-one	3.760	L3
5513	Heptan-3-one	3.776	L53
5514	Heptan-4-one	3.705	L56
5517	5-Methylhexan-2-one	3.605	L53
5525	4,4-Dimethylpentan-2-one	3.344	L53
5530	2,4-Dimethylpentan-3-one	3.403	L62
5535	Octan-2-one	4.257	L3
5536	Octan-3-one	4.264	L53
5544	5-Methylheptan-3-one	4.200	L20
5552	Nonan-2-one	4.735	L90
5553	Nonan-3-one	4.720	L28
5555	Nonan-5-one	4.698	L53
5560	2,6-Dimethylheptan-4-one	4.244	L53
5570	Decan-2-one	5.245	L53
5580	Undecan-2-one	5.732	L53
5584	Undecan-6-one	5.677	L53
5590	Dodecan-2-one	6.167	L90
5600	Nonadecan-2-one	9.554	L91
5705	Cyclopentanone	3.221	L55
5710	Cyclohexanone	3.792	L53
5711	2-Methylcyclohexanone	4.055	L53
5712	3-Methylcyclohexanone	4.093	L53
5713	4-Methylcyclohexanone	4.129	L53
5720	Cycloheptanone	4.376	L53
5725	Cyclooctanone	4.981	L40
5730	Cyclononanone	5.537	L40
5735	Cyclodecanone	6.063	L40
5740	Cycloundecanone	6.621	L40
5745	Cyclododecanone	7.222	L40
5750	Cyclotridecanone	7.783	L40
5755	Cyclotetradecanone	8.344	L40
5760	Carvone	5.330	L28
5770	But-1-ene-3-one	2.330	L19
5775	3-Methyl-but-3-ene-2-one	2.691	L63

Table 12. Log L16 Values in the Solute Database

No	Compound Name	Log L16	Ref
5780	Hex-5-ene-2-one	3.181	L63
5785	Mesityl oxide	3.300	L1
5800	Butan-2,3-dione (biacetyl)	1.639	L63
5801	Pentan-2,3-dione	2.209	L63
5802	Acetylacetone , pentan-2,4-dione	2.772	L63
5971	g-Butyrolactone	3.600	L27
6001	Methyl formate	1.285	L63
6002	Ethyl formate	1.845	L53
6003	Propyl formate	2.433	L53
6004	Isopropyl formate	2.230	L24
6005	n-Butyl formate	2.958	L53
6006	Isobutyl formate	2.789	L53
6007	s-Butyl formate	2.730	L42
6008	t-Butyl formate	2.546	L53
6009	Pentyl formate	3.488	L53
6010	2-Pentyl formate	3.250	L42
6011	3-Pentyl formate	3.266	L62
6012	Isoamyl formate	3.306	L53
6015	n-Hexyl formate	3.970	L62
6030	Allyl formate	2.256	L62
6051	Methyl acetate	1.911	L53
6052	Ethyl acetate	2.314	L53
6053	n-Propyl acetate	2.819	L53
6054	Isopropyl acetate	2.546	L53
6055	n-Butyl acetate	3.353	L53
6056	Isobutyl acetate	3.161	L53
6057	s-Butyl acetate	3.054	L54
6058	t-Butyl acetate	2.802	L53
6059	n-Pentyl acetate	3.844	L53
6061	3-Pentyl acetate	3.679	L53
6062	Isoamyl acetate	3.740	L24
6063	2-Methyl-2-butyl acetate	3.340	L62
6065	n-Hexyl acetate	4.351	L63
6068	4-Methyl-2-pentyl acetate	3.822	L62
6069	2-Ethyl-1-butyl acetate	4.178	L62
6079	2-Ethylhexyl acetate	5.025	L62
6080	Vinyl acetate	2.152	L63
6081	Allyl acetate	2.723	L63
6082	1-Propenyl acetate	2.741	L63
6083	Isopropenyl acetate	2.611	L63
6101	Methyl propanoate	2.431	L53
6102	Ethyl propanoate	2.807	L53
6103	n-Propyl propanoate	3.338	L53
6104	Isopropyl propanoate	3.028	L53
6105	n-Butyl propanoate	3.833	L53
6106	Isobutyl propanoate	3.635	L63
6107	s-Butyl propanoate	3.524	L53
6108	t-Butyl propanoate	3.244	L53
6109	n-Pentyl propanoate	4.331	L63
6110	2-Pentyl propanoate	4.024	L63
6112	Isopentyl propanoate	4.153	L53
6130	2-Ethyl-1-hexyl propanoate	5.486	L63
6141	Allyl propanoate	3.241	L63
6151	Methyl butanoate	2.893	L53
6152	Ethyl butanoate	3.271	L53
6153	Propyl butanoate	3.783	L53
6154	Isopropyl butanoate	3.482	L53
6155	Butyl butanoate	4.275	L53
6156	Isobutyl butanoate	4.097	L53
6157	s-Butyl butanoate	3.989	L53
6158	t-Butyl butanoate	3.695	L53
6159	Pentyl butanoate	4.764	L53
6160	2-Pentyl butanoate	4.472	L63
6162	Isopentyl butanoate	4.597	L53
6170	2-Ethyl-1-hexyl butanoate	5.856	L63
6180	Vinyl butanoate	3.191	L63
6201	Methyl pentanoate	3.442	L45
6251	Methyl hexanoate	3.984	L45
6252	Ethyl hexanoate	4.194	L60
6301	Methyl heptanoate	4.761	L60
6365	Methyl isobutanoate	2.636	L53
6366	Ethyl isobutanoate	3.072	L53
6367	n-Propyl isobutanoate	3.555	L53
6368	Isopropyl isobutanoate	3.249	L53
6369	n-Butyl isobutanoate	4.068	L53
6370	Isobutyl isobutanoate	3.885	L53
6371	s-Butyl isobutanoate	3.772	L53
6372	t-Butyl isobutanoate	3.471	L53
6373	n-Pentyl isobutanoate	4.539	L53
6380	Isoamyl isopentanoate	4.371	L53
6390	Methyl trimethylacetate	2.932	L1
6401	Methyl acrylate	2.360	L42
6402	Ethyl acrylate	2.758	L63
6403	Propyl acrylate	3.260	L42
6404	Isopropyl acrylate	2.950	L20
6405	Butyl acrylate	3.790	L42
6406	Isobutyl acryate	3.600	L20
6408	2-Ethyl-1-hexyl acrylate	5.445	L63
6410	Allyl acrylate	3.160	L63
6421	Methyl methacrylate	2.880	L42
6422	Ethyl methacrylate	3.255	L1
6423	n-Propyl methacrylate	3.770	L20
6424	Isopropyl methacrylate	3.460	L20
6425	n-Butyl methacrylate	4.280	L20
6426	Isobutyl methacrylate	4.090	L20
6432	Cyclohexyl acetate	4.454	L63
6451	2-Methoxyethylacetate	3.290	L42
6452	2-Ethoxyethylacetate	3.747	L1
6461	Ethyl acetoacetate	3.752	L1
6470	Methylene diacetate	3.419	L63
6472	Ethylene diacetate	3.937	L63
6474	Ethylene dipropanoate	4.914	L62
6480	Propylene diacrylate	4.979	L62
6547	Ethyl chloroacetate	2.559	L3
6601	Acetonitrile	1.739	L53
6602	Proprionitrile	2.154	L53
6603	1-Cyanopropane	2.604	L53
6605	1-Cyanobutane	3.108	L53

Table 12. Log L16 Values in the Solute Database

No	Compound Name	Log L16	Ref	No	Compound Name	Log L16	Ref
6609	1-Cyanopentane	3.608	L53	7616	Octanoic acid	5.000	L46
6610	1-Cyanohexane	3.980	L31	7617	Nonanoic acid	5.550	L46
6611	1-Cyanoheptane	4.480	L31	7618	Decanoic acid	6.090	L46
6612	1-Cyanooctane	4.970	L31	7619	Undecanoic acid	6.640	L46
6613	1-Cyanononane	5.460	L31	7620	Dodecanoic acid	7.180	L46
6614	1-Cyanodecane	5.940	L31	8000	Water	0.260	L47
6706	Trichloroacetonitrile	3.677	L1	8001	Methanol	0.970	L64
6800	Ammonia	0.680	L22	8002	Ethanol	1.485	L3
6801	Methylamine	1.300	L19	8003	Propan-1-ol	2.031	L63
6802	Ethylamine	1.677	L3	8004	Propan-2-ol	1.764	L63
6803	n-Propylamine	2.141	L3	8005	Butan-1-ol	2.601	L3
6804	Isopropylamine	1.908	L19	8006	2-Methylpropan-1-ol	2.413	L63
6805	n-Butylamine	2.618	L3	8007	Butan-2-ol	2.338	L17
6806	Isobutylamine	2.469	L19	8008	2-Methylpropan-2-ol	1.963	L63
6807	s-Butylamine	2.410	L3	8009	Pentan-1-ol	3.106	L3
6808	t-Butylamine	2.493	L3	8010	Pentan-2-ol	2.840	L3
6809	n-Pentylamine	3.086	L20	8011	Pentan-3-ol	2.860	L42
6811	n-Hexylamine	3.557	L20	8012	2-Methylbutan-1-ol	3.011	L1
6812	n-Heptylamine	4.050	L20	8013	3-Methylbutan-1-ol	3.011	L1
6813	n-Octylamine	4.520	L20	8014	2-Methylbutan-2-ol	2.630	L1
6831	Allylamine	2.268	L19	8015	3-Methylbutan-2-ol	2.793	L63
6842	Cyclohexylamine	3.574	L19	8016	2,2-Dimethylpropan-1-ol	2.650	L42
6851	Dimethylamine	1.600	L17	8017	Hexan-1-ol	3.610	L3
6852	Diethylamine	2.395	L17	8018	Hexan-2-ol	3.340	L3
6853	Di-n-propylamine	3.372	L17	8019	Hexan-3-ol	3.343	L63
6854	Di-isopropylamine	2.893	L17	8020	2-Methylpentan-1-ol	3.530	L42
6855	Di-n-butylamine	4.349	L19	8022	4-Methylpentan-1-ol	3.500	L20
6882	Methyl-n-propylamine	2.487	L17	8023	2-Methylpentan-2-ol	3.081	L1
6883	Methyl-isopropylamine	2.293	L17	8025	4-Methylpentan-2-ol	3.179	L63
6884	Methyl-n-butylamine	3.049	L17	8026	2-Methylpentan-3-ol	3.240	L42
6901	Trimethylamine	1.620	L3	8027	3-Methylpentan-3-ol	3.277	L1
6902	Triethylamine	3.077	L3	8028	2-Ethylbutan-1-ol	3.523	L53
6904	Tri-n-butylamine	6.050	L19	8029	2,2-Dimethylbutan-1-ol	3.320	L42
6921	Ethyldimethylamine	2.125	L19	8032	2,3-Dimethylbutan-2-ol	3.167	L63
7101	Nitromethane	1.892	L3	8033	3,3-Dimethylbutan-2-ol	3.090	L42
7102	Nitroethane	2.414	L53	8041	Heptan-1-ol	4.115	L3
7103	1-Nitropropane	2.894	L53	8042	Heptan-2-ol	3.842	L3
7104	2-Nitropropane	2.550	L3	8043	Heptan-3-ol	3.860	L42
7105	1-Nitrobutane	3.415	L54	8044	Heptan-4-ol	3.850	L42
7108	2-Methyl-2-nitropropane	2.710	L19	8054	3-Ethylpentan-3-ol	3.785	L63
7109	1-Nitropentane	3.938	L54	8055	2,2-Dimethylpentan-1-ol	3.780	L42
7115	Nitrocyclohexane	4.733	L53	8065	2,4-Dimethylpentan-3-ol	3.603	L63
7251	N,N-Dimethylformamide	3.173	L3	8071	Octan-1-ol	4.619	L3
7261	N,N-Dimethylacetamide	3.717	L3	8072	Octan-2-ol	4.343	L20
7602	Acetic acid	1.750	L46	8078	2-Methylheptan-2-ol	3.990	L40
7603	Propanoic acid	2.290	L46	8088	3-Methyl-3-heptanol	4.000	L19
7604	Butanoic acid	2.830	L46	8091	2-Ethylhexan-1-ol	4.433	L53
7605	2-Methylpropanoic acid	2.670	L63	8092	2-Ethyl-4-methylpentan-1-ol	4.266	L63
7606	Pentanoic acid	3.380	L46	8100	Nonan-1-ol	5.124	L20
7607	2-Methylbutanoic acid	3.260	L63	8130	Decan-1-ol	5.628	L20
7608	3-Methylbutanoic acid	3.140	L63	8131	Decan-2-ol	5.356	L20
7610	Hexanoic acid	3.920	L46	8140	Undecan-1-ol	6.130	L20
7611	2-Methylpentanoic acid	3.680	L63	8145	Dodecan-1-ol	6.640	L20
7615	Heptanoic acid	4.460	L46	8191	Cyclopentanol	3.241	L53

Table 12. Log L16 Values in the Solute Database

No	Compound Name	Log L16	Ref
8192	Cyclohexanol	3.758	L53
8193	Cycloheptanol	3.801	L63
8194	Cyclooctanol	5.054	L53
8200	1-Methylcyclopentanol	3.279	L53
8201	1-Methylcyclohexanol	3.806	L53
8202	2-Methylcyclohexanol	4.110	L42
8210	1-Methylcycloheptanol	4.402	L53
8211	1-Methylcyclo-octanol	4.916	L53
8251	Prop-2-yne-1-ol	2.050	L42
8252	Prop-2-en-1-ol (allyl alcohol)	1.951	L63
8253	But-2-en-1-ol (Crotylalcohol)	2.618	L63
8254	But-3-ene-1-ol	2.422	L63
8255	But-3-ene-2-ol	2.206	L63
8256	Pent-3-ene-1-ol	3.064	L63
8260	Pent-1-en-3-ol	2.752	L63
8265	Pent-1-ene-4-ol	2.710	L42
8266	2-Methylprop-2-ene-1-ol	2.509	L63
8267	2-Methyl-but-3-ene-2-ol	2.376	L63
8271	Hex-2-ene-1-ol	3.510	L20
8281	trans-Hept-2-ene-1-ol	4.010	L20
8291	trans-Oct-2-ene-1-ol	4.520	L20
8295	2-Methylbut-3-yne-2-ol	2.209	L63
8303	2,2,2-Trifluoroethanol	1.224	L3
8323	1,1,1,3,3,3-Hexafluoropropan-2-o	1.392	L3
8335	Dodecafluoroheptan-1-ol	3.089	L20
8351	2-Chloroethanol	2.630	L42
8431	2-Methoxyethanol	2.490	L42
8432	2-Ethoxyethanol	2.815	L63
8434	2-Butoxyethanol	3.806	L63
8436	2-Allyloxyethanol	3.283	L63
8440	2-Methoxypropan-1-ol	2.793	L63
8441	2-Ethoxypropan-1-ol	3.115	L63
8442	3-Ethoxypropan-1-ol	3.426	L63
8443	1-Methoxypropan-2-ol	2.655	L63
8445	1-Propoxypropan-2-ol	3.495	L63
8446	3-Methoxybutan-1-ol	3.398	L63
8447	1-Ethoxypentan-3-ol	4.102	L63
8448	4-Methoxy-4-methylpentan-2-ol	3.963	L63
8451	Ethan-1,2-diol	2.661	L62
8452	Propan-1,2-diol	2.918	L62
8453	Propan-1,3-diol	3.263	L62
8454	Butan-1,2-diol	3.525	L62
8455	Butan-1,3-diol	3.642	L62
8456	dl-Butan-2,3-diol	3.250	L62
8457	meso-Butan-2,3-diol	3.291	L62
8458	Butan-1,4-diol	3.795	L62
8459	2-Methyl-propan-1,2-diol	3.190	L62
8470	3-Hydroxybutan-2-one	2.771	L63
8471	4-Hydroxybutan-2-one	3.160	L63
8472	1-Hydroxy-2-methylbutan-3-one	3.573	L63
8473	2-Hydroxy-2-methylbutan-3-one	2.951	L63
8474	4-Hydroxy-4-methylpentan-2-one	3.475	L63
8490	Geraniol	5.020	L28
8500	Hydrogen sulphide	0.529	L10
8502	Ethanthiol	2.173	L47
8503	n-Propylthiol	2.685	L47
8504	Isopropylthiol	2.406	L47
8505	n-Butylthiol	3.243	L47
8506	Isobutylthiol	3.091	L63
8508	t-Butylthiol	2.558	L47
8509	n-Pentylthiol	3.720	L47
8510	Isopentylthiol	3.360	L47
8511	n-Hexylthiol	4.220	L47
8512	n-Heptylthiol	4.720	L47
8513	n-Octylthiol	5.270	L28
8514	n-Nonylthiol	5.790	L28
8515	n-Decylthiol	6.318	L63
8520	Allyl thiol	2.654	L63
8551	Dimethyl sulphide	2.238	L47
8552	Diethyl sulphide	3.104	L47
8553	Di-n-propyl sulphide	4.120	L47
8554	Di-isopropyl sulphide	3.600	L47
8555	Di-n-butyl sulphide	4.950	L47
8557	Di-s-butyl sulphide	4.490	L28
8558	Di-t-butyl sulphide	4.160	L47
8540	Di-isoamyl sulphide	5.540	L47
8571	Methylethyl sulphide	2.730	L47
8572	Methyl-n-propyl sulphide	3.240	L47
8573	Methyl isopropyl sulphide	2.920	L28
8574	Methyl n-butyl sulphide	3.590	L28
8581	Ethyl-n-propylsulphide	3.540	L47
8582	Ethylisopropyl sulphide	3.350	L28
8583	Ethyl n-butyl sulphide	4.030	L28
8585	Ethyl s-butyl sulphide	3.800	L28
8586	EThyl t-butyl sulphide	3.630	L28
8610	Diallyl sulphide	3.750	L40
8615	Propylene sulphide	2.870	L40
8622	Tetrahydrothiophen	3.660	L47
8681	Dimethyl disulphide	3.550	L20
8682	Diethyl disulphide	4.210	L20
8685	Di-n-butyl disulphide	6.030	L47
8701	Dimethylsulphoxide	3.437	L3
8790	Sulphur hexafluoride	-0.120	L34
8795	Carbon disulphide	2.353	L3
9112	Triethyl phosphate	4.750	L2
9131	Dimethylmethanephosphonate	3.977	L3
9151	Hexamethylphosphotriamide	5.110	L48
9501	Tetrametnylsilane	2.140	L48
9502	Tetraethylsilane	4.330	L48
9521	Tetramethyltin	2.920	L48
9522	Tetraethyltin	5.080	L48
9542	Tetraethyllead	5.200	L48
9990	Mercury	1.620	L34
10001	Benzene	2.803	L3
10002	Toluene	3.344	L3
10003	Ethylbenzene	3.789	L62
10004	o-Xylene	3.942	L62
10005	m-Xylene	3.864	L3

