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A New Method for the Characterization of Solutes & Solvent Phases Using Solvotochromic Parameters

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THIRD INTERIM PROGRESS REPORT

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Summary

Several hundred new secondary $\log L^{16}$ values, obtained by correlation with published data, are presented in this report. Additionally, there are 35 secondary $\log L^{16}$ values from data obtained experimentally on Apiezon L, by the gas chromatographic method and 26 new $\log L^{16}$ values determined directly on hexadecane. These are all collected in Section 1.

pi alpha beta

Now that we have an extended set of parameters, we have repeated the regressions on the Laffort data set for some 190 solutes, to obtain final equations in terms of the parameters π_2^H, α_2^H, β_2^H and V_x or $\log L^{16}$. There still remains the problem that a positive, statistically significant coefficient of β_2^H is found for liquid phases that have no acidic property. A start has been made on replacing the $\overset{\text{delta}}{\delta}/\alpha_2^H$ formalism by the dipole moment, and regressions on this basis are set out in Section 2. (sym)

(1)

SECTION 1

In the previous reports, we started to examine the characterisation of some solvent phases using equation (1) or equation (2), or some varient of these equations in which solute dipole moment could replace π_2^x. In equations (1) and (2), the solute parameters are δ, π_2^x, α_2, β_2, V_2 and $\log L^{16}$. Although we have found, in practice, that equation (2) nearly always yields better results than does equation(1), there is one drawback to the use of equation (2). Parameters δ, π_2^x, α_2 and β_2 are now known for literally hundreds of solutes and parameter estimation rules can be constructed so that further values can be deduced. The V_2 parameters in equation (1) can be taken as either the intrinsic volume V_I or the characteristic volume V_x, either of which can be calculated for any solute of known chemical structure. Hence equation (1) can be applied to a vast range of solutes. Unlike equation (1), equation (2) is restricted to those solutes for which $\log L^{16}$ values are experimentally available (240) or for which values can be estimated, that is a total of not more than 300. Although this is a rather large data base, it is much less than that for the other parameters in equation (1) and (2). Hence the drawback of equation (2) is that lack of data on $\log L^{16}$ values will restrict the use of this potentially very useful equation.

$$SP = C + s.\pi_2^x + a.\alpha_2 + b.\beta_2 + m.V_2 \qquad (1)$$

$$SP = C + s.\pi_2^x + a.\alpha_2 + b.\beta_2 + l.\log L^{16} \qquad (2)$$

The purpose of the first part of this report is to tabulate several hundred new $\log L^{16}$ values obtained from secondary sources and to show how these secondary values have been obtained. Additionally, we have carried on with our programme of determination of $\log L^{16}$ values directly. As a result of this activity, we now have available some 700 $\log L^{16}$ values thus bringing the $\log L^{16}$ data base up to or exceeding the level of the data base for the other parameters in equations (1) and (2).

Methodology

Correlation of published retention data in the form of log relative retention times, retention indices (I), or log retention volumes with $\log L^{16}$ provides equations from which further $\log L^{16}$ values can be obtained.

$$\log(\text{relative retention time, or volume}) = l.\log L^{16} + \text{CONSTANT} \qquad (1)$$

or alternatively:

$$I = l.\log L^{16} + \text{CONSTANT} \qquad (2)$$

Using the coefficient l and the constant, secondary values of $\log L^{16}$ (that is values which are not directly measured on hexadecane at 298K) can be calculated. The values obtained can be assumed to be fairly accurate if a number of conditions are met:-

a) The correlation of $\log L^{16}$ and the published data must be good, $r>0.99$, and the standard deviation must be low.

b) The published chromatographic data must be measured on a non-polar hydrocarbon stationary phase, similar to hexadecane.

c) The data has to all be measured at the same temperature and preferably be as near to 298.15K as possible.

It is useful to carry out a preliminary plot by hand of data against

$\log L^{16}$, to show compounds which are outliers, or to show if different correlations are needed for different classes of compound. For example, two separate equations were set up for retention indices (I) on Apiezon L at 403°C, see Table 3 and 4.

In a number of cases, outliers were observed on plots of retention data against $\log L^{16}$ and were further examined as follows. For a homologous series, or for a series of structurally related compounds, plots of $\log L^{16}$ against logP or of retention data against logP are always excellent straight lines, where P is the solute vapor pressure at 298K. Use of these logP plots showed in all cases examined that the retention data as reported were inaccurate (possibly due to trivial errors such as misprints, etc).

