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Throughout the summer the principal investigator and Dr. Marguerite S. Swain continued to work on the project, although Mr. Henry Bryndza was away during June, July and August.

As noted in previous reports, the major problem has been that of deciding between possible choices for the six subsidiary conditions that are needed, in addition to the linear model and least squares, to determine the derived solvent and reaction constants. To be physically significant, the two reaction constants for each reaction, which represent its sensitivity to solvent acidity and solvent basicity respectively, must be zero or greater (never negative). The derived order of solvent acidities must be $CF_3COOH > CH_3COOH > H_2O$, and the derived order of solvent basicities must be $H_2O > CH_3COOH > CF_3COOH$. Many initially attractive choices fail to satisfy these criteria and accordingly have now been rejected.

The choices excluded in this way include many that were formerly advocated by us and by others in the literature. Each of them can be characterized or summarized by a pair of critical conditions, since the other four conditions associated with each choice are invariably concerned only with the arbitrary and physically unimportant specification of reference solvents (for which one or both of the solvent constants is zero) and standard solvents or reactions (for which one or both of the constants is unity). Listed below are six typical untenable pairs of critical conditions, each with a derived order that violates one of the criteria in the paragraph above, and three more acceptable ones. Subscripts refer to the solvents (J) and reactions (I) in Tables I and II.

$A_1/B_1 = 3A_2/B_2$ and $A_2/B_2 = 3A_3/B_3$ (102)

gave very negative $B_7$

$B_1 = 0$ and $A_3 = 0$. (83)

gave very negative $B_7$

$B_6 = B_9$ and $A_3 = 0$. (87)

gave very negative $B_7$

$A_{\phi_3CCl} = A_2$ and $B_7 = 0$. (93)

gave negative $A_7$

$A_{\phi_3CCl} = A_{\phi_3COAc}$ and $B_7 = 0$. (70a)

gave $Y_{11} > Y_9 > Y_1$

$A_7 = A_9$ and $B_7 = 0$. (70b)

gave $Y_{11} > Y_9 > Y_1$

$A_3 = 0$ and $B_7 = 0$ (89)

gave $Y_{13} << Y_1$

$Y_{13} = Y_1$ and $B_7 = 0.$ (101)

gave possible values

$Y_9 = Y_{10}$ and $B_7 = 0.$ (103)

gave possible values

We have processed more than 75 different choices with our DOVE (dual obligate vector evaluation) computer program to obtain corresponding sets of solvent and reaction constants, but have now excluded, and have not even included in the above list, any that involve either orthogonality ($\Sigma XY = 0.$) or zero covariance between solvent acidity (X) and solvent basicity (Y) for all the solvents considered, because, as we recently discovered and demonstrated in our last (eighth) status report, such statistical statements are generally invalid. However, we can now additionally exclude many others including the first six in the above list. The first of them (conditions 102), used by us in our first dual factor analysis (with R. B. Mosely and D. E. Bown, J. Amer. Chem. Soc., 77, 3731 (1955)),can be excluded because Dimroth's $E_T$ series (not measured or available when our earlier analysis was done) acquires a negative A reaction constant (for sensitivity to solvent acidity) under these conditions. The last of them (103) gives results rather close to the preceding one (101), was used by Schleyer in recent analyses (J. W. Bentley, F. L. Schadt and P. v. R. Schleyer, J. Amer. Chem. Soc., 94, 991 (1972)),cannot be excluded by the criteria given in the second paragraph, and is probably only slightly in error, but we now believe that it is not sufficiently accurate to be acceptable for the following reasons: (1) since formic acid is considerably stronger than acetic acid, it is statistically unlikely that their basicities are exactly equal; (2) experimental results indicate that their basicities are significantly unequal, with the basicity of formic acid somewhat higher than that of acetic acid (P. E. Peterson and F. J. Waller, ibid., 94, 991 (1972)); (3) assumed equality leads to the conclusion that an ether (1,2-dimethoxyethane) is a stronger base than water, which seems unlikely.

Whether this last conclusion is unlikely or not depends, of course, on the relative importance of two influences, one of which could increase the basicity of water relative to ethers, and the other of which could reduce it. The first (probably more important) is hydrogen bonding, which would probably increase the basicity of water or alcohols by making them slightly resemble hydroxide or alkoxide ions. The second is the electron-supplying inductive effect of alkyl groups relative to hydrogen, which might make the ether a slightly stronger base, but which we would not expect to be significant here because in a previous analysis of substituent effects (C. G. Swain and E. C. Lupton, Jr., ibid., 90, 4328 (1968)), reinforced by more recent unpublished work, we found the electronic effect of alkyl groups to be negligible except in situations where they can supply electrons by resonance (not true in ethers).