Table 12. Log L16 Values in the Solute Database

No	Compound Name	Log L16	Ref
10006	p-Xylene	3.836	L62
10007	n-Propylbenzene	4.229	L62
10008	Isopropylbenzene	4.082	L62
10009	1,2,3-Trimethylbenzene	4.563	L62
10010	1,2,4-Trimethylbenzene	4.438	L62
10011	1,3,5-Trimethylbenzene (mesityle	4.316	L62
10012	2-Ethyltoluene	4.362	L49
10013	3-Ethyltoluene	4.274	L62
10014	4-Ethyltoluene	4.285	L49
10015	n-Butylbenzene	4.686	L20
10016	Isobutylbenzene	4.486	L62
10017	s-Butylbenzene	4.505	L62
10018	t-Butylbenzene	4.427	L62
10019	1,2-Diethylbenzene	4.690	L42
10020	1,3-Diethylbenzene	4.680	L19
10021	1,4-Diethylbenzene	4.680	L19
10022	1,2,4,5-Tetramethylbenzene	5.063	L49
10023	1,2,3,5-Tetramethylbenzene	5.092	L49
10024	1,2,3,4-Tetramethylbenzene	5.246	L49
10028	2-n-Propyltoluene	4.579	L49
10029	3-n-Propyltoluene	4.678	L49
10030	4-n-Propyltoluene	4.703	L49
10031	2-Isopropyltoluene	4.597	L49
10032	3-Isopropyltoluene	4.499	L49
10033	4-Isopropyltoluene	4.534	L53
10050	n-Pentylbenzene	5.152	L20
10060	t-Pentylbenzene	4.910	L60
10061	Pentamethylbenzene	5.847	L49
10070	4-t-Butyltoluene	4.870	L19
10080	n-Hexylbenzene	5.617	L20
10085	1,2-Di-isopropylbenzene	5.172	L49
10087	1,4-Di-isopropylbenzene	5.240	L49
10092	1,3,5-Triethylbenzene	5.375	L49
10180	n-Dodecylbenzene	8.600	L20
10300	Styrene	3.863	L61
10301	a-Methylstyrene, PhMeCCH2	4.322	L1
10302	trans-b-Methylstyrene	4.559	L49
10305	4-Vinyltoluene	4.480	L28
10308	1,4-Divinylbenzene	4.900	L28
10310	Phenylethyne	3.715	L1
10340	Allyl benzene	4.227	L20
10400	Naphthalene	5.149	L53
10440	Tetrahydronaphthalene	5.303	L49
10445	Indene	4.670	L49
10446	1-Methylindene	4.802	L49
10449	Indane	4.580	L60
10450	1-Methylindane	4.884	L49
10490	Azulene	5.993	L53
11501	Fluorobenzene	2.786	L53
11504	1,4-Difluorobenzene	2.766	L3
11510	Hexafluorobenzene	2.528	L3
11530	Benzotrifluoride	2.987	L52
11601	Chlorobenzene	3.640	L3
11602	1,2-Dichlorobenzene	4.489	L53
11603	1,3-Dichlorobenzene	4.419	L21
11604	1,4-Dichlorobenzene	4.446	L53
11613	2-Chlorotoluene	4.168	L53
11614	3-Chlorotoluene	4.176	L53
11615	4-Chlorotoluene	4.197	L53
11617	2,4-Dichlorotoluene	5.008	L60
11619	2,6-Dichlorotoluene	5.026	L60
11620	3,4-Dichlorotoluene	5.089	L60
11650	Benzyl chloride	4.320	L60
11651	2-Chlorobenzyl chloride	5.101	L60
11661	2-Chloroethylbenzene(b)	4.600	L19
11671	2-Chlorostyrene	4.785	L60
12601	Bromobenzene	4.035	L3
12613	2-Bromotoluene	4.542	L53
12614	3-Bromotoluene	4.576	L53
12615	4-Bromotoluene	4.581	L53
12650	Benzyl bromide	4.660	L3
12662	2-Bromo-1-phenylethane	5.134	L53
13601	Iodobenzene	4.454	L53
14001	Methylphenylether	3.859	L53
14002	Ethylphenylether	4.198	L53
14150	1,2-Dimethoxybenzene	4.967	L3
14151	1,3-Dimethoxybenzene	5.022	L3
14152	1,4-Dimethoxybenzene	5.044	L3
14401	Benzaldehyde	3.985	L1
14403	3-Methylbenzaldehyde	4.508	L53
14404	4-Methylbenzaldehyde	4.536	L53
14470	Furfural	3.262	L1
14480	Phenylacetaldehyde	4.287	L53
14481	3-Phenylpropanal	4.861	L53
14501	Acetophenone	4.483	L3
14601	Ethylphenylketone	4.937	L53
14602	n-Propylphenylketone	5.312	L53
14619	Benzylmethylketone	4.628	L53
14625	1-Phenylbutan-2-one	5.085	L53
14626	4-Phenylbutan-2-one	5.188	L53
14801	Methyl benzoate	4.634	L1
14951	Benzyl acetate	4.991	L1
15201	Benzonitrile	4.004	L1
15252	Phenylacetonitrile	4.578	L53
15301	Aniline	3.993	L3
15302	o-Toluidine	4.494	L60
15303	m-Toluidine	4.474	L60
15304	p-Toluidine	4.449	L60
15583	2,6-Dimethylaniline	5.037	L19
15601	N-Methylaniline	4.494	L1
15602	N-Ethylaniline	4.846	L60
15603	N-Propylaniline	5.338	L60
15651	N,N-Dimethylaniline	4.754	L2
15652	N,N-Diethylaniline	5.343	L60
15662	3-Methyl-N,N-dimethylaniline	5.332	L60
15663	4-Methyl-N,N-dimethylaniline	5.287	L60
15801	Nitrobenzene	4.511	L53
15802	2-Nitrotoluene	4.841	L53

Table 12. Log L16 Values in the Solute Database

No	Compound Name	Log L16	Ref
15803	3-Nitrotoluene	5.062	L53
15804	4-Nitrotoluene	5.117	L53
15901	b-Nitrostyrene	6.600	L28
15902	b-Methyl-b-nitrostyrene	6.900	L28
16501	Phenol	3.897	L52
16502	o-Cresol	4.242	L3
16503	m-Cresol	4.329	L3
16504	p-Cresol	4.307	L3
16505	2,3-Dimethylphenol	4.957	L60
16506	2,4-Dimethylphenol	4.762	L60
16508	2,6-Dimethylphenol	4.667	L60
16509	3,4-Dimethylphenol	4.935	L60
16516	2,4,6-Trimethylphenol	5.185	L1
16528	2-Isopropylphenol	4.921	L3
16544	4-t-Butylphenol	5.340	L1
16652	3-Fluorophenol	3.844	L3
16654	2-Chlorophenol	4.937	L1
16655	3-Chlorophenol	4.650	L1
16656	4-Chlorophenol	4.630	L46
16658	3-Bromophenol	5.050	L46
16659	4-Bromophenol	5.030	L46
16671	2,6-Difluorophenol	3.693	L3
16771	3-Cyanophenol	5.020	L46
16772	4-Cyanophenol	5.000	L46
16776	2-Nitrophenol	4.684	L3
16777	3-Nitrophenol	5.470	L46
16778	4-Nitrophenol	5.450	L46
16831	Salicylaldehyde	4.750	L24
17001	Benzyl alcohol	4.249	L52
17080	1-Phenylethanol	4.362	L53
17081	2-Phenylethanol	4.578	L53
17082	3-Phenylpropanol	5.149	L53
17083	2-Phenylpropan-2-ol	4.504	L53
17151	Thiophenol	4.118	L1
18501	Furan	1.830	L1
18502	2-Methylfuran	2.430	L42
18551	Benzofuran	4.393	L49
18651	Benzodioxan	4.985	L32
18761	Trioxan	2.650	L42
18762	Paraldehyde	3.169	L63
19001	Pyridine	3.003	L3
19002	2-Methylpyridine	3.437	L3
19003	3-Methylpyridine	3.603	L3
19004	4-Methylpyridine	3.593	L3
19006	2,4-Dimethylpyridine	4.050	L31
19007	2,5-Dimethylpyridine	4.050	L31
19008	2,6-Dimethylpyridine	3.860	L31
19009	3,4-Dimethylpyridine	4.360	L31
19010	3,5-Dimethylpyridine	4.250	L31
19015	2,4,6-Trimethylpyridine	4.200	L1
19016	2-Ethylpyridine	3.900	L31
19017	3-Ethylpyridine	4.130	L31
19018	4-Ethylpyridine	4.140	L31
19052	4-t-Butylpyridine	4.750	L31
19501	Pyrrole	2.865	L1
19562	N-Methyl-2-pyrrolidinone	4.320	L27
19802	N-Methylimidazole	3.805	L3
20501	Thiophene	2.943	L1
20502	2-Methylthiophen	3.302	L1
20505	2,5-Dimethylthiophen	3.806	L1

References For Table 12.

Ref Code	Reference
L1	Value measured by G. S. Whiting directly on n-hexadecane at 298.15 K.
L2	Retention data measured by G. S. Whiting on Apiezon L at 298.15 K, correlated to give Log L16 value.
L3	Value measured directly on n-hexadecane at 298.15 K by R. A. McGill; M. H. Abraham, P. L. Grellier, R. A. McGill, J. Chem. Soc., Perkin Trans. 2, 1987, 287.
L4	M. H. Abraham and E. Matteoli, survey of results.
L5	Solubility Data Project Series, vols. 1-10, Pergamon, Oxford.
L6	P. J. Lin and J. F. Parcher, J. Chromatogr. Sci., 1982, 20, 33.
L7	L5 and L6.
L8	L4 and L5.
L9	Estimated value using Abraham's Rg parameter.
L10	K. K. Tremper and J. M. Prausnitz, J. Chem. Eng. Data, 1976, 21, 295.
L11	D. Richon and H. Renon, J. Chem. Eng. Data, 1980, 25, 59.
L12	J.-Y. Lenoir, P. Renault, and H. Renon, J. Chem. Eng. Data, 1971, 16, 340.
L13	L4, L6, L11, and L12.
L14	L4, L11, L12, L21 and I. Kikic and H. Renon, Sep. Science, 1976, 11, 45.
L15	L11 and L12.
L16	A. Kwantes and G. W. A. Rijinders in 'Gas Chromatography 1958', ed. D. H. Desty, Butterworths, London, 1958.
L17	D. E. Martire and P. Riedl, J. Phys. Chem., 1968, 72, 3478;J. P. Sheridan, D. E. Martire, and Y. B. Tewari, J. Am. Chem. Soc., 1972, 94, 3294.
L18	N. Dimov, J. Chromatogr., 1985, 347, 366-374, (data corrected to 298 K using dI/dT given). Calculated value from correlation of Log L16 with retention data.
L19	Estimated from vapour pressure/log L16 correlations for closely similar compounds.
L20	Estimated from a correlation of log L with carbon number, for a homologous series.
L21	W. Hayduk and R. Castenada, Can. J. Chem. Eng., 1973, 51, 353; W. Hayduk, E. B. Walter, and P. Simpson, J. Chem. Eng. Data, 1972, 17, 59.
L22	From data in cyclohexane.
L23	L4 and L11.
L24	A. Wehrli and E. Kovats, Helv. Chim. Acta., 1959, 42, 2709-36. Calculated value from correlation of log L16 with retention data.
L25	L24, - the average of the cis and trans isomers.
L26	P. Allessi, I. Kikic, A. Alessandri and M. Fermeglia, J. Chem. Eng. Data, 1982, 24, 445, 448.
L27	Back-calculated from data in iso-octane by - D. J. W. Grant, T. Higuchi, Y. T. Hwang, and J. H. Rytting, J. Solution Chem., 1984, 13, 297.
L28	Approximate estimation.
L29	U. Weldlich and J. Grehling, J. Chem. Eng. Data, 1987, 32, 138-142. Calculated value from correlation of log L16 with retention data.
L30	Y. Miyano and W. Hayduk, Can. J. Chem. Engl., 1981, 59, 746.
L31	F. Riedo, D. Fritz, G. Tarjan, and E. Kovats, J. Chromatogr., 1976, 126, 63-83, (data corrected to 343 K using dI/dT given). Calculated value from correlation of log L16 with retention data.
L32	C. F. Poole, R. M. Pomaville, and T. A. Dean, Analyt. Chim. Acta., 1989, 225, 193.
L33	Estimated from log L olive oil/log L16 correlations for closely similar compounds.
L34	From log L values in alkanes.
L35	L19 and L33.
L36	M. Laffosse and M. Dreux, J. Chromatogr., 1980, 193, 9-18. Calculated value from correlation of log L16 with retention data.
L37	From data by P. Perez, J. Valero, M. Gracia and C. G. Losa, J. Chem. Thermodyn., 1989, 21, 259.
L38	L31 and L36. Average or adjusted value of 2 or more values.
L39	A. Lebert and D. Richon, J. Food Sci., 1984, 39, 1301.
L40	P. Laffort and F. Patte, J. Chromatogr., 1987, 406, 51-74. Calculated value from correlation of log L16 with retention data.
L41	A. Ya. Aarna, L. J. Melder, and A. V. Ebber, Zhur. Prikl. Khim., 1979, 52, 1640 (English Translation p. 1558).
L42	W. O. McReynolds in 'Gas Chromatographic Retention Data', Preston Technical Abstracts Company, USA, 1966. Calculated value from correlation of log L16 with retention data on Squalane at 80°C.

References For Table 12.