The $\log L^{16}$ values are presented in Tables as follows:-

Table 1 Experimentally determined $\log L^{16}$ values on hexadecane at 298K.

Table 2 Secondary $\log L^{16}$ values from experimentally determined retention times on Apiezon L at 298K.

Table 3-10 Secondary $\log L^{16}$ values from published data.

Experimental

$\log L^{16}$ values were determined on hexadecane in exactly the same way as that described in Progress Report 1, at 298.15 on a stationary phase of hexadecane by the gas-chromatographic method. Results are given in Table 1.

Relative retention times were determined on Apiezon L at the standard temperature of 298.15K. A short column was used of length 50 cm and internal diameter 2 mm, containing 25% W/W of Apiezon L on chromosorb WHP, and relative retention times were obtained for other solutes using a flame ionisation detector. Log (relative retention time) was correlated against $\log L^{16}$ and secondary $\log L^{16}$ values are given in Table 2.

TABLE 1 Further values of $\log L^{16}$ obtained on hexadecane at 298K.

isoprene	2.086
2-butyne	1.856
1-bromopentane	3.611
1-iodobutane	3.573
1,3-dichloropropane	3.194
1,4-dichlorobutane	3.775
benzyl bromide	4.283
phenyl acetylene	3.715
4-chlorotoluene	4.194
trans-B-nitrostyrene	3.181
furan	1.830
furfural	3.262
benzyl acetate	4.991
valeronitrile	3.057
2-Me-2-butanol	2.630
3-Me-1-butanol	3.011
cyclopentanol	3.270
allyl alcohol	1.960
crotyl alcohol	2.610
pentafluorophenol	4.330
4-fluorophenol	3.904
thiophene	2.784
2-Me-thiophene	3.302
2,5-diMe-thiophene	3.806
thiophenol	4.118
dimethyl disulphide	3.112

TABLE 2 **Secondary values of LogL^{16} from Apiezon L at 298K (experimentally determined).**

Correlation equation: Log (Relative Retention Time) = 1.037 LogL^{16} - 3.705

r = 0.9949 sd = 0.09 n = 23

2-octene	3.59		
1-decene	4.42		
1,2,3,4-tetraMe-benzene	5.15		
		N,N-diethylaniline	5.38
i-butyl ether	3.42		
2,6-diMe-anisole	4.64	di-*i*-Pr-methylphosphonate	4.61
3-Me-2-butanone	2.66	*o*-isopropyl-*t*-butylfluorophosphonate	4.08
2,4-diMe-3-pentanone	3.32	di-*i*-Pr phosphite	4.37
3-nonanone	4.73	triethyl phosphate	4.75
5-nonanone	4.64	2-chloroethylethylsulphide	4.01
2,6-diMe-4-heptanone	4.18	2-chloroethylpropylsulphide	4.44
		2-chloroethylbutylsulphide	4.89
methyl-trimethylacetate	2.91	*t*-Bu_2S_2	4.85
methyl-2-methylbutanoate	3.22		
diethyl malonate	4.37		
diethyl methylmalonate	4.50		
diethyl ethylmalonate	4.85		
diethyl succinate	4.89		
dimethyl glutarate	4.69		
diethyl fumurate	5.01		
2(-dimethylamino)ethyl methacrylate	4.59		
dimethyl chloromalonate	4.26		
diethyl chloromalonate	4.88		
ethyl acetoacetate	3.84		
methyl cyanoacetate	3.53		
ethyl cyanoacetate	3.85		

TABLE 3 Secondary values of LogL^{16} from Apiezon L at 403K (ref. 1)