In any case, it appeared to us that the most practical way to settle this issue would be to allow for either result but use 52 data to settle the point. The difference

in solvent basicity between HOH and $CH_3OH$ should be the same as the difference between $CH_3OH$ and $CH_3OCH_3$, regardless of which influence is dominant, because the number of hydrogen bonds decreases steadily (2, 1, 0) and the number of alkyl substitutions increases steadily (0, 1, 2) over this range of structure. There are no suitable data for $CH_3OCH_3$ (because it is a liquid only above atmospheric pressure), but $(CH_3OCH_2)_2$ is a reasonable approximation, having two reasonably independent and non-interacting functions of the same type in a molecular unit of approximately twice the molecular weight. Therefore we assumed conditions 104,

$$Y_1 - Y_2 = Y_2 - Y_{13} \text{ and } B_7 \approx 0. \qquad (104)$$

The results are presented in Tables I and II. From the fact that Y values for methanol and 1, 2-dimethoxyethane are calculated to be less than for water, we conclude that the dominant influence is indeed hydrogen bonding, as we expected, rather than the inductive effect of alkyl groups.

Table I. Solvent Constants from 52 Data and Conditions 104.

| J | Solvent | Solvent acidity X | Solvent basicity Y |
|---|---|---|---|
| 1 | $H_2O$ | (1.000)[a] | (1.000)[a] |
| 2 | $CH_3OH$ | 0.765 | (0.889)[d] |
| 3 | 97% $CH_3OH$ | 1.047 | 0.838 |
| 4 | $C_2H_5OH$ | 0.651 | 0.881 |
| 5 | 80% $C_2H_5OH$ | 0.706 | 0.932 |
| 6 | 60% $C_2H_5OH$ | 1.453 | 0.806 |
| 7 | 80% $CH_3COCH_3$ | 0.107 | 1.033 |
| 8 | 70% $CH_3COCH_3$ | (0.000)[b] | 1.087 |
| 9 | $CH_3CO_2H$ | 2.648 | 0.441 |
| 10 | $HCO_2H$ | 2.739 | 0.573 |
| 11 | $CF_3CO_2H$ | 5.456 | (0.000)[c] |
| 13 | $CH_3OCH_2CH_2OCH_3$ | 0.226 | (0.777)[d] |

[a] Unity chosen for water for both X and Y to give units and values convenient sizes. [b] Made zero (this solvent reference for X values) because this solvent has the lowest X of the 12 solvents listed. [c] Made zero (this solvent reference for Y values) because this solvent has the lowest Y of the 12 solvents listed. [d] Made $Y_1 - Y_2 = Y_2 - Y_{13}$ (fifth one of conditions 104) for reasons given in text.

Table II. Reaction Constants from 52 Data and Conditions 104

| I | Reaction | n[a] | A | B | %B[b] | R[c] |
|---|---|---|---|---|---|---|
| 1 | $(C_6H_5)_3CF + H_2O$ | 6 | 7.41 | 25.79 | 23.9 | 0.9998 |
| 2 | $(CH_3)_3CCl + H_2O$ | 10 | 5.86 | 26.85 | 29.3 | 0.9789 |
| 3 | $CH_3OTs + H_2O$ | 7 | 0.75 | 8.26 | (50.0)[b] | 0.9988 |
| 4. | Adamantyl OTs + $H_2O$ | 7 | 5.52 | 23.07 | 27.4 | 0.9950 |
| 5 | $(CH_3)_2CHOTs + H_2O$ | 6 | 3.50 | 17.05 | 30.6 | 0.9836 |
| 6 | Pyridinium iodide Z | 8 | 19.32 | 85.68 | 28.6 | 0.9662 |
| 7 | Dimroth $E_T$ | 5 | 32.14 | (0.00)[d] | 0.0 | 1.0000[e] |
| 8 | Pyridine oxide Z | 3 | 5.42 | 22.65 | 27.4 | —[f] |
| | Over-all: | 52 | | | | 0.9861 |

[a] Number of data. [b] Relative importance of B relative to reaction 3, defined as $100|B_I|/(R|A_I| + |B_I|)$, where $R = |B_3|/|A_3|$. [c] Correlation coefficients, corrected for sample size (degrees of freedom) and magnitudes of numbers (status report 4). [d] Made zero (sixth one of conditions 104) because this reaction has the lowest B of the 8 reactions listed. [e] To two more figures, this is 0.999974. [f] Not calculable because based on only 3 data.

Although a few X values are somewhat surprising, (e. g., the lowest value for 70% acetone and a slightly higher value for the supposedly anhydrous ether), we consider the results in these tables now acceptable, and a suitable basis for analysis of a wider range of solvents and reactions, which we now propose to undertake, using other data accumulated by Dr. A. L. Powell and ourselves. This can be done in two ways, which we propose to explore successively. First, we will apply ordinary multiple least squares to determine X and Y values for other solvents and A and B values for other reactions, without changing the 24 solvent constants and 16 reaction constants already assigned. Second, we will pool all of the seemingly reliable data to reassess all of the constants in one DOVE analysis. Finally, we hope to translate the results into individual ionic activity coefficients for many organic and inorganic ions in these solvents and solvent mixtures.