Ref Code	Reference
L43	R. I. Sidorov, A. A. Khvostikova, and G. I. Vakhursheva, J. Anal. Chem. USSR, 1973, 28, 1420-1424. Calculated value from the correlation of log L16 with retention data.
L44	L24 corrected slightly to be more in line with homologous series.
L45	R. N Featherstone, C. Muehlbaecher, F. L. De Bon, and J. A. Forssith, Anesthesiology, 1961, 22, 977.
L46	From log L (water) plus log P for partition between water and n-hexadecane.
L47	R. V. Golovnya and Y. N. Arsen'ev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1972, 1350-52; R. V. Golovnya, V. G. Garbuzov, and T. A. Misharina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1976, 2114-2117. Data corrected to 333 K using dI/dT given. Value calculated from log L16 correlation.
L48	From data by M. H. Abraham, P. L. Grellier, and R. A. McGill, J. Chem. Soc., Perkin Trans. 2, 1988, 339.
L49	T.-C. L. Chang and C. Karr,Jr., Analyt. Chim. Acta, 1959,21,474 (Calculated from a correlation for aromatic hydrocarbons on Apiezon)
L50	G.f.Harrison, in Vapour Phase Chromatography, ed by D.L.Desty, Butterworths, London, 1957. Calculated through a number of regressions.
L51	G. Castello and T.C.Gerbino, J.Chromatogr.,1988,437,33, using a correlation for a nonpolar phase.
L52	R. Fellous, L. Lizzani-Cuvelier, and R. Luft, Analyt. Chim. Acta. 1985 174, 53. Calculated through a number of regressions.
L53	A. Wehrli and E. Kovats, Helv. Chim. Acta, 1959,42,2709, from a regression equation for apiezon.
L54	Average values from ref L31 and L53
L55	P. Urone, J. E. Smith, and R. J. Katnik, Anal. Chem., 1962,34,476, from several regression equations.
L56	D. H. Desty and C. L. Harbourn, Anal. Chem., 1959, 31, 1965 from the average of two regressions.
L57	E. F. Meyer, K. S. Stec, and R. D. Hotz, J.Phys.Chem., 1973,77,2140, from a correlation with n-tetracosane.
L58	Average of values from regressions using data in ref 51, and J. P. Sheridan, D. E. Martire, and Y. B. Tewari, J. Am. Chem. Soc., 1972, 94, 3294.
L59	Average of values in ref L3, and from D. E. Martire and L. Z. Pollara, J. Chem. Eng. Data, 1965, 10, 40.
L60	Correlations using data in 'Gas Chromatography Data Compilation',ed O. E. Schupp and J. S. Lewis, ASTM series DS 25A,Philadelphia, 1967.
L61	Average of values in L3, L53, and L60.
L62	A. J. Lubeck and D. L. Sutton, J. High Res. Chromatog, 1983, 6, 328.
L63	Calculated using the inverse matrix method on McReynolds data set, ref 133.
L64	Average of ten back-calculated values, M. H. Abraham and G. S. Whiting, unpublished work.
L65	Value obtained using a correlation with retention data on Apiezon at various temperatures, this work.

APPLICATION OF THE NEW SOLUTE PARAMETERS TO THE CHARACTERISATION OF SOLVENTS AND SOLVENT/WATER PARTITION COEFFICIENTS

One of the major undertakings of this work has been to characterise important solvents and to analyse water to solvent partitions. As well as the detailed characterisation of some N-substitued amides, by analysing log L and V^o_G for the partition process gas ⇨ solvent[63], other solvents were also characterised in this way, using log L (gas ⇨ solvent). The partition between water and these solvents has also been examined, using log P (water ⇨ solvent). Some of the amides examined before[63] are again presented here. The solvents have been analysed using equations 28 and 35; where the new solvation parameters (π^H_2, $\Sigma\alpha^H_2$ and $\Sigma\beta^H_2$) are available, they have been used.

$$\log L\ (\text{gas} \Rightarrow \text{solvent}) = c + r.R_2 + s.\pi^H_2 + a.\Sigma\alpha^H_2 + b.\Sigma\beta^H_2 + l.\log L^{16} \qquad [28]$$

$$\log P\ (\text{water} \Rightarrow \text{solvent}) = c + r.R_2 + s.\pi^H_2 + a.\Sigma\alpha^H_2 + b.\Sigma\beta^H_2 + v.V_X \qquad [35]$$

Application of these equations using MLRA is entirely straightforward, yielding coefficients in the usual way. Note the use of preferred equation 35 (with the term $v.V_X$), for processes occuring within condensed phases. Values of log L for the solubility of gases or vapours in solvents have been extensively collected [+], along with log L_W[±]. If log L for water and solvent is known, then from $P = L_2/L_1$, where log L_W is the gas ⇨ water value of log L, the value of P (water ⇨ solvent) can be found,

$$P\ (\text{water} \Rightarrow \text{solvent}) = L_{\text{SOLVENT}}/L_W \qquad [36]$$

$$\therefore \quad \log P\ (\text{water} \Rightarrow \text{solvent}) = \log L_{\text{SOLVENT}} - \log L_W \qquad [37]$$

[+] The Solubility Data Project Series referenced in Tables 15,17 and 18 for values of log L, published by Pergamon Press, Oxford. Vol 1: Helium & Neon, ed. H. L. Clever, 1979. Vol 2: Krypton, Xenon & Radon, ed. H. L. Clever, 1979. Vol 4: Argon, ed. H. L. Clever, 1980. Vol &: Oxygen & Ozone, ed. R. Battino, 1981. Vol 8: Oxides of Nitrogen, ed. C. L. Young, 1981. Vol 9: Ethane, ed. W. Hayduk, 1982. Vol 10: Nitrogen & Air, ed. R. Battino, 1982. Vol 21: Ammonia, Amines, Phosphine, Arsine, Stibine, Silane, Germane & Stannane in Organic Solvents, ed. C. L. Young and P. G. T. Fugg, 1985. Vol 27,28: Methane, ed. H. L. Clever and C. L. Young, 1987. Vol 12: Suplhur Dioxide, Chlorine, Fluorine & Chlorine Oxides, ed. C. L. Young, 1983. Vol 24: Propane, Butane and 2-Methylpropane, ed. W. Hayduk, 1986. [±] All values of log L_W are taken from references 64-66.

AMIDES

Solvents examined were N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF), N-methylpyrrolidinone (NMP), and N-formylmorpholine (NFM). Summaries of the obtained regression equations are given in Table 13.

Table 13. Characterisation of Amide Solvents.

(A) Correlations of log L (gas ⇨ solvent) Using Equation 28.

	c	r	s	a	b	l	R	SD	N
DMA[a]	-0.032	0.138	2.020	5.070	-	0.787	0.9987	0.063	28
NMP[a]	-0.306	0.351	2.098	4.975	-	0.838	0.9969	0.107	61
DMF[a]	-0.239	0.084	2.259	4.362	-	0.827	0.9929	0.159	55
NFM[b]	-0.439	0.008	2.567	4.324	-	0.730	0.9955	0.069	45

(B) Correlations of log P (water ⇨ solvent) Using Equation 35.

	c	r	s	a	b	v	R	SD	N
DMA[a]	0.142	0.535	0.030	0.880	-4.590	3.944	0.9960	0.120	26[c]
NMP[a]	-0.019	0.885	0.209	1.314	-4.889	3.859	0.9958	0.146	55[c]
DMF[a]	0.018	0.566	0.386	0.588	-4.791	3.845	0.9924	0.193	51[c]
NFM[b]	0.017	0.457	0.390	0.418	-4.713	3.389	0.9977	0.115	45

[a] Values from reference 63, with additional values for 2-chloro-2-methylpropane and 2-bromo-2-methylpropane from reference 67.

[b] Same compound set as in reference 63.

[c] N for log P is less than N for log L because some values of log L_W are not available.

From the log L analysis, see Table 13(a), the $b.\Sigma\beta^H_2$ term is shown to be insignificant. All the amides are shown to be reasonably dipolar, *s* ranging from 2.57 for NFM to 2.02 for DMA, and are strong hydrogen bond bases, DMA being the strongest hydrogen bond base, *a* = 5.07. They are all medium dispersion interactors, with $l < 1.00$ (by definition, $l = 1.00$ for n-hexadecane).

Equation 35 gives constants that are generally chemically reasonable and might be expected, Table 13(b). All the amides have a *v*-constant around + 4, showing solute volume leads to a preference for amides. The *b*-constant is large, *b* = -4.59 for DMA to -4.89 for NMP, leading to solute preference, as might be expected, for water. The *s*-constant is small but positive (solute preference for amide), and r-constants are reasonably large and positive. The *a*-constants range from 0.42 (NFM) to 1.31 (NMP), showing solute preference for amide; amides are stronger hydrogen bond bases than water. Comparing solvent β_1 values[68], β_1 for water is 0.18, β_1 for DMF and DMA is 0.69 and 0.76 respectively.

ALKANES

The alkanes examined were pentane, hexane, heptane, octane, decane, *iso*-octane and cyclohexane. All these solvents should be reasonably close to our standard non-polar solvent n-hexadecane, but application of equation 28 can still yield useful information, and additionally serve as a check on the method. Summaries of the obtained regression coefficients are in Table 14, and the log L and log P values for alkane solvents are set out in Table 15.

Table 14. Characterisation of Alkane Solvents.

(A) Correlations of log L (gas ⇨ solvent) Using Equation 28.

	c	r	s	l	R	SD	N
Pentane	0.376	-0.130	-0.229	0.969	0.9989	0.071	30
Hexane	0.313	-0.127	-0.153	0.978	0.9977	0.098	83[a]
Heptane	0.283	-0.193	-0.271	1.032	0.9991	0.093	78[a]
Octane	0.238	-0.103	-0.156	0.988	0.9990	0.062	59
Decane	0.168	-0.104	-0.071	0.993	0.9995	0.053	40
Iso-octane	0.283	-0.138	-0.135	0.977	0.9983	0.078	63[a]
Cyclohexane	0.206	-0.022	-0.040	1.031	0.9983	0.090	71
Cyclohexane	0.203	-	-	1.024	0.9983	0.089	71

(B) Correlations of log P (water ⇨ solvent) Using Equation 35.

	c	r	s	a	b	v	R	SD	N
Pentane	0.344	0.145	-1.478	-3.419	-5.299	4.631	0.9989	0.108	30
Hexane	0.369	0.635	-1.699	-3.410	-5.034	4.362	0.9971	0.175	81[b]
Heptane	0.267	0.560	-1.771	-3.439	-5.032	4.594	0.9980	0.120	76[b]
Octane	0.210	0.574	-1.775	-3.215	-4.954	4.563	0.9978	0.132	58[b]
Decane	0.099	0.446	-1.496	-3.417	-4.935	4.676	0.9989	0.118	40
Hexadecane [c]	0.076	0.887	-1.773	-3.605	-4 805	4.422	0.9965	0.158	256
Iso-octane	0.273	0.341	-1.580	-3.444	-5.152	4.527	0.9982	0.125	62[b]
Cyclohexane	0.162	0.847	-1.750	-3.411	-4.773	4.683	0.9967	0.167	66[b]

[a] Less than the number of solutes given in Table 15, as there are still a few log L^{16} values missing.

[b] Less than the log L regression, as some log L_W values are not available

[c] Data from reference 66, provisional regression equation.

In equation 28, the coefficients obtained are all similar to those for solvent n-hexadecane, see Table 14(a), for which *r*, *s*, *a*, and *b* are zero and *l* is 1 by definition. Two regressions have been generated for cyclohexane, the first in *r*, *s*, and *l*, the second in solely *l*. The correlation coefficient and standard deviation are virtually identical, showing clearly that *l*.log L^{16} is the only relevant term, as might be expected. Equation 35, see Table 14(b), which in effect compares the (zero) coefficients for alkanes from equation 28 with those of water, again gives coefficients of similar magnitude to those for n-hexadecane. Solute dipolarity, hydrogen bond acidity and basicity favour partition to water, and solute volume partition to alkane solvent.

Table 15. Log L and Log P For Alkane Solvents.

	Pentane		Hexane		Heptane		Octane	
	log L	Log P	Log L	Log P	Log L	Log P	Log L	Log P
Helium	-1.26 [a]	0.76	-1.315 [a]	0.71	-1.38 [a]	0.64	-1.45 [a,b]	0.57
Neon	-1.06 [a]	0.90	-1.162 [a]	0.80	-1.23 [a]	0.73	-1.27 [a,b]	0.69
Argon	-0.22 [a]	1.25	-0.328 [a]	1.14	-0.38 [a]	1.09	-0.44 [a,b]	1.03
Krypton	0.22 [a]	1.44	0.110 [a]	1.32	0.07 [a]	1.28	0.02 [b]	1.23
Xenon	0.71 [c]	1.68	0.683 [a]	1.65	0.64 [a,c]	1.61	0.51 [a,c]	1.48
Radon			1.137 [a]	1.78				
Hydrogen	-0.85 [a]	0.87	-0.909 [a]	0.81	-0.94 [a]	0.78	-0.99 [a]	0.73
Deuterium					-0.93 [a]	0.80	-0.98 [a]	0.75
Oxygen	-0.36 [d]	1.15	-0.419 [d]	1.09	-0.47 [d]	1.04	-0.50 [b,d]	1.01
Nitrogen	-0.53 [d]	1.27	-0.588 [d]	1.21	-0.65 [d]	1.15	-0.71 [b]	1.09
Nitrous oxide	0.61 [a]		0.540 [a]	0.77	0.48 [a]	0.71	0.44 [a]	0.67
Nitric oxide								
Carbon monoxide			-0.494 [e]	1.14	-0.54 [f]	1.09	-0.59 [b]	1.04
Carbon dioxide					0.30 [g]	0.38	0.26 [b]	0.34
Sulphur dioxide					1.00 [h]	-0.55		
Methane			-0.012 [i]	1.44			-0.12 [b]	1.33
Ethane	0.74 [k]	2.08	0.76 [i,k]	2.10	0.73 [k]	2.07	0.70 [k]	2.04
Propane	1.33 [k]	2.77	1.31 [i,k]	2.75	1.30 [k]	2.74	1.28 [k]	2.72
n-Butane	1.91 [k]	3.43	1.84 [i,k]	3.39	1.96 [k,m]	3.48	1.83 [k]	3.35
2-Methylpropane	1.75 [k]	3.45	1.71 [i,k]	3.41	1.69 [k]	3.39	1.68 [k]	3.38
n-Pentane	2.49 [o]	4.19	2.43 [i]	4.13	2.36 [p]	4.06	2.30 [q]	4.00
2,2-Dimethylpropane			2.12 [a]	3.96				
n-Hexane	3.02 [o]	4.84	3.02 [i]	4.84	2.91 [p]	4.73	2.83 [q]	4.65
2,2-Dimethylbutane			2.67 [a]	4.57				
n-Heptane			3.45 [i]	5.41	3.44 [o]	5.40	3.39 [o]	5.35
n-Octane	3.99 [u]	6.10	4.00 [i]	6.11	3.95 [p,u]	6.06	3.91 [o]	6.02
2,2,4-Trimethylpentane							3.27 [q]	5.44
3,3-Diethylpentane			4.31 [i]	5.94				
n-Decane								
Cyclopropane			1.45 [v]	2.00				
Cyclopentane			2.71 [i]	3.59				
Methylcyclopentane								
Cyclohexane			3.24 [i]	4.14	3.12 [s]	4.02	3.03 [w]	3.93
Methylcyclohexane								
Ethene	0.51 [k]	1.45	0.53 [k,x]	1.47	0.52 [x]	1.46	0.44 [k]	1.38
Propene	1.31 [k]	2.28	1.29 [k]	2.26	1.28 [k]	2.25	1.26 [k]	2.23
But-1-ene	1.85 [k]	2.86	1.83 [k]	2.84	1.82 [k]	2.83	1.80 [k]	2.81
Iso-butene	1.82 [k]	2.68	1.78 [k]	2.63	1.79 [k]	2.65	1.77 [k]	2.63
Pent-1-ene					2.31 [s]	3.54	2.27 [s]	3.50
Buta-1,3-diene					1.96 [y]	2.41		
2-Methylbuta-1,3-diene					2.36 [s]	2.86	2.33 [s]	2.83
Ethyne			0.38 [n]	0.37				
Fluoroethane					1.06 [z]			
Tetrafluoromethane			-0.40 [e]	1.88	-0.45 [g]	1.83	-0.52 [b]	1.76
Perfluoroethane								
Perfluoropropane								
Perfluorocyclobutane								
Dichloromethane	2.13 [w]	1.17			2.13 [s]	1.17	2.10 [s]	1.14
Trichloromethane			2.65 [s]	1.86	2.65 [s]	1.86	2.58 [s,aa]	1.79
Tetrachloromethane			3.03 [s]	3.09	3.00 [s]	3.06	2.92 [ab]	2.98
Chloroethane			1.91 [ad]	1.45				
1,2-Dichloroethane			2.74 [ae,af]	1.43	2.71 [s,ag]	1.40	2.71 [s]	1.40
1-Chloropropane			2.47 [ad]	2.23	2.41 [s]	2.17	2.36 [s]	2.12
1,2-Dichloropropane			3.05 [ah]	2.12				
1,3-Dichloropropane			3.25 [ah]	1.86				

Table 15 (cont). Log L and Log P For Alkane Solvents.