Correlation equation $I/1000 = 0.202 \text{ Log}L^{16} + 0.071$

$r = 0.9977$ $sd = 0.012$ $n = 44$

2-Me-1-butene	2.12
3-Me-1-butene	1.87
2-Me-2-butene	2.25
<u>trans</u>-4-Me-2-pentene	2.42
<u>cis</u>-4-Me-2-pentene	2.42
isoprene	2.19
diamyl ether	4.86
5-Me-2-hexanone	3.67
2,4-diMe-2-pentanone	3.39
5-nonanone	4.77
2,6-diMe-2-heptanone	4.28
6-undecanone	5.74
propyl formate	2.49
2-propyl formate	2.25
2-butyl formate	2.77
2-Me-1-propyl formate	2.83
2-Me-2-propyl formate	2.56
pentyl formate	3.54
3-Me-1-butyl formate	3.35
2-butyl acetate	3.07
2-Me-1-propyl acetate	3.18
2-Me-2-propyl acetate	2.80
3-Me-1-butyl acetate	3.70
propyl propanoate	3.37
2-propyl propanoate	3.03
2-butyl propanoate	3.53
2-Me-1-propyl propanoate	3.65
2-Me-2-propyl propanoate	3.24
pentyl propanoate	4.35
3-Me-1-butyl propanoate	4.17
propyl butanoate	3.81
2-propyl butanoate	3.48
butyl butanoate	4.30
2-butyl butanoate	3.99
2-Me-1-propyl butanoate	4.10
2-Me-2-propyl butanoate	3.68
pentyl butanoate	4.79
3-Me-1-butyl butanoate	4.61
methyl isobutanoate	2.67
ethyl isobutanoate	3.08
propyl isobutanoate	3.56
2-propyl isobutanoate	3.23
butyl isobutanoate	4.07
2-butyl isobutanoate	3.75
2-Me-1-propyl isobutanoate	3.88
2-Me-1-propyl isobutanoate	3.43
pentyl isobutanoate	4.54
3-Me-1-butyl isobutanoate	4.37
nitropentane	3.56
nitrohexane	4.08
propionitrile	2.24
butanonitrile	3.04
pentanonitrile	3.56
hexanonitrile	4.08

TABLE 4 **Secondary values of $\log L^{16}$ from Apiezon L at 403K (ref. 1)**

Correlation equation: $I/1000 = 0.246 \log L^{16} - 0.022$

$r = 0.9919$ $sd = 0.019$ $n = 20$

Me cycloheptane	3.78		
Me cyclooctane	4.23		
cyclononane	4.53	p-dichlorobenzene	4.40
cyclodecane	4.96	o-chlorotoluene	4.14
cyclaindecane	5.34	m-chlorotoluene	4.13
cyclododecane	5.72	p-chlorotoluene	4.14
trans-decalin	4.66	benzyl bromide	4.66
cis-decalin	4.85	o-bromotoluene	4.52
cyclopentene	2.45	m-bromotoluene	4.54
cyclohexene	2.99	p-bromotoluene	4.54
1-Me-1-cyclopentene	2.83	iodobenzene	4.58
cycloheptene	3.50		
1-Me-1-cyclohexene	3.37	ethoxybenzene	4.14
cyclooctene	3.93	tetrahydropyran	2.99
1-Me-1-cycloheptene	3.78		
1-Me-1-cyclooctene	4.25	phenylacetaldehyde	4.27
chlorocyclopentane	3.36	m-tolualdehyde	4.48
chlorocyclohexane	3.84	p-tolualdehyde	4.52
chlorocycloheptane	4.43	salicylaldehyde	4.75
chlorocyclooctane	4.96		
bromocyclopentane	3.77	cycloheptanone	4.19
bromocyclohexane	4.25	2-Me-cyclohexanone	3.90
bromocycloheptane	4.79	3-Me-cyclohexanone	3.92
bromocyclooctane	5.20	4-Me-cyclohexanone	3.95
nitrocyclohexane	4.49	cyclooctanone	4.62
p-cumene	4.36	1-Ph-2-propanone	4.55
2-Br-1-phenyl ethane	5.05	1-Ph-2-butanone	4.93
napthalene	5.22	1-Ph-3-butanone	5.05
anthracene	5.78	propiophenone	4.82
fluorobenzene	2.86	butyrophenone	5.13

continued

TABLE 4 continued

m-dichlorobenzene	4.39
o-nitrotoluene	4.78
m-nitrotoluene	4.97
p-nitrotoluene	5.02
phenylacetonitrile	4.55
1-Me-cyclopentanol	3.22
1-Me-cyclohexanol	3.67
1-Me-cycloheptanol	4.19
1-Me-cyclooctanol	4.65
1-Ph-ethanol	4.33
2-Ph-ethanol	4.52
3-Ph-1-propanol	5.00
2-Ph-2-propanol	4.46