	Decane		Iso-octane		Cyclohexane	
	Log L	Log P	Log L	Log P	Log L	Log P
Helium	-1.53 [b]	0.49	-1.34 [a]	0.68	-1.561 [a]	0.47
Neon	-1.37 [b]	0.59	-1.17 [a]	0.79	-1.382 [a]	0.58
Argon	-0.51 [b]	0.96	-0.37 [a]	1.10	-0.475 [a]	0.99
Krypton	-0.03 [b]	1.18	0.07 [a]	1.28	0.025 [a]	1.24
Xenon	0.57 [c]	1.54	0.60 [a]	1.57	0.673 [a]	1.65
Radon						
Hydrogen	-1.09 [a]	0.63	-0.94 [a]	0.78	-1.031 [a]	0.69
Deuterium			-0.93 [a]	0.80		
Oxygen	-0.56 [b]	0.95	-0.41 [a]	1.10	-0.556 [d]	0.95
Nitrogen	-0.82 [b]	0.98	-0.64 [a]	1.15	-0.760 [d]	1.04
Nitrous oxide	0.36 [a]	0.59	0.49 [a]	0.72	0.283 [a]	0.51
Nitric oxide					-0.350 [a]	
Carbon monoxide	-0.68 [b]	0.95			-0.652 [g]	0.98
Carbon dioxide	-0.20 [b]	-0.12			0.233 [g]	0.31
Sulphur dioxide			0.86 [a]	-0.69	0.900 [a]	-0.65
Methane	-0.18 [b]	1.27	-0.10 [j]	1.35	-0.133 [g]	1.32
Ethane	0.65 [k]	1.99	0.65 [a]	1.98	0.72 [a]	2.06
Propane	1.25 [k]	2.69	1.25 [l]	2.69	1.35 [a]	2.79
n-Butane	1.79 [k]	3.31	1.79 [l]	3.30	1.95 [n]	3.47
2-Methylpropane	1.64 [k]	3.34			1.71 [e]	3.41
n-Pentane	2.28 [r]	3.98	2.35 [s,t]	4.05	2.42 [e]	4.12
2,2-Dimethylpropane						
n-Hexane	2.82 [r]	4.64	2.82 [t]	4.64	2.99 [e]	4.81
2,2-Dimethylbutane	2.48 [r]	4.38				
n-Heptane	3.33 [r]	5.29	3.38 [t]	5.34	3.53 [e]	5.49
n-Octane	3.82 [u]	5.93	3.89 [u]	6.00	4.09 [e,u]	6.20
2,2,4-Trimethylpentane			3.36 [s]	5.53		
3,3-Diethylpentane						
n-Decane	4.84 [o]	7.16				
Cyclopropane					1.50 [v]	2.05
Cyclopentane	2.54 [r]	3.42			2.73 [e]	3.61
Methylcyclopentane	2.88 [r]	4.05				
Cyclohexane	3.02 [r]	3.92			3.24 [o]	4.14
Methylcyclohexane	3.35 [r]	4.60				
Ethene	0.42 [k]	1.36				
Propene	1.23 [k]	2.20				
But-1-ene	1.77 [k]	2.78				
Iso-butene	1.73 [k]	2.59				
Pent-1-ene			2.25 [s]	3.48		
Buta-1,3-diene						
2-Methylbuta-1,3-diene			2.33 [s]	2.83		
Ethyne					0.33 [n]	0.32
Fluoroethane						
Tetrafluoromethane	-0.63 [b]	1.65	-0.37 [g]	1.92	-0.63 [g]	1.65
Perfluoroethane					-0.26 [g]	2.62
Perfluoropropane					0.14 [g]	3.34
Perfluorocyclobutane					0.69 [g]	3.22
Dichloromethane			2.09 [s]	1.13		
Trichloromethane			2.59 [s]	1.80		
Tetrachloromethane					3.06 [ac]	3.12
Chloroethane						
1,2-Dichloroethane					2.83 [ac]	1.52
1-Chloropropane			2.36 [s]	2.12	2.52 [ac]	2.28
1,2-Dichloropropane					3.15 [ah]	2.23
1,3-Dichloropropane					3.31 [ah]	1.92

Table 15 (cont). Log L and Log P For Alkane Solvents.

	Pentane		Hexane		Heptane		Octane	
	Log L	Log P	Log L	Log P	Log L	Log P	Log L	Log P
1-Chlorobutane	2.99 [ai]	2.87	2.94 [a]	2.82	2.91 [ag]	2.79		
2-Chloro-2-methylpropane			2.46 [ae,aj]	3.26	2.48 [s]	3.28		
1-Chloropentane			3.51 [ad]	3.46				
Bromoethane			2.27 [s,ad]	1.73	2.23 [s]	1.69	2.19 [s]	1.65
2-Bromo-2-methylpropane			2.75 [aj]	3.37				
Iodomethane					2.22 [s]	1.57	2.19 [s]	1.54
Iodoethane			2.72 [s,ad,ak]	2.18	2.70 [s]	2.16	2.68 [s]	2.14
1-Iodopropane								
1-Iodobutane								
Difluorodichloromethane Freon 12					1.32 [g]	2.46	1.29 [g]	2.43
Trifluorochloromethane Freon 13					0.44 [g]	2.15	0.39 [g]	2.10
1,2-Difluorotetrachloroethane			3.25 [n]		3.20 [al]	3.80		
Diethylether								
Di-n-propylether								
Di-n-butylether								
Methyl-n-butylether								
Ethyl-n-butylether								
Dimethoxymethane								
Diethoxymethane								
1,2-Dimethoxyethane								
1,2-Diethoxyethane								
Diethyleneglycol dimethylether								
Tetrahydrofuran [CH2]4 O	2.62 [ao]	0.07	2.69 [s,ao]	0.14	2.55 [ao]	0.00	2.68 [s]	0.13
Dioxan	2.96 [u]	-0.75	2.98 [v]	-0.73	2.95 [u,ao]	-0.76		
Acetaldehyde								
Propionaldehyde							1.86 [q]	-0.66
Butyraldehyde							2.37 [q]	0.04
Pentanal							2.91 [q]	0.69
Hexanal							3.49 [q]	1.43
Propanone							1.85 [q]	-0.94
Butanone	2.51 [u]	-0.21	2.54 [s,u]	-0.18	2.52 [u]	-0.20	2.37 [q]	-0.35
Pentan-2-one							2.84 [q]	0.26
4-Methylpentan-2-one							3.18 [q]	0.94
Cyclopentanone					3.32 [ar]	-0.13		
Cyclohexanone			3.65 [s]	0.05	3.80 [ar]	0.20		
Methyl formate								
Ethyl formate								
Propyl formate								
Ethyl acetate			2.64 [s]	0.48	2.59 [s,as]	0.43	2.56 [q,s]	0.40
n-Butyl acetate					3.61 [as]	1.67		
Acetonitrile			1.77 [s,ad]	-1.08	1.62 [s,as]	-1.23	1.58 [s,aa]	-1.27
Proprionitrile			2.22 [s,ad]	-0.60	2.10 [s,as]	-0.72	2.08 [s]	-0.74
1-Cyanopropane			2.75 [ad]	0.08				
1-Cyanobutane			3.26 [ad]	0.68				
Ammonia			0.433 [a]	-2.72				
Methylamine			1.20 [a]	-2.14				
Ethylamine			1.68 [af]	-1.62				
n-Propylamine			2.26 [af]	-0.96				
Isopropylamine			2.04 [af]					
n-Butylamine	2.71 [at]	-0.40			2.98 [p]	-0.13		
n-Pentylamine					3.48 [p]	0.48		
n-Hexylamine					3.99 [p]	1.09		
n-Heptylamine					4.52 [p]	1.74		
n-Octylamine					5.04 [p]	2.36		
Dimethylamine			1.82 [a]	-1.33				

Table 15 (cont). Log L and Log P For Alkane Solvents.

	Decane		Iso-octane		Cyclohexane	
	Log L	Log P	Log L	Log P	Log L	Log P
1-Chlorobutane					3.05 [ac]	2.93
2-Chloro-2-methylpropane					2.47 [ac]	3.27
1-Chloropentane						
Bromoethane			2.18 [s]	1.64		
2-Bromo-2-methylpropane					2.84 [ac]	3.46
Iodomethane			2.16 [s]	1.50		
Iodoethane			2.66 [s]	2.12	2.97 [ak]	2.43
1-Iodopropane					3.39 [ac]	3.00
1-Iodobutane					3.77 [ac]	3.59
Difluorodichloromethane Freon 12					1.32 [g]	2.46
Trifluorochloromethane Freon 13					0.35 [g]	2.06
1,2-Difluorotetrachloroethane					3.31 [am]	
Diethylether					2.29 [an]	1.12
Di-n-propylether					3.36 [an]	2.51
Di-n-butylether					4.35 [an]	3.74
Methyl-n-butylether					2.88 [an]	1.75
Ethyl-n-butylether					3.36 [an]	2.06
Dimethoxymethane					2.16 [an]	0.01
Diethoxymethane					3.20 [an]	
1,2-Dimethoxyethane					2.75 [an]	-0.79
1,2-Diethoxyethane					3.40 [an]	0.82
Diethyleneglycol dimethylether					4.12 [an]	
Tetrahydrofuran [CH2]4 O			2.71 [s]	0.16	2.66 [ao,ap]	0.11
Dioxan	2.91 [u]	-0.80	2.93 [u]	-0.78	3.04 [ap,aq]	-0.67
Acetaldehyde			1.38 [t]	-1.19		
Propionaldehyde			1.95 [t]	-0.57		
Butyraldehyde			2.42 [t]	0.09		
Pentanal						
Hexanal						
Propanone			1.84 [s]	-0.95		
Butanone	2.40 [u]	-0.32	2.47 [u]	-0.25	2.55 [aq]	-0.17
Pentan-2-one						
4-Methylpentan-2-one						
Cyclopentanone					3.39 [ar]	-0.06
Cyclohexanone					3.93 [ar]	0.33
Methyl formate			1.53 [t]	-0.51		
Ethyl formate			2.12 [t]	0.24		
Propyl formate			2.68 [t]	0.86		
Ethyl acetate			2.59 [s]	0.43	2.69 [ao]	0.53
n-Butyl acetate						
Acetonitrile			1.60 [s]	-1.25		
Proprionitrile			2.10 [s]	-0.72		
1-Cyanopropane						
1-Cyanobutane						
Ammonia					0.896 [a]	-2.25
Methylamine						
Ethylamine			1.72 [t]	-1.58		
n-Propylamine			2.22 [t]	-1		
Isopropylamine						
n-Butylamine			2.83 [t]	-0.28		
n-Pentylamine						
n-Hexylamine						
n-Heptylamine						
n-Octylamine						
Dimethylamine	1.69 [a]	-1.46				

Table 15 (cont). Log L and Log P For Alkane Solvents.

	Pentane		Hexane		Heptane		Octane	
	Log L	Log P	Log L	Log P	Log L	Log P	Log L	Log P
Diethylamine			2.62 [at]	-0.37				
Trimethylamine			1.93 [a]	-0.42	1.79 [a]	-0.56		
Triethylamine			3.30 [s,ak]	0.94	3.28 [at]	0.92		
Nitromethane	1.97 [u]	-0.98	2.00 [s,u]	-0.95	1.92 [s,as]	-1.03	1.99 [s,aa]	-0.96
Nitroethane			2.51 [s]	-0.21	2.45 [s,as]	-0.27	2.47 [s]	-0.25
1-Nitropropane			2.97 [s]	0.52	2.91 [as]	0.46		
2-Nitropropane					2.79 [as]	0.49		
Water	0.50 [au]	-4.14	0.54 [au]	-4.10	0.43 [av]	-4.21	0.50 [aw]	-4.14
Methanol			1.15 [ad]	-2.59	1.20 [p,s]	-2.54	1.06 [s,aa]	-2.68
Ethanol	1.63 [az]	-2.04	1.63 [u]	-2.02	1.64 [p,u]	-2.03	1.61 [s,aa]	-2.06
Propan-1-ol			2.21 [s,ad]	-1.35	2.20 [p,ba]	-1.36		
Propan-2-ol			2.02 [am]	-1.46	1.91 [p,ba]	-1.57		
Butan-1-ol			2.74 [ad]	-0.72	2.75 [p]	-0.71		
2-Methylpropan-1-ol					2.58 [p]	-0.72		
Butan-2-ol					2.39 [p]	-1.00		
2-Methylpropan-2-ol					2.21 [p]	-1.07		
Pentan-1-ol					3.33 [p]	-0.02		
Hexan-1-ol			3.55 [bd]	0.32	3.87 [p]	0.64		
2-Methylpentan-3-ol								
Decan-1-ol			5.64 [bd]	2.97				
Sulphur hexafluoride			0.28 [s]	2.51	0.22 [g]	2.45	0.15 [s]	2.38
Carbon disulphide					2.44 [s]		2.41 [s]	
Hexamethylphosphotriamide			5.41 [bg]		5.33 [bg]		5.10 [bg]	
Tetramethylsilane			2.32 [i]	4.55				
Tetraethylsilane			4.64 [i]	6.67				
Tetramethyltin			3.03 [i]	4.65				
Tetraethyltin			5.14 [i]	6.96				
Mercury	1.74 [a]	1.28	1.78 [a]	1.32	1.79 [a]	1.33	1.79 [a]	1.33
Benzene	2.94 [w]	2.29	3.00 [w,ae]	2.35	2.93 [bh]	2.28	2.88 [q,w,bi]	2.23
Toluene	3.46 [u]	2.88	3.48 [u,ae]	2.90	3.47 [u]	2.89		
Hexafluorobenzene								
Chlorobenzene					3.79 [bk]	2.95		
Pyridine			3.07 [ae]	-0.37				
2-Methylpyridine								
3-Methylpyridine								
4-Methylpyridine								
2,6-Dimethylpyridine								

Table 15 (cont). Log L and Log P For Alkane Solvents.

	Decane		Iso-octane		Cyclohexane	
	Log L	Log P	Log L	Log P	Log L	Log P
Diethylamine						
Trimethylamine						
Triethylamine					3.39 [ar]	1.03
Nitromethane	1.92 [u]	-1.03	1.97 [u]	-0.98	2.02 [aq]	-0.93
Nitroethane			2.47 [u]	-0.25		
1-Nitropropane						
2-Nitropropane					2.84 [ae]	0.54
Water	0.35 [au]	-4.29	0.26 [aw]	-4.38	0.37 [aw]	-4.27
Methanol	1.03 [ax]	-2.71	1.06 [a]	-2.68	1.50 [ay]	-2.24
Ethanol	1.58 [u]	-2.09	1.63 [a]	-2.04	1.80 [e,am]	-1.87
Propan-1-ol			2.24 [l]	-1.32		
Propan-2-ol					2.08 [e,am]	-1.40
Butan-1-ol			2.75 [bb]	-0.71	2.80 [e,am]	-0.66
2-Methylpropan-1-ol			2.60 [bb]	-0.7		
Butan-2-ol			2.47 [bb]	-0.92	2.59 [bc]	-0.80
2-Methylpropan-2-ol			2.19 [bb]	-1.09	2.24 [bc]	-1.04
Pentan-1-ol					3.37 [e,am]	0.02
Hexan-1-ol						
2-Methylpentan-3-ol			3.31 [be]	0.46		
Decan-1-ol						
Sulphur hexafluoride	0.04 [b]	2.27	0.35 [g]	2.58	0.09 [h]	2.32
Carbon disulphide			2.38 [a]		2.55 [bf]	
Hexamethylphosphotriamide						
Tetramethylsilane						
Tetraethylsilane						
Tetramethyltin					3.10 [e]	4.72
Tetraethyltin						
Mercury	1.81 [a]	1.35	1.60 [a]	1.14	2.05 [a]	1.59
Benzene	2.92 [r]	2.27	2.91 [l]	2.26	3.04 [ac,ae]	2.39
Toluene	3.42 [u]	2.84	3.40 [u]	2.82	3.58 [aq]	3.00
Hexafluorobenzene			2.75 [bj]			
Chlorobenzene						
Pyridine			3.10 [bc]	-0.34	3.23 [bm]	-0.21
2-Methylpyridine			3.44 [bc]	0.05		
3-Methylpyridine			3.64 [bc]	0.14		
4-Methylpyridine			3.63 [bc]	0.02		
2,6-Dimethylpyridine			3.88 [bc]	0.51		