TABLE 5 Secondary values of $\log L^{16}$ from Squalane (corrected to 298K (ref. 2)

Correlation equation: $I/1000 = 0.203 \log L^{16} + 0.059$

$r = 0.9993$ $sd = 0.004$ $n = 26$

trans-2-pentene	2.18
3,3-diMe-1-butene	2.20
cis-2-pentene	2.19
2-Me-2-butene	2.24
4-Me-1-pentene	2.41
3-Me-1-pentene	2.42
4-Me-*cis*-2-pentene	2.44
2,3-diMe-1-butene	2.45
4-Me-*trans*-2-pentene	2.48
2-Me-1-pentene	2.56
cis-3-hexene	2.63
2-Et-1-butene	2.63
trans-3-hexene	2.63
trans-2-hexene	2.65
4,4-diMe-1-pentene	2.68
2-Me-2-pentene	2.65
3-Me-*cis*-2-pentene	2.67
cis-2-hexene	2.68
3-Me-*trans*-2-pentene	2.73
3,3-diMe-1-pentene	2.78
2,2,3-triMe-1-butene	2.79
2,3-diMe-2-butene	2.78
4,4-diMe-*cis*-2-pentene	2.83
3,4-diMe-1-pentene	2.84
2,4-diMe-1-pentene	2.84
2,4-diMe-2-pentene	2.87
3-Me-1-hexene	2.88
5-Me-1-hexene	2.91
2-Me-*trans*-3-hexene	2.90
4-Me-*cis*-2-hexene	2.93
4-Me-*trans*-2-hexene	2.94
4-Me-1-hexene	2.94
1,1-diMe cyclopentane	3.01
3,4-diMe-*cis*-2-pentene	3.01
1-cis-3-diMe cyclopentane	3.05
2-Me-1-hexene	3.05
1-*trans*-3-diMe cyclopentane	3.07
1-heptene	3.07
2-Et-1-pentene	3.07
1-*trans*-2-diMe cyclopentane	3.09
trans-3-heptene	3.10
cis-3--heptene	3.11
2-Me-2-hexene	3.12
3-Me-*cis*-2-hexene	3.12
3-Et-2-pentene	3.14
trans-2-heptene	3.15
2,3-diMe-2-pentene	3.17
cis-2-heptene	3.17
2,2-diMe-*cis*-3-hexene	3.23
1-*cis*-2-diMe-cyclopentane	3.24
2,2,4-triMe-2-pentene	3.23
2,2,3,3-tetraMe-butane	3.25
1,1,3-triMe-cyclopentane	3.25
2,2-diMe-hexane	3.25

continued

TABLE 5 continued

3-Et-1-pentene	2.89	Et-cyclopentane	3.30
2,3-diMe-1-pentene	2.90	2,5-diMe-hexane	3.29
2,2,3-triMe-pentane	3.32	isopropylcyclopentane	3.68
2,4-diMe-hexane	3.31	cis-2-octene	3.65
1-*trans*-2-*cis*-4-triMe-cyclopentane	3.34		
3,3-diMe-hexane	3.35	2,3,5-triMe-hexane	3.70
1-*trans*-2-*cis*-3-triMe-cyclopentane	3.37	2,2,3,4-tetraMe-pentane	3.72
2,3,4-triMe-pentane	3.40	1-Me-*cis*-2-Et-cyclopentane	3.73
2,3,3-triMe-pentane	3.42	2,2-diMe-3-Et-pentane	3.73
1,1,2-triMe-cyclopentane	3.43	2,2-diMe-heptane	3.72
2-Me-3-Et-pentane	3.44	2,2,3-triMe-hexane	3.74
2,3-diMe-hexane	3.45	1-*cis*-2-diMe-cyclohexane	3.76
1-*cis*-2-*trans*-4-triMe cyclopentane	3.49	2,4-diMe-heptane	3.75
3-Me-3-Et-pentane	3.50	Et-cyclohexane	3.79
2-Me-heptane	3.48	Pr-cyclopentane	3.78
2,2,4,4-tetraMe-pentane	3.50	4,4-diMe-heptane	3.77
3-Et-hexane	3.51	2-Me-4-Et-hexane	3.77
3-Me-heptane	3.51	*2,6-diMe-heptane*	3.78
1,1-diMe-cyclohexane	3.55	1,1,3-triMe-cyclohexane	3.82
1-*trans*-4-diMe-cyclohexane	3.55	1,1,1-triMe-cyclohexane	3.82
2,2,5-triMe-hexane	3.53	2,4-diMe-3-Et-pentane	3.81
1-*cis*-3-diMe-cyclohexane	3.55	2,3,3-triMe-hexane	3.82
1-octene	3.55	3,5-diMe-heptane	3.81
1-Et-*trans*-2-Me-cyclopentane	3.58	3,3-diMe-heptane	3.82
1-Me-1-Et-cyclopentane	3.59	2,5-diMe-heptane	3.81
2,2,4-triMe-hexane	3.58	2-Me-3-Et-hexane	3.85
trans-4-octene	3.57	2,3,4-triMe-hexane	3.86
cis-3-octene	3.59	2,2,3,3-tetraMe-pentane	3.88
cis-4-octene	3.58	3,3,4-triMe-hexane	3.89
1-*cis*-2-*cis*-3-triMe-cyclopentane	3.63	3-Me-3-Et-hexane	3.89
1-*trans*-2-diMe-cyclohexane	3.63	2,3,3,4-tetraMe-pentane	3.91
trans-3-octene	3.60	3-Me-4-Et hexane	3.90
1-cis-4-diMe-cyclohexane	3.64	2,3-diMe-heptane	3.91

continued

TABLE 5 continued

1-trans-3-diMe-cyclohexane	3.65	3,4-diMe-heptane	3.92
trans-2-octene	3.64		
4-Et-heptane	3.93		
2,3-diMe-3-Et-pentane	3.97		
4-Me-octane	3.95		
2,2,4-triMe-heptane	3.99		
2-Me-octane	3.97		
3-Et-heptane	3.98		
3-Me-octane	3.99		
1-nonene	4.05		
cis-4-nonene	4.06		
trans-4-nonene	4.06		
cis-3-nonene	4.07		
trans-3-nonene	4.08		
3,3,5-triMe-heptane	4.15		
cis-2-nonene	4.13		
trans-2-nonene	4.12		

Secondary values from results on Squalane (ref. 3)

n-butyl nitrate	3.19
n-pentyl nitrate	3.63

TABLE 6 Secondary values of $\log L^{16}$ from $C_{87}H_{176}$, corrected to 343K (ref. 4)

Correlation equation: $I/1000 = 0.205 \log L^{16} + 0.072$

$r = 0.9953$ $sd = 0.017$ $n = 68$

2,2-diMe-hexane	3.14	n-DecCl	5.66
2,3-diMe-hexane	3.36	n-PrBr	2.64
2,4-diMe-hexane	3.21	n-PeBr	3.64
3,4-diMe-hexane	3.42	n-HexBr	4.13
2,3,4-triMe-pentane	3.34	n-HepBr	4.60
2,2-diMe-heptane	3.61	n-OctBr	5.09
2,2,4,6,6-pentaMe-heptane	4.42		
1-nonene	3.96	n-NonBr	5.56
1-decene	4.44	n-DecBr	6.04
1-undecene	4.93	n-PrI	3.16
1-dodecene	5.41	n-BuI	3.64
1-tridecene	5.90	n-PeI	4.13
1-pentyne	2.01	n-HexI	4.62
1-hexyne	2.51	n-HepI	5.09
1-heptyne	3.00	n-OctI	5.60
1-octyne	3.48		
1-nonyne	3.96		
1-decyne	4.44	Pe_2O	4.80
cyclodecane	5.19		
cycloundecane	6.05	heptyl acetate	4.73
cis-hydrindane	4.51	octyl acetate	5.20
trans-hydrindane	4.35	nonyl acetate	5.68
cis-decalin	5.06		
trans-decalin	4.87	2-undecanone	5.64
tetralin	5.25		
napthalene	5.34	$n\text{-}BuNO_2$	3.33
azulene	5.86	$n\text{-}PeNO_2$	3.82