[a] Solubility Data Project Series. [b] R. J. Wilcock, R. Battino, W. F. Danforth and E. Wilhelm, *J. Chem. Thermodyn.*, **10**, 817 (1978). [c] G. L. Pollack and J. F. Hinn, *J. Chem. Phys.*, **77**, 3221 (1982). [d] R. Battino, T. R. Rettich and T. Tominaga, *J. Phys. Chem. Ref. Data*, **12**, 163 (1983); **13**, 563 (1984). [e] M. H. Abraham, *J. Am. Chem. Soc.*, **104**, 2085 (1982). [f] R. G. Linford and D. G. T. Thornhill, *J. Appl. Chem. Biotech.*, **27**, 479 (1977). [g] E. Wilhelm and R. Battino, *Chem. Rev.*, **73**, 1 (1973). [h] R. L. Benoit and E. Milanova, *Can. J. Chem.*, **57**, 1319 (1979). [i] M. H. Abraham, P. L. Grellier and R. A. McGill, *J. Chem. Soc., Perkin Trans. 2*, 339 (1989). [j] W. Gerrard, *J. Appl. Chem. Biotechnol.*, **23**, 1 (1973). [k] R. Jadot, *J. Chim. Phys.*, 1036 (1972). [l] Interpolated value. [m] W. Hayduk and R. Castenada, *Can. J. Chem. Eng.*, **51**, 353 (1973). [n] Y. Miyano and W. Hayduk, *J. Chem. Eng. Data*, **31**, 77 (1986). [o] Using $\Phi^{\infty} = 1$. [p] J. H. Rytting, L. P. Huston and T. Higuchi, *J. Pharm. Sci.*, **67**, 615 (1978). [q] D. W. Arnold, R. A. Greenkorn and K. -C. Chao, *J. Chem. Eng. Data*, **27**, 123 (1982). [r] T. Hofstee, A. Kwantes and G. W. A. Rijnders, *International Sym. on Distillation*, Brighton, 1960. [s] E. R. Thomas, B. A. Newman, T. C. Long, D. A. Wood and C. A. Eckert, *J. Chem. Eng. Data*, **27**, 399 (1982). [t] R. E. Pecsar and J. J. Martin, *Anal. Chem*, **38**, 1661 (1966), from Φ^{∞} at 293K and 303K in 2,3,4-trimethylpentane. [u] J. H. Park, A. Hussam, P. Couasnan, D. Fritz and P. W. Carr, *Anal. Chem.*, **59**, 1970 (1987). [v] C. L. de Ligny and J. C. Van Houwelingen, *Fluid Phase Eq.*, **27**, 263 (1986). [w] T. M. Letcher and P. J. Jerman, *J. South Afr. Chem. Inst.*, **29**, 55 (1976). [x] A. Sahgal, H. M. La and W. Hayduk, *Canad. J. Chem. Eng.*, **56**, 354 (1978). [y] W. Hayduk and B. S. Minhas, *J. Chem. Eng. Data*, **32**, 285 (1987). [z] R. G. 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Soc., Perkin Trans 2*, 1717 (1988). [ak] M. H. Abraham and P. L. Grellier, *J. Chem. Soc., Perkin Trans 2*, 1737 (1976). [al] V. Dohnal and M. Novotna, *Fluid Phase Eq.*, **23**, 303 (1985). [am] D. M. Trampe and C. A. Eckert, *J.Chem. Eng. Data*, **35**, 156 (1990). [an] L. Lepori, E. Matteoli and B. Marongiu, *Fluid Phase. Eq.*, **42**, 229 (1988). [ao] K. A. Pividal and S. I. Sandler, *J. Chem. Eng. Data*, **33**, 438 (1988). [ap] H. Arm and D. Bánkay, *Helv. Chim. Acta.*, **52**, 279 (1969). [aq] J. Park, T. R. Rettich, R. Battino, D. Peterson and E. Wilhelm, *J. Chem. Eng. Data*, **27**, 324 (1982). [ar] E. Matteoli and L. Lepori, *J. Chem. Eng. Data*, **33**, 247 (1988). [as] S. Afrashehfar and G. C. B. Cave, *Can. J. Chem.*, **64**, 198 (1986). [at] R. Siedler and H. -J. Bittrich, *J. Prakt. Chem.*, **311**, 721 (1969). [au] W. F. Hoot, A. Azarnoosh and J. J. McKetta, *Petroleum Ref.*, **36**, 255 (1957). [av] P. Schatzberg, *J. Phys. Chem.*, **67**, 776 (1963). [aw] S. 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Acta*, **75**, 85 (1984). [bh] C. H. Deal and E. L. Derr, *Ind. Eng. Chem., Process Des. Dev.*, **3(4)**, 394 (1964). [bi] D. V. S. Jain, V. K. Gupta and B. S. Lark, *J. Chem. Therm.*, **5**, 451 (1973). [bj] J. Arancil, R. G. Rubro, M. Caceres, M. D. Pena and J. A. R. Renuncio, *J. Chem. Soc., Faraday Trans. 1*, **84**, 539 (1988). [bk] H. J. Paul, J. Krug and H. Knapp, *Fluid Phase Eq.*, **39**, 307 (1988). [bl] S. Warycha and J. H. Rytting, *J. Soln. Chem.*, **13**, 589 (1984). [bm] S. Malanowski, R. Patz, M. T. Ratzseh and C. Wohlfarth, *Fluid Phase Eq.*, **3**, 291 (1979).

The application of equations 28 and 35 are summarised in Table 16, and log L and log P values for methanol and ethanol are set out in Table 17.

Table 16. Characterisation of Methanol and Ethanol.

(A) Correlations of log L (gas ⇨ solvent) Using Equation 28.

	c	r	s	a	b	l	R	SD	N
Methanol	-0.059	0.304	0.823	3.753	1.717	0.778	0.9963	0.140	73
Ethanol	-0.004	0.033	0.738	3.662	1.295	0.838	0.9968	0.136	60

(B) Correlations of log P (water ⇨ solvent) Using Equation 35.

	c	r	s	a	b	v	R	SD	N
Methanol	0.302	0.694	-0.997	0.177	-3.048	3.517	0.9934	0.170	71[a]
Ethanol	0.205	0.575	-0.904	0.056	-3.530	3.829	0.9939	0.120	59[a]

[a] Less than the log L regression, as some log L_W values are not available

In equation 28, both alcohols are shown to be strong hydrogen bond bases, *a* = 3.75 for methanol, and 3.67 for ethanol, whilst being somewhat weaker hydrogen bond acids, *b* = 1.72 and 1.30 for methanol and ethanol respectively. Both alcohols are reasonably dipolar, and are weaker dispersion interactors than n-hexadecane. Equation 35 gives *s*-constants which show solute preference for water, which suggests that any dipolarity parameter, π^*_1, for water should be larger than π^*_1 for methanol and ethanol. This is the case[68], π^*_1 = 1.09 for water, and 0.60 and 0.54 for methanol and ethanol. The *a*-coefficients obtained for either alcohol are very small, which indicates that the alcohols are of about the same basicity as water and is quite contrary to the solvatochromic β_1 values of 0.18 for water and 0.62 and 0.77 for methanol and ethanol[68]. The *b*-coefficients are large, -3.05 for methanol and -3.53 for ethanol, showing hydrogen bond base solute preference for water, suggesting that water is more acidic than methanol or ethanol. (compare α_1 of 1.17 for water with α_1 of 0.93 and 0.83 for methanol and ethanol [68]). The *v*-coefficients show solute preference for the alcohols.

Table 17. Log L and Log P For Methanol and Ethanol

	log Lmeoh	log Pmeoh	log Letoh	log Petoh
Helium	-1.447[a]	0.58	-1.481[a]	0.55
Neon	-1.314[a]	0.64	-1.342[a]	0.62
Argon	-0.571[a]	0.90	-0.583[a]	0.88
Krypton	-0.264[b]	0.95	-0.210[b]	1.00
Xenon	0.319[c]	1.29	0.371[c]	1.34
Radon	0.684[a]	1.33	0.745[a]	1.39
Hydrogen	-1.015[a]	0.70	-1.066[a]	0.65
Oxygen	-0.603[d]	0.90	-0.614[e]	0.89
Nitrogen	-0.785[f]	1.01	-0.827[e]	0.97
Nitrous oxide	0.507[a]	0.74	0.449[a]	0.68
Carbon monoxide	-0.644[g]	0.99	-0.695[h]	0.93
Carbon dioxide	0.524[h]	0.60	0.424[h]	0.50
Methane	-0.27[g]	1.18	-0.278[g]	1.17
Ethane	0.37[g]	1.71	0.44[a]	1.78
Propane	0.83[g]	2.26	0.91[g]	2.35
n-Butane	1.27[g]	2.79	1.40[g]	2.92
2-Methylpropane	1.07[g]	2.77	1.20[g]	2.90
n-Pentane	1.54[g]	3.24	1.78[g,i]	3.48
2,2-Dimethylpropane	1.40[g]	3.24	1.61[g]	3.45
n-Hexane	2.09[g]	3.91	2.25[g,i]	4.07
n-Heptane	2.52[g]	4.48	2.72[g,i]	4.68
n-Octane	2.82[g,j]	4.93	3.20[i,j]	5.31
n-Nonane			3.51[i,j]	5.82
3,3-Diethylpentane	3.15[g]	4.78	3.49[g]	5.12
n-Decane			3.91[k]	6.23
Cyclopentane	1.92[g]	2.80	2.04[g]	2.92
Cyclohexane	2.43[g]	3.33	2.55[g]	3.45
Ethene	0.39[l]	1.33	0.41[h]	1.35
Ethyne	1.04[m]	1.03		
Dichloromethane	2.55[n]	1.59		
Trichloromethane			3.06[o]	2.27
Tetrachloromethane	2.70[p]	2.76	2.75[p]	2.81
2-Chloro-2-methylpropane	2.19[g]	2.99	2.22[g]	
1,1-Dichloroethene	2.16[q]	2.34	2.38[q]	2.56
Bromoethane			2.22[r]	1.68
2-Bromo-2-methylpropane	2.36[g]	2.98	2.49[g]	
Iodomethane	2.35[g]	1.69	2.19[s]	1.53
Iodoethane	2.62[g]	2.08	2.59[s]	2.05
2-Iodopropane			2.92[t]	2.58
1,2-Difluorotetrachloroethane	2.76[r]			
1,2-Dichlorotetrafluoroethane			2.87[r]	4.57
Diethylether	2.39[u]	1.22		
Methyl-t-butylether	2.77[v]			
Dioxan	3.56[w]	-0.14	3.44[g,j]	-0.26
Propionaldehyde	2.79[v]	0.27		
Butyraldehyde	3.18[x]	0.85		
Pentanal	3.57[v]	1.35		
Propanone	2.77[v]	-0.02	2.77[s,t]	-0.02
Butanone	3.31[j,y]	0.59	3.16[g,j]	0.44
Pentan-2-one	3.43[v]	0.85		
Hexan-2-one	3.82[v]	1.41		
Heptan-2-one	4.38[v,z]	2.33		
Heptan-3-one	4.26[z]	2.12		
Heptan-4-one	4.23[z]	2.09		
Methyl acetate	2.92[v]	0.62		
Methyl propanoate	3.17[v,aa]	1.02	3.04[aa]	0.89
Methyl butanoate	3.55[v]	1.47		
Methyl pentanoate	3.91[v]	2.03		
Methyl hexanoate	4.28[v]	2.45		
Acetonitrile	2.81[ab]	-0.04	2.90[ac,ad]	0.05
Ammonia	2.26[a]	-0.89	2.01[a]	-1.14
Dimethylamine	2.57[a]	-0.58	2.40[a]	-0.75
Diethylamine	3.73[ae]	0.74		
Trimethylamine	2.85[g]	0.50	2.67[af]	0.32
Triethylamine	3.84[g]	1.48	3.57[ag]	1.21
Tri-n-propylamine			4.10[t]	
Nitromethane	3.35[j,n,y]	0.40	3.12[g,j,n]	0.17
Water	4.07[ah]	-0.57	3.72[ah]	-0.92
Methanol	3.55[ai]	-0.19	3.40[aj]	-0.34
Ethanol	3.89[ai]	0.22	3.73[ai]	0.06
Propan-1-ol	4.36[ai]	0.80	4.20[ak]	0.64
Propan-2-ol			3.86[ak]	0.38

Table 17 (cont). Log L and Log P For Methanol and Ethanol

	log Lmeoh	log Pmeoh	log Letoh	log Petoh
Ethanthiol	2.20 [al]	1.36		
Dimethylsulphoxide	6.52 [w]			
Carbon disulphide			2.27 [o]	
Tetramethylsilane	1.47 [g]	3.70		
Tetraethylsilane	3.30 [g]	5.33	3.62 [g]	5.65
Tetramethyltin	2.13 [g]	3.75	2.28 [g]	3.90
Tetraethyltin	3.90 [g]	5.72	4.13 [g]	5.95
Mercury	1.43 [a]	0.97		
Benzene	2.79 [g]	2.14	2.78 [am]	2.13
Toluene	3.20 [j,y]	2.62	3.28 [j]	2.70
p-Xylene			3.73 [an]	3.19
Chlorobenzene	3.67 [ao]	2.83	3.68 [n,t]	2.84
Benzyl chloride			4.63 [g]	3.22
Benzyl bromide			4.85 [g]	3.11
Pyridine	4.40 [ap]	0.96	4.18 [g,t]	0.74
2-Methylpyridine	4.78 [ap]	1.39		
2,6-Dimethylpyridine	5.05 [ap]	1.68		

[a] Solubility Data Project Series. [b] V. N. Prorokov, V. V. Dolatov and G. A. Krestov, *Zhur. Fiz. Khim.*, **58**, 1888 [Eng. 1153] (1984). [c] G. L. Pollack, J. F. Hinn and J. J. Enyeart, *J. Chem. Phys.*, **81**, 3239 (1984). [d] Y. Miyano and W. Hayduk, *J. Chem. Eng. Data*, **31**, 77 (1986). [e] R. Battino, T. R. Rettich and T. Tominaga, *J. Phys. Chem. Ref. Data*, **12**, 163 (1983); **13**, 563 (1984). [f] I. Endler, G. Hradetzky and H. -J. Bittrich, *J. Prakt. Chem.*, **327**, 693 (1985). [g] M. H. Abraham and P. L. Grellier, *J. Chem. Soc., Perkin Trans* 2, 1856 (1975); M. H. Abraham, P. L. Grellier and R. A. McGill, *J. Chem. Soc., Perkin Trans* 2, 339 (1988). [h] E. Wilhelm and R. Battino, *Chem. Rev.*, **73**, 1 (1973). [i] L. Cori and P. Deloga, *Fluid Phase Eq.*, **27**, 103 (1986). [j] J. H. Park, A. Hussam, P. Cousasnun, D. Fritz and P. W. Carr, *Anal. Chem.*, **59**, 1970 (1987). [k] C. J. Pierotti, C. H. Deal and E. L. Durr, *Ind. Eng. Chem.*, **51**, 95 (1959). [l] S. Zeck and H. Knapp, *fluid Phase Eq.*, **20**, 37 (1986). [m] Y. Miyano and W. Hayduk, *Canad. J. Chem. Eng.*, **59**, 746 (1981). [n] J. R. Kharma, O. Mutha, S. Munjal and B. D. Smith, *J. Chem. Eng. Data*, **28**, 110, 113, 119, 412 (1983). [o] I. M. Barclay and J. A. V. Butler, *Trans. Faraday Soc.*, 34, 1445 (1938). [p] E. Matteoli and L. Lepori, *J. Chem. Thermodyn.*, 18, 1065 (1986). [q] A. Kovac, J. Svoboda and L. Ondrus, *Chem. Zvesti*, 39, 729 (1985). [r] V. Dohnal and M. Novotna, *Fluid Phase Eq.*, **23**, 303 (1985). [s] E. R. Thomas, B. A. Newman, T. C. Long, D. A. Wood and C. A. Eckert, *J. Chem. Eng. Data*, **27**, 399 (1982). [t] E. R. Thomas, B. A. Newman, G. L. Nicolaides and C. A. Eckert, *J. Chem. Eng. Data*, **27**, 233 (1982). [u] R. Srivasteva, G. Natarajan and B. D. Smith, *J. Chem. Eng. Data*, **31**, 89 (1986); R. Srivasteva and B. D. Smith, idem p.94. [v] R. A. Djerki and R. J. Laub, *J. Liq. Chromatog.*, **11**, 585 (1988). [w] K. Quitzch, H. Ulbrecht and G. Geiseler, *Z. Phys. Chem.*, **234**, 33 (1967). [x] Interpolated value. [y] D. M. Trampe and C. A. Eckert, *J. Chem. Eng. Data*, **35**, 156 (1990). [z] R. G. Rubin, J. A. R. Renuncio and M. D. Pena, *J. Chem. Thermodyn.*, 15, 779 (1983). [aa] J. Polak and B. C. -Y. Lu, *J. Chem. Eng. Data*, 17, 457 (1972). [ab] B. G. Cox, A. J. Parker and W. E. Waghorne, *J. Am. Chem. Soc.*, **95**, 1010 (1973). [ac] V. Dohnal, F. Vesely, R. Hobab and J. Pick, *Coll. Czech. Chem. Comm.*, **47**, 3177 (1982). [ad] O. Muthu, P. J. Maher and B. D. Smith, *J. Chem. Eng. Data*, **25**, 163 (1980). [ae] Activity coefficient (no temperature given) quoted by K. Nakanishi, R. Toba and H. Shirai, *J. Chem. Eng. Japan*, **2(1)**, 4 (1969). [af] M. H. Abraham, *J. Chem. Soc. (B)*, 299 (1971). [ag] M. H. Abraham and P. L. Grellier, *J. Chem. Soc., Perkin Trans.* 2, 1735 (1976). [ah] J. A. V. Butler, D. W. Thomson and W. H. Maclennan, *J. Chem. Soc.*, 674 (1933). [ai] From $\Phi^{\infty} = 1$. [aj] A. C. Morris, L. T. Munn and G. Anderson, *Canad. J. Research*, **20B**, 207 (1942). [ak] G. S. Parks and K. K. Kelly, *J. Phys. Chem.*, **29**, 727 (1925). [al] P. W. Rousseau and J. Y. Kim, AICHE Symposium, **83**, 42 (1987). [am] S. -C. Hwang and R. L. Robinson, *J. Chem. Eng. Data*, **22**, 319 (1977). [an] R. H. Stokes and H. T. French, *J. Chem. Soc., Faraday Trans. 1*, **76**, 537 (1980). [ao] P. J. Maher and B. D. Smith, *J. Chem. Eng. Data*, **24**, 363 (1979). [ap] C. H. Rochester and J. A. Waters, *J. Chem. Soc., Faraday Trans. 1*, **78**, 631 (1982).