continued

TABLE 6 continued

PhF	2.82		
n-HexCl	3.71	n-HexNO$_2$	4.31
n-HepCl	4.21		
n-OctCl	4.70	n-PrCN	2.51
n-NonCl	5.17	n-BuCN	3.01
n-PeCN	3.50		
n-HexCN	3.98		
n-HepCN	4.48		
n-OctCN	4.97		
n-NonCN	5.46		
n-DecCN	5.94		
2,4-diMe-pyridine	4.05		
2,5-diMe-pyridine	4.05		
2,6-diMe-pyridine	3.86		
3,4-diMe-pyridine	4.36		
3,5-diMe-pyridine	4.25		
2-Et-pyridine	3.90		
3-Et-pyridine	4.13		
4-Et-pyridine	4.14		
2-Pr-pyridine	4.31		
4-Pr-pyridine	4.57		
4-*t*-Bu-pyridine	4.75		
2-Me-2-butanol	2.56		
2-Me-2-hexanol	3.46		
2-Me-2-heptanol	3.94		
2-Me-2-octanol	4.43		

TABLE 7 **Secondary values of $\log L^{16}$ from Apiezon M corrected to 333K (ref. 5 and 6)**

Correlation equation: $I/1000 = 0.196 \log L^{16} + 0.081$

$r = 0.9995$ sd $= 0.006$ $n = 19$

*iso*amylSH	3.36	EtSDecyl	6.98
tert-amylSH	3.16	PrSBu	4.48
HexSH	4.22	PrSPe	4.96
HepSH	4.72	PrSHex	5.45
NonSH	5.89	PrSHep	5.94
AllylSH	2.51	PrSOct	6.43
n-Pr_2S	4.12	PrSNonyl	6.92
i-Pr_2S	3.60	BuSPe	5.43
Bu_2S	4.95	BuSHex	5.92
t-Bu_2S	4.16	BuSHep	6.41
Am_2S	5.91	BuSOct	6.90
i-am_2S	5.54	PeSHex	6.40
Hex_2S	6.88	PeSHep	6.90
BuSMe	3.75	PeSOct	7.38
MeSPe	4.14	EtSMe	2.73
HexSMe	4.63	MeSPr	3.24
HepSMe	5.13	Et_2S_2	4.21
MeSOct	5.62	n-Pr_2S_2	5.12
MeSNonyl	6.12	i-Pr_2S_2	4.67
MeSDecyl	6.61	n-Bu_2S_2	6.03
MeSUndecyl	7.11	i-Bu_2S_2	5.57
MeSDodecyl	7.60	t-Bu_2S_2	5.17
EtSPr	3.54	t-am_2S_2	6.26
BuSEt	4.03	tetrahydrothiophene	3.66
EtSPe	4.52		
EtSHex	5.01		
EtSHep	5.50		
EtSOct	6.00		
EtSNonyl	6.49		

TABLE 8 Secondary values of $\log L^{16}$ from Squalane at 353K (ref. 7)

Correlation equation: Log Relative Retention Volume = 0.74 $\log L^{16}$ - 2.304

$r = 0.9984$ sd = 0.037 $n = 38$

2,5-diMe-5-hexadiene	3.38
cyclohexadiene	2.92
diallyl	2.44
α-pinene	4.20
β-pinene	4.40
tricyclene	4.15
camphene	4.24
myrcene	4.40
Δ^3-carene	4.55
dioxane	2.84
methyl propargyl ether	2.04
dimethylethinylcarbinol methylether	2.46
dimethylethinylcarbinol	2.19
diacetyl	2.20
allylacetone	3.17
propyl formate	2.42
isopropyl formate	2.21
isobutyl acetate	3.14
tert-butyl acetate	2.81
propyl propanoate	3.32

TABLE 9 **Secondary values of $\log L^{16}$ from Octacosane at 353.35K (ref. 8)**

Correlation equation: $\log V_g^o = 0.729 \log L^{16} - 0.16$

$r = 0.9984$ $sd = 0.03$ $n = 32$

furfurol	3.29
crotonaldehyde	2.57
2-Me-propanal	2.15
vinyl acetate	2.22
3-Me-1-butanol	3.01

TABLE 10 Secondary values of $\log L^{16}$ from $C_{87}H_{176}$ at 393K (ref. 9)

Correlation equation: $I/1000 = 0.201 \log L^{16} + 0.082$

$r = 0.9948$ $sd = 0.018$ $n = 35$

1-octyne	3.51
cis-hydrindane	4.71
cis-decalin	5.29
1-chlorohexane	3.79
1-bromopentane	3.73
1-iodobutane	3.77
2-undecanone	5.73
1-cyanopropane	2.27
1-cyanobutane	3.05
2-Me-2-heptanol	3.99