BUTANONE

Log L and log P values for butanone are set out in Table 18. Application of equation 28 to log L (gas ⇨ butanone) yields the relationship,

$$\text{Log L} = 0.171 - 0.453R_2 + 1.694\pi^H_2 + 2.699\Sigma\alpha^H_2 + 0.891\log L^{16} \quad [38]$$
$$R = 0.9898 \quad SD = 0.134 \quad N = 34$$

Equation 35 applied to log P (water ⇨ solvent) on butanone gives equation 39.

$$\log P = 0.354 + 0.003R_2 - 0.164\pi^H_2 - 0.979\Sigma\alpha^H_2 - 4.706\Sigma\beta^H_2 + 4.160V_X \quad [39]$$
$$R = 0.9985 \quad SD = 0.115 \quad N^+ = 32$$

Equation 38 shows butanone to be a solvent of moderate dipolarity (s = 1.70), and a medium to strong hydrogen bond base (a = 2.70). As is required on chemical grounds, no statistically significant coefficient in b is generated, as of course, butanone can have no hydrogen bond acidity at all. Butanone is a medium dispersion interactor, somewhat less so than n-hexadecane. V_X in equation 39 favours solute partition to butanone, but all other coefficients of significance favour partition to water, especially solute basicity. Again this is chemically sensible, as water is a hydrogen bond acid, and butanone is not.

WATER

Extensive data in log L_W (gas ⇨ water) is available[66], and this was analysed using equation 28.

$$\text{Log } L_W \text{ (gas} \Rightarrow \text{water)} = -1.217 + 0.743R_2 + 2.729\pi^H_2 + 3.984\Sigma\alpha^H_2 + 4.781\Sigma\beta^H_2 - 0.210\log L^{16} \quad [40]$$
$$R = 0.9895 \quad SD = 0.238 \quad N = 256$$

None of these coefficients are unexpected. The s-coefficient at 2.729 shows water solvent to be of medium to high dipolarity. With a = 3.984 and b = 4.781, while water is both a hydrogen bond acid and base, its hydrogen bond acid strength is the greater of the two. Abraham *et. al.*[68] list β_1 for water of 0.18, and α_1 of 1.17. The coefficients from equation 106 suggest there is a difference between the hydrogen bond acid and base strength of water, but not of the large magnitude previously found [68].

[+] Less than regression in log L, as some log L_W values not available.

Table 18. Log L and Log P For Butanone

	log L	log P
Oxygen	-0.562 [a]	0.95
n-Butane	1.70 [b]	3.25
n-Pentane	2.06 [c.d,e]	3.76
n-Hexane	2.53 [c,d]	4.35
n-Heptane	3.01 [c,e]	4.97
n-Octane	3.42 [c,f]	5.53
n-Decane	4.40 [e]	6.72
Cyclohexane	2.79 [e]	3.69
Methylcyclohexane	3.02 [g]	4.27
Pent-1-ene	2.11 [d]	3.34
3-Methylbut-1-ene	1.99 [d]	3.33
2-Methylbuta-1,3-diene	2.41 [d]	2.91
Dichloromethane	2.98 [d]	2.02
Tetrachloromethane	3.07 [d]	3.13
1,2-Dichloroethane	3.55 [g]	2.24
1-Chloropropane	2.72 [d]	2.48
Bromoethane	2.60 [d,g]	2.06
Iodomethane	2.56 [d]	1.90
Iodoethane	3.01 [d]	2.47
1,2-Difluorotetrachloroethane	3.31 [h]	
Dioxan	3.68 [f]	-0.03
Propanone	2.94 [d]	0.15
Butanone	3.36 [i]	0.64
Ethyl acetate	3.29 [g]	1.13
Acetonitrile	3.25 [g]	0.40
Nitromethane	3.66 [g]	0.71
Water	3.04 [j]	-1.60
Methanol	2.81 [g]	-0.93
Ethanol	3.17 [f]	-0.50
2,2,2-Trifluoroethanol	4.29 [k]	1.14
Carbon disulphide	2.29 [d]	
Benzene	3.29 [e]	2.64
Toluene	3.73 [f]	3.15
Ethylbenzene	4.09 [e]	3.61

[a] R. Battino, T. R. Rettich and T. Tominaga, *J. Phys. Chem. Ref. Data,* **12**, 163 (1983). [b] Solubility Data Project Series. [c] M. H. Abraham, *J. Am. Chem. Soc.*, **104**, 2085 (1982). [d] E. R. Thomas, B. A. Newman, T. C. Long, D. A. Wood and C. A. Eckert, *J. Chem. Eng. DAta,* **27**, 399 (1982). [e] G. J. Pierotti, C. H. Deal and E. L. Durr, *Ind. Eng. Chem.*, **51**, 95 (1959). [f] J. H. Park, A. Hussam, P. Couasnon, D. Fritz and P. W. Carr, *Anal. Chem.*, **59**, 1970 (1987). [g] E. R. Thomas, B. A. Newman, G. L. Nicolaides and C. A. Eckert, *J. Chem. Eng. Data,* **27**, 233 (1982). [h] V. Dohnal and M. Novotna, *Fluid Phase Eq.*, **23**, 303 (1985). [i] Taking $\Phi^{\infty} = 1$. [j] K. Tochigi and K. Kojima, *J. Chem. Eng. Japan,* **9**, 267 (1976). [k] This work by headspace analysis.

Water is the only solvent characterised with a negative *l*-coefficient, -0.210, indicating that the exoergic solvent-solute dispersion interactions set up in the dissolution of the solute do not compensate for, or exceed the energy required for the endoergic formation of a cavity in the solvent. This again is not surprising, considering the very extensive self-association of water because of its high degree of inter-molecular hydrogen bonding and dipolar interactions.

As can be seen, the application of equation 28 can usefully characterise common solvents in terms of the solvation parameters. The analysis of log P (water ⇨ solvent) via equation 35 in the cases of the amides, methanol, ethanol and butanone is a 'hypothetical' or 'theoretical' procedure, as water and these solvents are in fact completely miscible in all proportions. However, application of equation 35 to log P (water ⇨ solvent) values for these solvents can still usefully characterise them, as in effect, equation 35 will compare the solvents to water in terms of the solvation parameters. The alkanes are to all extents and purposes insoluble in water, so equation 35 provides information about a 'real' partition process between water and alkane. This partition process is akin to that in biological membranes[64], between water and a phospholipid layer. The correlations of all the solvents studied using equations 28 and 35 are summarised for ease of comparison in Table 19.

Table 19. Summary of Solvent Characterisation

(A) Correlations of log L (gas ⇨ solvent) Using Equation 28.

	c	r	s	a	b	l	R	SD	N
DMA	-0.03	0.14	2.02	5.07	-	0.787	0.9987	0.063	28
NMP	-0.31	0.35	2.10	4.98	-	0.838	0.9969	0.107	61
DMF	-0.24	0.08	2.26	4.36	-	0.827	0.9929	0.159	55
NFM	-0.44	0.01	2.57	4.32	-	0.730	0.9955	0.069	45
Pentane	0.38	-0.13	-0.23	-	-	0.969	0.9989	0.071	30
Hexane	0.31	-0.13	-0.15	-	-	0.978	0.9977	0.098	83
Heptane	0.28	-0.19	-0.27	-	-	1.032	0.9991	0.093	78
Octane	0.24	-0.10	-0.16	-	-	0.988	0.9990	0.062	59
Decane	0.17	-0.10	-0.07	-	-	0.993	0.9995	0.053	40
Hexadecane [a]	0	0	0	0	0	1	-	-	-
Isooctane	0.28	-0.14	-0.13	-	-	0.977	0.9983	0.078	63
Cyclohexane	0.21	-0.02	-0.04	-	-	1.031	0.9983	0.090	71
Methanol	-0.06	0.30	0.82	3.75	1.73	0.778	0.9963	0.140	73
Ethanol	0	0.03	0.738	3.66	1.30	0.838	0.9968	0.136	60
Butanone	0.17	-0.45	1.69	2.70	-	0.891	0.9898	0.134	34
Water	-1.22	0.74	2.73	3.98	4.78	-0.210	0.9895	0.238	256

[a] By definition.

(B) Correlations of log P (water ⇨ solvent) Using Equation 35.

	c	r	s	a	b	v	R	SD	N
DMA	0.14	0.53	0.03	0.88	-4.59	3.94	0.9960	0.120	26
NMP	-0.02	0.88	0.21	1.31	-4.89	3.86	0.9958	0.146	55
DMF	0.02	0.56	0.39	0.59	-4.79	3.85	0.9924	0.193	51
NFM	0.02	0.46	0.39	0.42	-4.71	3.39	0.9977	0.115	40
Pentane	0.34	0.15	-1.48	-3.42	-5.30	4.63	0.9989	0.108	30
Hexane	0.37	0.04	-1.70	-3.41	-5.03	4.36	0.9971	0.175	81
Heptane	0.27	0.56	-1.77	-3.44	-5.03	4.59	0.9980	0.120	76
Octane	0.21	0.57	-1.75	-3.22	-4.95	4.56	0.9978	0.132	58
Decane	0.10	0.45	-1.50	-3.42	-4.94	4.68	0.9989	0.118	40
Hexadecane	0.08	0.89	-1.77	-3.60	-4.81	4.42	0.9965	0.158	256
Isooctane	0.27	0.34	-1.58	-3.44	-5.15	4.53	0.9982	0.125	62
Cyclohexane	0.16	0.85	-1.75	-3.41	-4.77	4.68	0.9967	0.167	66
Methanol	0.30	0.69	-1.00	0.18	-3.05	3.52	0.9934	0.170	71
Ethanol	0.21	0.58	-0.90	0.06	-3.53	3.83	0.9939	0.210	59
Butanone	0.35	0.00	-0.16	-0.98	-4.71	4.16	0.9985	0.115	32

The generation of coefficients from equation 28 and 35 also provides the opportunity to assess the validity of solvent parameters [68] π^*_1, β_1, and α_1, by comparison with coefficents *s*, *a* and *b* respectively, Table 20.

Table 20. Comparison of Coefficients *S*, *A*, and *B* With Solvent Parameters π^*_1, β_1 and α_1.

(A) Comparison of Coefficents From Equation 28.

Solvent	*s*	π^*_1	*a*	β_1	*b*	α_1
Alkanes	≈0	0	(0)	0	(0)	0
DMA	2.02	0.88	5.07	0.76	(0)	0
NMP	2.10	0.92	4.98	0.77	(0)	0
DMF	2.26	0.88	4.36	0.69	(0)	0
NFM	2.57	-	4.32	-	(0)	0
Methanol	0.82	0.60	3.75	0.62	1.73	0.93
Ethanol	0.74	0.54	3.66	0.77	1.30	0.83
Butanone	1.69	0.67	2.70	0.48	(0)	0
Water	2.73	1.09	3.98	0.18	4.78	1.17

(B) Comparison of Coefficients From Equation 35.

Solvent	s	π^*_1	a	β_1	b	α_1
n-Alkanes (av.)	-1.66	0	-3.42	0	-5.01	0
DMA	0.03	0.88	0.88	0.76	-4.59	0
NMP	0.21	0.92	1.31	0.77	-4.89	0
DMF	0.39	0.88	0.59	0.69	-4.79	0
NFM	0.39	-	0.42	-	-4.71	0
Methanol	-1.00	0.60	0.18	0.62	-3.05	0.93
Ethanol	-0.90	0.54	0.06	0.77	-3.53	0.83
Butanone	-0.16	0.67	-0.98	0.48	-4.71	0
Water	0	1.09	0	0.18	0	1.17

There are sufficient data points in s and π^*_1, and a and β_1 to generate informative XY-plots. The s-coefficients in log L and log P can be plotted against the solvent parameter π^*_1, Figure 1, and the a-coefficient in log L and log P similarly plotted against β_1, Figure 2.

S-coefficients for amides for the log L (gas ⇨ solvent) process, Table 20(a), show that amides are all a bit less dipolar than water, and that methanol and ethanol are much less dipolar than either amides or water, see also Figure 1. However, s-coefficients for the log P (water ⇨ solvent) process, Table 20(b), suggest amides are rather *more* dipolar than water, although again, methanol and ethanol are quite a bit less dipolar than water, Figure 1. There is in general reasonable agreement between the s-coefficient and π^*_1 .

Amide a-coefficients for the log L (gas ⇨ solvent) and log P (water ⇨ solvent) process show they are more basic than water. From log L (gas ⇨ solvent), methanol and ethanol are slightly less basic than water, but a-coefficients from log P (water ⇨ solvent) suggest methanol and ethanol are very slightly more basic than water. The β_1 = 0.18 for water is very considerably out of line with the other coefficients for either process, see Figure 2, suggesting β_1 for water to be far too low. A more reasonable value would seem to be no less than around 0.65 units.

The b-coefficients for methanol and ethanol for log L (gas ⇨ solvent) are considerably less than for water, showing some agreement here with the α_1 values. Again, b-coefficients for log P (water ⇨ solvent) for methanol and ethanol, Table 20(b), show they are considerably less acidic than water. The b-coefficients for amides and butanone are quite near those of the alkanes, as would be expected since these solvents have no hydrogen bond acidity at all.