Secondary values of $\log L^{16}$ from results on Squalane at 333K (ref 10)

allyl iodide (1-iodo-2-propene)	3.01
allyl cyanide (1-cyano-2-propene)	3.34
cyclohexene	2.97

TABLE 11 **Secondary values of $\log L^{16}$ from n-Heptadecane at 318.15K (ref 10)**

Correlation equation: $\log V_G = 0.895535 \log L^{16} - 0.007886$

$r = 0.9974$ $n = 29$

trans-2-hexene	2.664	1-chloropropane	2.202[b]
cis-2-hexene	2.668	1-bromopropane	2.605
trans-2-heptene	3.151	1-iodopropane	3.099
cis-2-heptene	3.168	1-chloro-2-methylpropane	2.566
trans-3-heptene	3.095	2-bromopropane	2.391
cis-3-heptene	3.104	2-bromobutane	2.933
4-methyl-1-pentene	2.398	1-bromo-2-methylpropane	2.961
2-methyl-2-pentene	2.552	2-bromo-2-methylpropane	2.616[b]
3,3-dimethyl-1-butene	2.185		
2-methyl-1-hexene	3.045		
5-methyl-1-hexene	2.908		
4,4-dimethyl-1-pentene	2.681		

[b] Revised values

TABLE 12 **Secondary values of $\log L^{16}$ from Squalane at 298.15K (ref 12)[a]**

Correlation equation: $\log L^{16} = 0.00504645 I - 0.36018$

1,3 - cyclopentadiene	2.25[b]
2-methyl	2.77[c]
1-methyl	2.79
5-methyl	2.88
2-ethyl	3.28
1-ethyl	3.30
5-ethyl	3.40
2-isopropyl	3.58
1-isopropyl	3.59
2-n-propyl	3.73
1-n-propyl	3.75
5-n-propyl	3.84
2-isobutyl	3.98
1-isobutyl	3.99
2-n-butyl	4.23
1-n-butyl	4.25
5-n-butyl	4.34
2-n-pentyl	4.71
1-n-pentyl	4.73
5-n-pentyl	4.81
2-n-hexyl	5.21
1-n-hexyl	5.23
5-n-hexyl	5.32
2-n-heptyl	5.71
1-n-heptyl	5.73
5-n-heptyl	5.82
2-n-ocytl	6.21
1-n-octyl	6.23
5-n-octyl	6.32
2-n-nonyl	6.72
1-n-nonyl	6.73
2-n-decyl	7.22
1-n-decyl	7.24
exo-dicyclopentadiene	4.58
endo-dicyclopentadiene	4.59
1-methyl-1-cyclopentene	2.88
1-ethyl-1-cyclopentene	3.39
1-n-propyl-1-cyclopentene	3.84
1-n-butyl-1-cyclopentene	4.34
1-n-pentyl-1-cyclopentene	4.83
1-n-hexyl-1-cyclopentene	5.32
1-n-heptyl-1-cyclopentene	5.82
1-n-octyl-1-cyclopentene	6.32
3-methyl-1-cyclopentene	2.67
3-ethyl-1-cyclopentene	3.23
3-n-propyl-1-cyclopentene	3.72
3-n-butyl-1-cyclopentene	4.22
3-n-pentyl-1-cyclopentene	4.72
3-n-hexyl-1-cyclopentene	5.28
3-n-heptyl-1-cyclopentene	5.72
3-n-octyl-1-cyclopentene	6.23

[a] Corrected from 337.15K by the given values of dI/dT

[b] Compare our original value of 2.222 (data base)

[c] Values for alkyl-1,3-cyclopetadienes

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SECTION 2

In our previous report we examined the extensive GLC data of Laffort,[1] and showed that equation (1) reproduced results quite well, using about 90 out of the 240 total solutes, for which all the solute parameters were available. We now have a much larger parameter data base and set out equations for 189 out of the 240 solutes. The present regressions include solutes containing most of the simple functional groups, and it is now unlikely that any further regressions will be substantially different. Equations are given in terms of $\log L^1$, where L^1 is the Ostwald solubility coefficient relative to n-decane.

$$\log L^1 = c + d.\delta + s.\pi_2^* + a.\alpha_2 + b.\beta_2 + l.\log L^{16} \qquad (1)$$

Results are given in Table 1. The correlation coefficients are not as high as usual, but it should be remembered that the regressions include data for solutes such as carboxylic acids, thiols, sulphides, etc that are not generally included. However, the sign and magnitude of the coefficients all make generally good chemical sense, with the exception of the $b.\beta_2$ term. None of the phases, with the exception of zonyl E7, are hydrogen-bond acids, and hence the b-coefficient should be zero. For TCEP, DEGS, and possibly for polyphenylether, the b-coefficient is nonzero, as can be seen from the % confidence levels shown in Table 1.

In order to resolve this, and also to attempt to separate the dipolarity and polarisability contributions in the π_2^* term, we have now embarked on a detailed analysis via equation (2)

$$\log L^1 = c + p.P_2 + q.\mu_2 + a.\alpha_2 + b.\beta_2 + l.\log L^{16} \qquad (2)$$

In this equation, the solute dipole moment, μ, replaces π_2^*, and a new parameter P_2 replaces δ_2. Our method is to construct equations for a series of solutes for which we expect P_2 to be zero, namely a series of simple aliphatic solutes with single dominant dipoles. Then using the resulting coefficients of c, q, a, b and l, it is possible to back-calculate the $p.P_2$ term for any other solute (eg aromatics, halogenated solutes) and then to examine the dependence of p on solute type.

The equations we have constructed are set out in Table 2, in terms of our new equation (1). Results are quite encouraging. Thus for the four phases given, all of which have no hydrogen-bond acidity at all, the correlation constants are excellent without the necessity of inclusion of the $b.\beta_2$ term (compare Table 1 with Table 2). We can now use these regression in Table 2 to back-calculate the $p.P_2$ term in equation (2) for other solutes, taking P_2 relative to benzene, $P_2 = 1.0$. We find quite reasonable values, viz for example:

benzene	1.0
toluene	0.83
o-xylene	0.99
mesitylene	1.02
anisole	0.89
m-nitrotoluene	0.48
benzonitrile	0.33
thiophene	0.86

We need further iterative calculations, but there is good hope that by using equation (2), not only can we provide equations that have the chemically sensible value of $b = 0$, but that will also have much better fits to the data. In Table 2, the regressions must be quite close to the "level of exhaustive fit", with sd ranging from 0.05 to 0.09 log units.

Now that we have a reasonably full data base, we will apply equation (2) not only to the Laffort phases, but to other solvent phases, and then attempt to deduce a comprehensive set of $p.P_2$ values.

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TABLE 1 Regression parameters for the Laffort phases, using equation (1)

	c	$d.\delta$	$s\pi_2^*$	$a.\alpha_2$	$b.\beta_2$	$l.\log L^{16}$	n	r	sd	CL %				
										d	s	a	b	l
Carbowax														
	-2.03	0.13	1.33	2.08	0.07	0.45	189	0.983	0.16	99	100	100	50	100
Tricyanoethoxypropane														
	-1.68	0.14	1.81	1.58	0.57	0.32	189	0.978	0.19	99	100	100	100	100
Polyphenyether														
	-2.51	0.12	0.90	0.54	0.17	0.55	189	0.987	0.14	100	100	100	95	100
Diethylenglycolsuccinate														
	-1.76	0.18	1.59	1.64	0.30	0.40	189	0.974	0.20	100	100	100	97	100
Zonyl E7														
	-2.08	-0.01	1.07	0.50	0.69	0.44	189	0.985	0.14	25	100	100	100	100

TABLE 2 Regression parameters for the Laffort phases, using equation (2)[a] with solutes that are simple dipoles with $P_2 = 0$

	c	$q.\mu$	$a.\alpha_2$	$1.\log L^{16}$	n	r	sd	CL % q	CL % a	CL % 1
Carbowax	-1.97	0.32	2.19	0.43	90	0.995	0.08	100	100	100
Tricyanoethoxypropane	-1.68	0.50	2.51	0.36	90	0.994	0.09	100	100	100
Polyphenyether	-2.43	0.22	0.80	0.53	90	0.998	0.05	100	100	100
Diethleneglycolsuccinate	-1.77	0.40	2.27	0.39	90	0.994	0.09	100	100	100

[a] Note that in all cases the $b.\beta_2$ coefficient is zero