Figure 1. Plot of S in Log L and Log P against Π*1

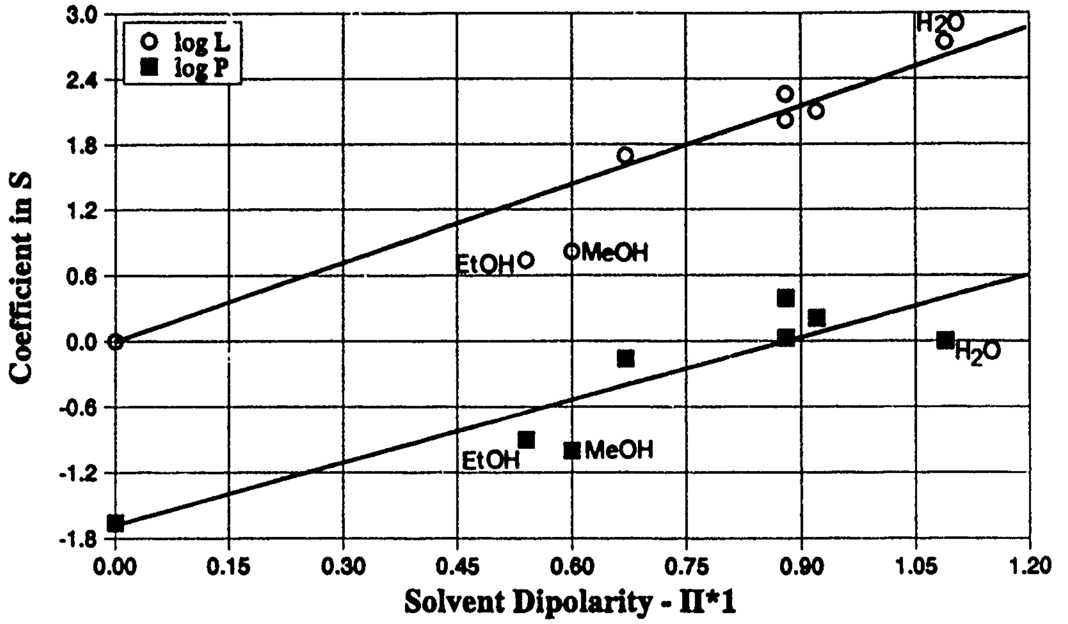
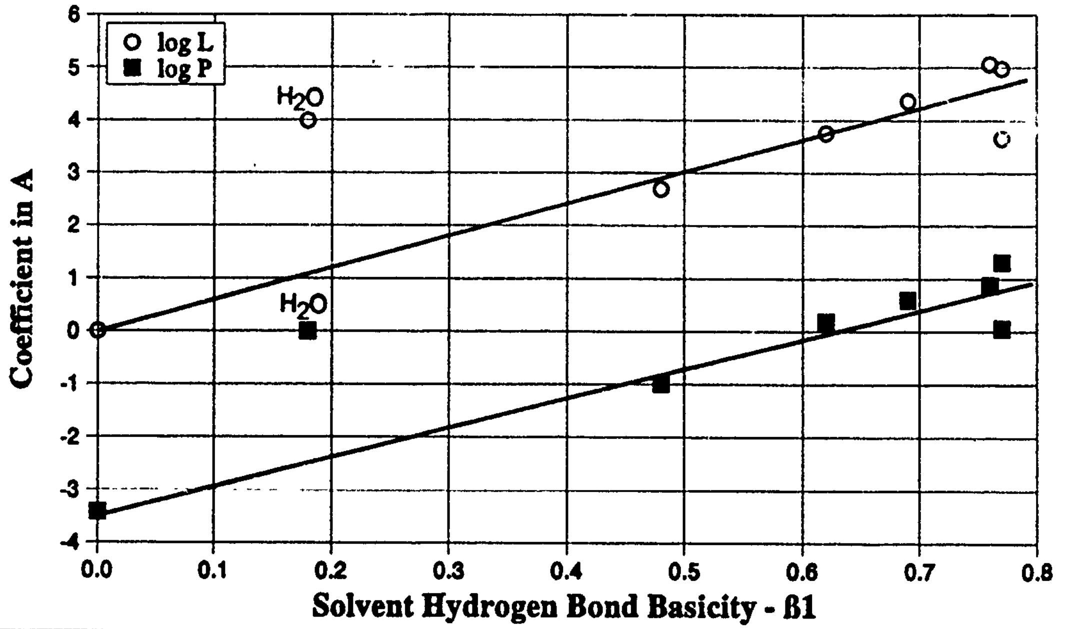


Figure 2. Plot of A in Log L and Log P against ß1



APPLICATION OF THE NEW SOLUTE PARAMETERS TO CHARACTERISATION OF THE GLC PHASES STUDIED BY POOLE *et. al*[69]

There have been a number of interesting new developments in recent years on the characterisation of gas-liquid chromatographic (GLC) stationary phases. Poole and his co-workers[70,71] have pointed out several deficiences in the McReynolds system of classification, and have suggested that the use of McReynolds numbers be abandoned. Following several other workers[72-74], Poole suggested that the Gibbs energy of solvation of a gaseous methylene increment into a stationary phase, $\Delta G_S°(CH_2)$, could be used as a measure of the `polarity' of the phase[70,71]. More recently, Poole[69,75] defined a solvent strength parameter, SSP, as SSP = $\Delta G_S°(CH_2)/\rho_1$ where ρ_1 is the density of the stationary phase at the column temperature. Although $\Delta G_S°(CH_2)$, or alternatively SSP, might well be the best "single parameter" that can be used to classify stationary phases, it cannot possibly reflect the various solute/solvent interactions that determine the retention of a solute by a given stationary phase. The use of various test solutes as probes cannot be used to identify such interactions either, because there are no test solutes that possess, for example, a singular quality of "polarity" without also possessing some other quality. Thus a test solute such as l-nitropropane, although certainly dipolar, is also quite basic, whereas a test solute like butan-l-ol is acidic, basic, and dipolar! Poole[71,69,75] recognised this difficulty, although no easy solution to the problem seemed to be available.

It has already been shown how solvation equations can be used to characterise stationary phases in the McReynolds and Laffort series[46,51], and how retention data in these two series may then be used to obtain π^H_2 and $\Sigma\alpha^H_2$ solute parameters. Since these two activities are interdependent, it seems obligatory to test equation 28 with a quite independent set of retention data.

$$\log SP = c + rR_2 + s\pi^H_2 + a\Sigma\alpha^H_2 + b\Sigma\beta^H_2 + l\log L^{16} \qquad [28]$$

The retention data, as log K values, obtained by Poole and his colleagues[69] on 24 stationary phases at 121.4°C can be used as a first test for solvation equation 28. There are two main reasons for this choice. Firstly, the data obtained by Poole[69] is amongst the most reliable GLC data ever reported, with considerable care being taken to exclude contributions from interfacial adsorption. Secondly, the stationary phases studied by Poole include seven molten salts, and it is of some interest to analyse results on these novel stationary phases using the general solvation equation 28.

The stationary phases used by Poole are shown in Table 21, together with $\Delta G_S°(CH_2)$

and SSP values given by Poole[69]. Solute parameters were all taken from Table 8; for convenience they are set out in Table 22.

Note that not all solutes were examined on all phases, so that for any particular phase the number of solutes studied (N) is less than 42. When equation 28 was first applied to the Poole data set, it was noted that one of the Poole solutes, oct-1-yne, was always out of line, and consistently behaved in a manner more expected of oct-2-yne. On contacting Professor Poole over this problem, it was gratifying to receive confirmation that compound oct-l-yne in the Poole data set was indeed oct-2-yne[76]. Hence, oct-2-yne is listed in Table 22 .

For each stationary phase, regression coefficients were generated using exactly the solutes studied by Poole[69]. Of the 24 phases with an average of some 35 solutes each, only one data point was excluded. The result for 2,6- dimethylaniline on phase V was out-of-line by over four standard deviations, with log K(obs) = 2.947 and log K(calc) = 3.416 units.

Table 21. The Stationary Phases Examined by Poole at 121.4°C.

Code	Stationary phase	ΔGS°(CH2)	SSP
A	Squalane	-530	-728
B	SE-30	-463	-578
C	OV-3	-458	-523
D	OV-7	-467	-504
E	OV-11	-475	-478
F	OV-17	-470	-463
G	OV-22	-458	-439
H	OV-25	-431	-396
I	OV-105, poly (cyanopropylmethyl dimethylsiloxane)	-461	-523
J	OV-225, poly (cyanopropylmethyl phenyl methylsiloxane)	-418	-410
K	OV-275, poly (dicyanoallylsiloxane)	-265	-243
L	OV-330, a poly (dimethylsiloxane)-carbowax copolymer	-418	-407
M	Poly (trifluoropropylmethylsiloxane), QF-1	-393	-337
O	Carbowax 20M	-400	-387
P	Poly (diethyleneglycol succinate), DEGS	-324	-275
Q	1,2,3-Tris(2-cyanoethoxy)propane, TCEP	-280	-273
R	Poly (phenylether) five rings, PPE-5	-487	-436
S	Tetraethylammonium 4-toluenesulphonate	-286	-267
T	Tributylammonium 4-toluenesulphonate	-384	-384
U	Tetrabutylammonium 4-toluenesulphonate	-377	-377
V	Tetrabutylammonium picrate	-411	-381
W	Tetrabutylammonium methanesulphonate	-398	-406
X	Tetrabutylammonium N-(2-acetamido)-2-aminoethanesulphonate	-319	-312
Y	Tetrabutylammonium 3-[tris(hydroxymethyl) methylamino]-2-hydroxy-1-propanesulphonate	-290	-276

As a necessary preliminary, the full equation 28 was applied to all 24 phases, and it was found that is no case was the *b*-coefficient statistically significant as judged by the t-test. The simpler equation, equation 41, can then be used. The solute parameters used in regression equation 41 follow, Table 22.

$$\log K = c + rR_2 + s\pi^H_2 + a\Sigma\alpha^H_2 + l\log L^{16} \qquad [41]$$

Table 22. Solute Parameters Used In The Regression Equation 41.

Solute	R_2	π^H_2	$\Sigma\alpha^H_2$	$\log L^{16}$
n-Heptane	0.000	0.00	0.00	3.173
n-Octane	0.000	0.00	0.00	3.677
n-Nonane	0.000	0.00	0.00	4.182
n-Decane	0.000	0.00	0.00	4.686
n-Undecane	0.000	0.00	0.00	5.191
n-Dodecane	0.000	0.00	0.00	5.696
n-Tridecane	0.000	0.00	0.00	6.200
n-Tetradecane	0.000	0.00	0.00	6.705
n-Pentadecane	0.000	0.00	0.00	7.209
n-Hexadecane	0.000	0.00	0.00	7.714
Butanone	0.166	0.70	0.00	2.287
Pentan-2-one	0.143	0.68	0.00	2.755
Hexan-2-one	0.136	0.68	0.00	3.262
Heptan-2-one	0.123	0.68	0.00	3.760
Octan-2-one	0.108	0.68	0.00	4.257
Nonan-2-one	0.119	0.68	0.00	4.735
Benzene	0.610	0.52	0.00	2.803
n-Butylbenzene	0.600	0.52	0.00	4.686
cis-Hydrindane	0.439	0.20	0.00	4.610
Oct-2-yne	0.225	0.30	0.00	3.850
Dodec-1-yne	0.133	0.23	0.13	5.657
Butan-1-ol	0.224	0.42	0.37	2.601
2-Methylpentan-2-ol	0.169	0.30	0.31	3.081
Dodecafluoroheptan-1-ol	-0.640	0.55	0.60	3.089
Octan-1-ol	0.199	0.42	0.37	4.619
Phenol	0.805	0.88	0.60	3.897
2,4,6-Trimethylphenol	0.860	0.83	0.37	5.185
Benzonitrile	0.742	1.07	0.00	4.004
1-Nitropropane	0.242	0.95	0.02	2.894
1-Nitropentane	0.210	0.95	0.00	3.938
Nitrobenzene	0.871	1.10	0.00	4.511
1,1,1,2-Tetrachlorethane	0.542	0.63	0.10	3.641
Pyridine	0.631	0.82	0.00	3.003
2,4,6-Trimethylpyridine	0.634	0.72	0.00	4.200
Aniline	0.955	0.96	0.26	3.993
N-Methylaniline	0.948	0.94	0.17	4.494
N,N-Dimethylaniline	0.957	0.82	0.00	4.754
2,6-Dimethylaniline	0.967	0.93	0.20	5.037
Dioxan	0.329	0.75	0.00	2.892
Methylphenylether	0.708	0.73	0.00	3.859
Di-n-hexylether	0.000	0.25	0.00	5.938
Benzodioxan	0.874	1.01	0.00	4.985
Nonanal	0.150	0.65	0.00	4.900

Results of application of equation 41 to all 24 phases are summarised in Table 23, As judged by the values of S.D. and R, the regression equations for the 24 phases are of excellent quality. Most values of S.D. are below 0.08 log units, and in the case of the four phases with S.D. larger than 0.08, viz. P, U, W, and X, errors in log K quoted by Poole[69] are much larger than for the other phases. It can therefore be concluded that the solvation parameters obtained previously, can, indeed, be used to characterise other GLC stationary phases. Whether such characterisation is useful or not, will depend at least in part on whether the characteristic constants r, s, a, and l in equation 41 make general chemical sense.

Table 23. Regression Equations For The Phases In Table 21.

Code	*c*	*r*	*s*	*a*	*l*	SD	R	N
A	-0.202	0.125	0.018	-0.097	0.581	0.033	0.9985	39
B	-0.194	0.024	0.190	0.125	0.498	0.022	0.9989	39
C	-0.181	0.033	0.328	0.152	0.503	0.021	0.9992	39
D	-0.231	0.056	0.433	0.165	0.510	0.025	0.9989	39
E	-0.303	0.097	0.544	0.174	0.516	0.029	0.9985	39
F	-0.326	0.128	0.612	0.147	0.509	0.036	0.9978	38
G	-0.328	0.201	0.664	0.190	0.489	0.034	0.9979	38
H	-0.273	0.277	0.644	0.182	0.472	0.042	0.9973	39
I	-0.212	-0.038	0.395	0.368	0.499	0.026	0.9987	39
J	-0.509	0.015	1.214	0.964	0.462	0.035	0.9979	39
K	-0.635	0.388	1.902	1.644	0.241	0.080	0.9935	32
L	-0.430	0.104	1.056	1.419	0.481	0.051	0.9954	36
M	-0.251	-0.362	1.101	0.054	0.416	0.077	0.9853	39
O	-0.558	0.285	1.292	1.803	0.450	0.059	0.9957	39
P	-0.498	0.351	1.683	1.718	0.311	0.096	0.9899	38
Q	-0.489	0.278	1.913	1.679	0.290	0.056	0.9972	40
R	-0.395	0.230	0.829	0.337	0.527	0.044	0.9972	39
S	-1.008	0.362	2.059	3.609	0.340	0.076	0.9941	29
T	-0.717	0.110	1.546	2.917	0.466	0.069	0.9922	30
U	-0.617	0.009	1.659	3.360	0.440	0.106	0.9885	34
V	-0.542	0.100	1.557	1.424	0.445	0.061	0.9935	36[a]
W	-0.631	0.095	1.595	3.408	0.437	0.097	0.9895	34
X	-0.666	0.283	1.809	3.417	0.329	0.100	0.9902	34
Y	-0.690	0.281	1.821	2.859	0.305	0.080	0.9932	29

[a] Excluding solute 2,6-dimethylaniline that is out by over four standard deviations, calc. log K = 3.416, obs. log K = 2.947

The $r.R_2$ term generally makes only a minor contribution, but nevertheless the r-constant seems well-behaved. Phases with a substantial proportion of phenyl groups lead to an increase in the r-constant, as expected if this is an index of π- and n-electron pair interaction. Thus along the OV series of poly (methylphenylsiloxane), the r-constant increases as the % phenyl group increases. The only substantially negative value of the r-constant, with phase M, corresponds to the only phase that contains fluorine, again as expected.

More important is the $s.\pi^H_2$ term in which the *s*-constant reflects dipole/dipole and dipole/induced dipole interactions, and so may be taken as a measure of stationary phase dipolarity. Of the conventional phases, phase K (OV-275), P(DEGS), and Q(TCEP) have the largest *s*-constants of around 1.7-1.9 units. The ionic salts (S - Y) all have *s*-constants that approach or equal those for the most dipolar conventional phases, and which are very much larger than the unsubstituted poly (methylphenylsiloxane) phases (C - H). The SSP parameter, see Table 21, is very nearly the same, however, for phase H as for phases (T - W).

All the phases in Tables 21 and 23, other than Squalane (A), are hydrogen bond bases and so give rise to significant values of the *a*-constant. Of the conventional phases K, L, O, P, and Q are the most basic, and hence will preferentially interact with solutes that are hydrogen bond acids. But all the ionic salts except phase V are significantly stronger hydrogen bond bases than any of the conventional phases. This is clearly due to the negatively charged counter-anions. It is not coincidental that where charge dispersion in the anion is very large, as with phase V, the *a*-constant decreases considerably.

The *l*-constant, on its own, is equivalent to $\Delta G_S°(CH_2)$ in that both quantities describe the ability of a phase to separate adjacent members of an homologous series. For the 24 phases, a regression of $\Delta G_S°(CH_2)$ against *l* gives,

$$\Delta G_S°(CH_2) = -44.9 - 816l \qquad [42]$$

with S.D. = 17 cal mol^{-1}, R = 0.9739, and N = 24. Thus general solvation equations 28 or 41, includes, via the *l*-constant, all the information contained in $\Delta G_S°(CH_2)$.

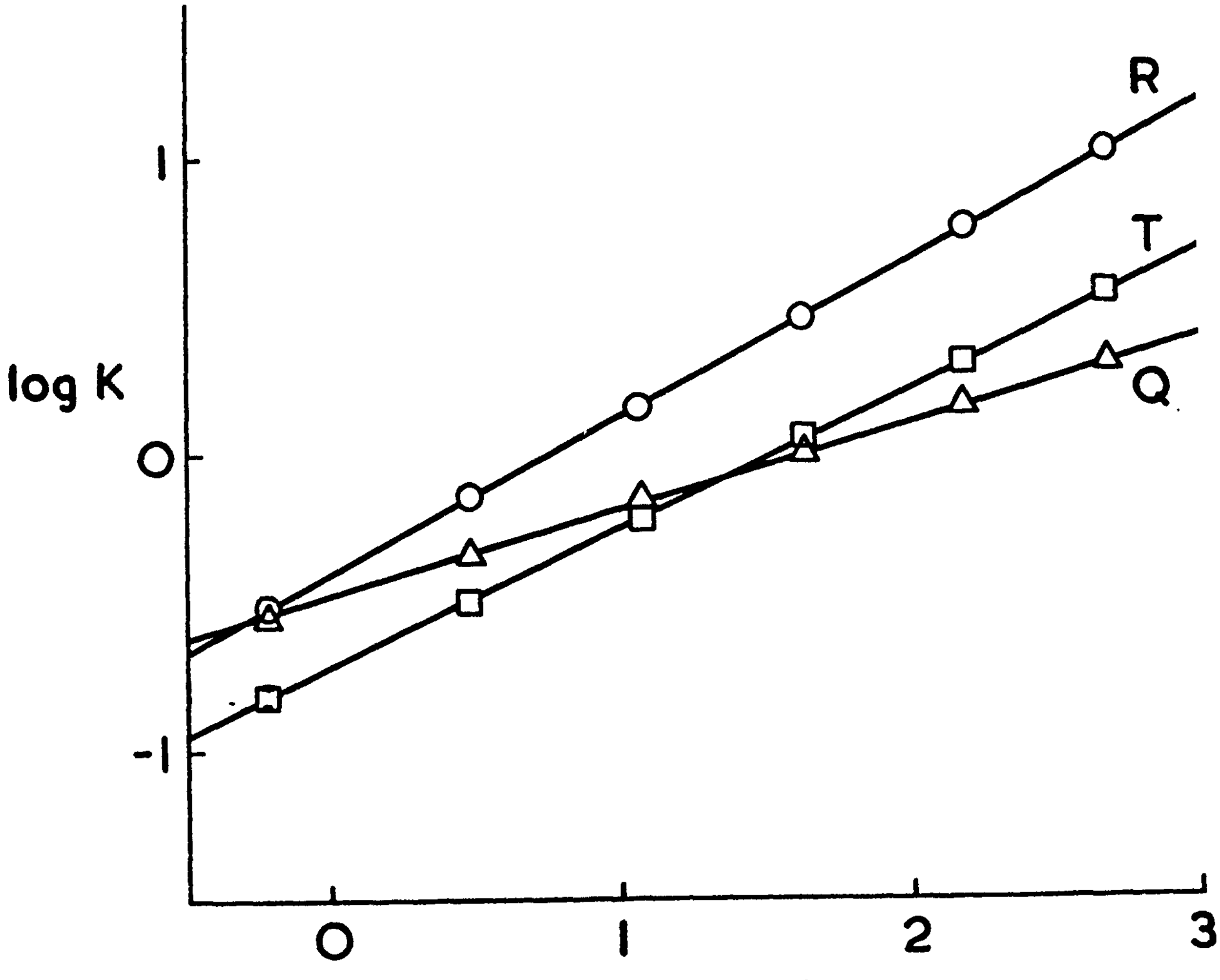
If the dependent variable, log SP, in equation 28 is based on retention times, then the characteristic constants *r, s, a, b,* and *l* will be the same as if log K had been used as the dependent variable. Only the *c*-constant will change. For many purposes, the *c*-constant is not needed in the set of characteristic constants, but if log K is used as the dependent variable, combination of the *c*-constant and the *l*-constant can lead to extra information.

Considering only the rare gases and the alkanes, for which $R_2 = \pi^H_2 = \Sigma\alpha^H_2 = \Sigma\beta^H_2 = 0$, so that equation 41 will then become,

$$\log K \text{ (inert solute)} = c + l.\log L^{16} \qquad [43]$$

The value of *c* is now identical to log K for an inert solute with log L^{16} = 0, *i.e.* a rare gas between krypton (-0.211) and xenon (0.378) or an alkane between methane (-0.323) and ethane (0.492). It is now possible to combine the *c*-constant and the *l*-constant, via equation 43, to show exactly how the affinity of a stationary phase for an inert solute depends on the L^{16} value of the solute. In Figure 3 is a plot of log K calculated through equation 43 against log L^{16} for a series of *n*-alkanes on phases R, T, and Q. For any alkane, phase R always has the highest log K value, i.e. highest affinity, of the three phases. But for phases T and Q there is a "cross-over" point between propane and *n*-butane, so that for small alkanes phase Q has more affinity, but for larger alkanes phase T has the greater affinity.

FIGURE 3: Plot of Log K Against Log L^{16} for the N-Alkanes Methane to Hexane on Phases R, T and Q.



The l-constant, as with $\Delta G_S°(CH_2)$, gives only the slopes of the lines in Figure 3. Combination of the l-constant with the c-constant leads to extra information on the affinity of the stationary phase for inert solutes.

The interaction of solutes with stationary phases can be quantified by calculating each term in equation 28, or, for the present purpose, each term in equation 41. The results are given in Table 24, using three particular solutes suggested by Poole[69] as test probes. *n*-Butylbenzene was used as a test probe for dispersive interactions, octan-l-ol for solvent basicity, benzodioxan for solvent acidity (not relevant here), and nitrobenzene for 'orientation interactions'. However, examination of Table 24 shows that it is not possible to define a set of test probes in which each probe corresponds to a unique interaction. Thus octan-l-ol, the test probe for solvent basicity (the $a.\Sigma\alpha^H_2$ term) actually interacts with most solvents more through dipolar interactions (the $s.\pi^H_2$ term) than through solute hydrogen bond acid/solvent hydrogen bond base interactions.

Table 24. A Term-By-Term Quantitative Evaluation Of The Solute/Stationary Phase Interactions That Contribute to Log K In Equation 41.

Phase	c	$r.R_2$	$s.\pi^H_2$	$a.\alpha^H_2$	$l.\log L^{16}$	Dispersion[a]	Cavity[a]
Solute n-butylbenzene							
C	-0.18	0.02	0.17	0	2.36	4.63	-2.27
K	-0.64	0.23	0.99	0	1.13	2.22	-1.09
M	-0.25	-0.22	0.57	0	1.95	3.83	-1.88
Q	-0.49	0.17	0.99	0	1.36	2.67	-1.31
R	-0.40	0.14	0.43	0	2.47	4.85	-2.38
T	-0.72	0.07	0.80	0	2.18	4.28	-2.10
Solute octan-1-ol							
C	-0.18	0.01	0.14	0.06	2.32	4.79	-2.47
K	-0.64	0.08	0.80	0.61	1.11	2.29	-1.18
M	-0.25	-0.07	0.46	0.02	1.92	3.96	-2.04
Q	-0.49	0.06	0.80	0.62	1.34	2.77	-1.43
R	-0.40	0.05	0.35	0.12	2.43	5.02	-2.59
T	-0.72	0.02	0.65	1.08	2.15	4.44	-2.29
Solute nitrobenzene							
C	-0.18	0.03	0.36	0	2.27	4.16	-1.89
K	-0.64	0.34	2.09	0	1.09	2.00	-0.91
M	-0.25	-0.32	1.21	0	1.88	3.45	-1.57
Q	-0.49	0.24	2.10	0	1.31	2.40	-1.09
R	-0.40	0.20	0.91	0	2.38	4.36	-1.98
T	-0.72	0.10	1.70	0	2.10	3.85	-1.75

[a] These represent a breakdown of the $l.\log L$ term according to reference 33.

It is useful to break down the $l.\log L^{16}$ term into an exoergic dispersion contribution to the Gibbs energy of solution, leading to a positive contribution to log K, and an endoergic cavity contribution to the Gibbs energy of solution, leading to a negative contribution to log K. Abraham and Fuchs[33] dissected log L^{16} values into various contributions, and if these contributions are calculated for the test solutes in hexadecane, assuming that the proportions are relatively the same in the phases studied here, the results in the last two columns of Table 24 are obtained. Now even if these dispersive and cavity interactions are only very approximate, they do show that the main exoergic contribution to solution of gaseous solutes in nearly all liquid phases (except water perhaps) is through solute/solvent dispersion interactions. Unfortunately it is very difficult to devise a simple experimental solute parameter that will reflect only the ability of a solute to interact via dispersion forces. Hence the combined dispersion plus cavity term, log L^{16}, has to be used in the general solvation equation, and then broken down approximately into its constituents.

Finally, considering a few individual phases, it can be shown how the characteristic constants can be used to select phases for particular separations. Phases A - J are not exceptional; their dipolarity and hydrogen bond basicity gradually increase along the series. Phase K has a very high dipolarity and basicity but the very low value of the *l*-constant would tend to reduce the general usefulness of the phase. Phase M is exceptional, in that it has a moderate dipolarity ($s = 1.101$) but has effectively zero basicity, a most unusual occurance. Of the molten salts, the tributylammonium salt, phase T, is of interest in that the Bu_3NH^+ group would be expected to be a powerful hydrogen bond acid, but for this phase, as with all others, the *b*-constant turns out to be zero. No doubt intramolecular hydrogen bonding between the Bu_3NH^+ group and the counter-anion takes place, so that the potential for intermolecular hydrogen bonding is reduced to zero. A comparison of the phases S, T, and U shows that the *a*-constant is somewhat reduced in phase T even though all three phases contain the 4-toluenesulphonate anion. This would be the result if there were intramolecular hydrogen bonding in phase T, because the anion would not then be totally available for intermolecular hydrogen bonding to a solute that was a hydrogen bond acid.

For the separation of rather nonpolar solutes, the only relevant characteristic constant is *l*. Phases A-F and phase R all have $l \geq 0.50$ and will be the best phases in the set to use. In order to separate compounds that are dipolar and nonacidic, a phase with a large *s*-constant (and preferably a large *l*-constant) is required. Phases J, L, M, O, and the molten salts T, U, V, and W satisfy these criteria. These phases, except phase M, will also selectively absorb hydrogen-bond acids because they all have large *a*-constants. To absorb acids rather than simply dipolar compounds requires $a >> s$, if possible, and here the molten salts seem to be preferred, see Table 24.

Again, this analysis shows that general solvation equation 28 (or 41), can be used to analyse GLC retention data, both to classify stationary phases and to select phases for particular separations. The method is quantitative in that specific solute/stationary phase interactions can be identified and their contribution to the overall retention process can be evaluated, Table 24.

SUMMARY DISCUSSION AND CONCLUSIONS

A much improved solvation equation, equation 28, has successfully been developed, and already applied to a variety of solubility and solubility related processes.

$$\log SP = c + r.R_2 + s.\pi^H_2 + a.\Sigma\alpha^H_2 + b.\Sigma\beta^H_2 + l.\log L^{16} \qquad [28]$$

For processes occurring within condensed phases, *eg*. log P (solvent1 ⇨ solvent2), a substitute term $m.V_X$, instead of $l.\log L^{16}$, has been found to give improved results over equation 28.

$$\log SP = c + r.R_2 + s.\pi^H_2 + a.\Sigma\alpha^H_2 + b.\Sigma\beta^H_2 + v.V_X \qquad [44]$$

By relating solubility and solubility related processes to solute characteristics, a wide range of processes can be characterised, and the contributions of the individual terms in equation 28 (or 44) quantified in a way which has previously been rather difficult. No attempt has, or should be made to simplify these equations, as they reflect the complexity of the solute-solvent interactions which are possible in the solvation of a solute. A single solvent strength parameter [69,75] cannot successfully model all the possible interactions in a solubility or solubility related process.

Solvation equations have enabled the characterisation of a large number of 'typical' GLC stationary phases[46,51], other more unusual GLC phases (such as the molten salts studied by Poole[69], polymers, more 'typical' solvents, and partition processes - some akin to those taking place inside living organisms. The systematic evaluation of gas-liquid stationary phases has been one of the largest ever attempted, notably looking at the phases of McReynolds[44] and Laffort[45]. Application of solvation equations to these and other GLC phases has shown just how similar many of these phases are. GLC phases can now be chosen in a very precise way for their solute selectivity ability. The equations have also assessed the suitability of candidate phases for use in SAW devices. Solvation equations are also invaluable for the calculation or estimation of solubility and solubility related phenomena. The scope of their application is clearly wide-ranging, the previous two sections specifically giving examples of applications of the improved solvation equations, 28 and 44. It has also been noted, see Table 11, page 44, that the newer solvation equations will give essentially the same value of the coefficients as older equations for a given solubility process, but correlation coefficients and standard deviation will be improved using the newer equations.

Substitute parameters for δ_2 and π^*_2 have been investigated, $f(\eta)$ and μ^2 respectively. The use of these two parameters has been dismissed, as their use not only generates poorer standard deviation and correlation coefficients, but leads to cross-correlations between $f(\eta)$ and log L^{16}, and μ^2 and β^H_2.

The back-calculation techniques developed during the course of this work, including the novel 'inverse' MLRA approach has been very effective in calculating new parameters, and firming up existing ones. A major aim of the project has been achieved in extending the application of the solvation equations by vastly increasing the database on log L^{16} for mono- and multifunctional compounds, to a point where the lack of a log L^{16} value is no longer a major consideration. The development and extension of the database on the effective or 'summation' solvation parameters for mono- and multifunctional compounds, π^H_2, $\Sigma\alpha^H_2$ and $\Sigma\beta^H_2$ clearly improves the ability of the solvation equations to reflect solute-solvent interactions in real solubility situations. The π^H_2 scale has been set up based on an experimental procedure and is no longer based on the solvent π^*_1 value as it used to be. The $\Sigma\alpha^H_2$ and $\Sigma\beta^H_2$ scales are also based on experimental procedure, and while they may be very similar or identical to α^H_2 and β^H_2 values for non-associated liquids, many important molecules are multifunctional in real solubility situations and the $\Sigma\alpha^H_2$ and $\Sigma\beta^H_2$ values reflect this fact. The main terms in the solvation equations, *viz.* π^H_2, $\Sigma\alpha^H_2$, $\Sigma\beta^H_2$ and log L^{16} are all related to Gibbs energy, and form a thermodynamically consistent set of explanatory variables.

The molar refraction parameter developed, R_2, is a substantial improvement over the trivial polarisability 'correction factor', δ_2, more especially since R_2 has a degree of rationale behind it and is calculable for any molecule (knowing $f(\eta)$ and V_X). The refractive index is either known, or can be measured or estimated for the majority of molecules that might be encountered, and V_X can be easily calculated for any molecule if its constituent atoms and number of bonds are known [28,29-31].

FURTHER WORK

We have now established a basic framework for the determination of solute parameters for use in two general LSER or QSAR equations, and have all the necessary parameters for a rather large number of common solutes. There are, however, still gaps in our solute parameter database. Thus we have but few parameters for sulphur compounds, especially those which might model mustard gas, and we have few parameters for phosphorous compounds, or for a variety of possible model compounds, such as derivatives of malonic acid, haloesters, *etc.* Since we now have an exact methodology that can be applied in a straight-forward way to parameter determinations, it would not be difficult to determine solute parameters for a wide variety of model compounds. Indeed, if funds are available, this would be a straight-forward extension of some of the work we have carried out.

Secondly, it is clearly possible to apply our general equations to solubilty data for solutes in any given solvent, just as we have done for solvents water, methanol, ethanol, butanol, amides and alkanes. Extension of this work to further solvents would establish the connection between Kamlet-Taft solvent solvatochromic parameters, and the characteristic constants in our solvation equations.

Thirdly, there is the possible extension of this work to solubilities in polymer phases and to the adsorption of gases and vapours in solids. The solubility of gaseous solutes in polymers can be determined by inverse GC, and application of our solvation equations would then lead to characteristic constants for polymers. A modified GC method, available at UCL, can also be used to determine adsorption isotherms of gaseous solutes on adsorbents at low partial pressure, and the derived gas/solid partition coefficients can then be analysed using our general solvation equation. Both solubility in polymers and adsorption on solids are of great practical importance, and application of the methodology we have now set out would enable considerably more information and understanding to be obtained on these systems.

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