# Solvent Effects on Chemical Processes. Part 7.‡ Quantitative Description of the Composition Dependence of the Solvent Polarity Measure $E_T(30)$ in Binary Aqueous–Organic Solvent Mixtures

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The solvation effect component of the phenomenological model of solvent effects is applied to $E_T(30)$, the molar transition energy of the Dimroth–Reichardt betaine, in binary aqueous–organic solvents. The dependence of $E_T(30)$ on $x_2$, the mole fraction of organic cosolvent, can be quantitatively described for all 17 systems studied. New data are given for 9 of these systems. It is found that a 1-parameter model suffices to describe the composition dependence of the highly polar cosolvents, whereas a 2-parameter model is needed to account for other cosolvents, which yield a nonhyperbolic composition dependence. The solvation parameters, which are exchange equilibrium constants, yield correlations suggesting their positive dependence on cosolvent hydrophobicity and electron-pair donor ability.

The phenomenological model of solvent effects developed in our laboratory writes the overall effect as the sum of effects arising from solvent–solvent interactions (the *general medium* effect), solvent–solute interactions (the *solvation* effect), and solute–solute interactions (the *intersolute* effect). The parameters of the model, which are given physical meaning by the theory, are extracted by fitting the appropriate equation to experimental data consisting of free energy changes as a function of solvent composition. This approach provides excellent descriptions of solvent effects, in aqueous–organic mixtures, on solubility,[1–3] surface tension[4] and molecular complex formation.[5–6] In the present paper we extend the approach to the description of solvent effects on electronic absorption spectra. For this purpose we choose to study the Dimroth–Reichardt pyridinium *N*-phenoxide betaine, whose molar transition energy, commonly symbolized $E_T(30)$, is widely used as an empirical measure of solvent polarity.[7,8] [For typographical simplicity we will usually represent $E_T(30)$ as $E_T$.]

We are concerned here with the dependence of $E_T$ on solvent composition in binary aqueous–organic solvent mixtures covering the entire composition range. Bosch and Rosés[9] and Langhals[10,11] have been able to describe the composition dependence of $E_T$ for certain solvent mixtures, but heretofore a general quantitative description has not been available. We apply our phenomenological model to this problem.

*Theory.*—The concentration of the solute (the Dimroth–Reichardt betaine) is always very low, so solute–solute interactions are negligible and the intersolute effect makes no significant contribution to the observed solvent effect. Moreover, because of the Franck–Condon principle, according to which the atomic nuclei undergo no sensible motion on the time scale of the electronic transition, the cavity containing the solute molecule does not change its size or shape, so the general medium effect (which we model in terms of a cavity approach) likewise makes no contribution. We are left only with the solvation effect.

Our theory treats the solvation effect in terms of competitive exchange equilibria between solvent component 1 (water, W, in the present study) and solvent component 2 (organic cosolvent, M) for solute (R). A general treatment can be given, but is not needed, for the two simplest cases suffice to describe all systems. First consider this 1-step (2-state) exchange process, shown as Scheme 1.

$$\mathrm{RW} + \mathrm{M} \overset{K_1}{\rightleftharpoons} \mathrm{RM} + \mathrm{W}$$

**Scheme 1**

Here $K_1$ is the exchange constant for the competition between the fully hydrated (RW) and fully cosolvated (RM) states. Defining the fractions in these two states as $F_W$ and $F_M$, where $F_W + F_M = 1$, it is easily possible to relate the fractions to $K_1$ and the mole fractions $x_1$ and $x_2$ of solvent components 1 and 2 by eqn. (1).

$$F_W = \frac{x_1}{x_1 + K_1x_2}; \quad F_M = \frac{K_1x_2}{x_1 + K_1x_2} \qquad (1)$$

We proceed by writing $E_T$ at any cosolvent concentration $x_2$ as an average of $E_T$ for RW and $E_T$ for RM, weighted by the fractions of these species [eqn. (2)].

$$E_T(x_2) = F_WE_T(\mathrm{W}) + F_ME_T(\mathrm{M}) \qquad (2)$$

Algebraic combination and rearrangement leads to eqn. (3)

$$\Gamma = \frac{E_T(x_2) - E_T(\mathrm{W})}{E_T(\mathrm{M}) - E_T(\mathrm{W})} = \frac{K_1x_2}{x_1 + K_1x_2} \qquad (3)$$

$E_T(\mathrm{W})$ and $E_T(\mathrm{M})$ are experimentally accessible as the values of $E_T$ when $x_2 = 0$ and 1, respectively. Thus $\Gamma$ is measured as a function of $x_2$, and $K_1$ is obtained by fitting eqn. (3) to the data. The method of Bosch and Rosés[9] is formally similar to the above treatment.

Many systems cannot be described by eqn. (3) over the entire composition range, and in these cases we expand the solvation description to a 2-step (3-state) process, shown in Scheme 2.

$$\mathrm{RW_2} + \mathrm{M} \overset{K_1}{\rightleftharpoons} \mathrm{RWM} + \mathrm{W} \qquad (a)$$

$$\mathrm{RWM} + \mathrm{M} \overset{K_2}{\rightleftharpoons} \mathrm{RM_2} + \mathrm{W} \qquad (b)$$

**Scheme 2**

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‡ Parts 1–6, see refs. 1–6.

A similar treatment[1] gives eqns. (4) and (5) for the fractions $F_{WM}$ and $F_{MM}$.

$$F_{WM} = \frac{K_1x_1x_2}{x_1^2 + K_1x_1x_2 + K_1K_2x_2^2} \quad (4)$$

$$F_{MM} = \frac{K_1K_2x_2^2}{x_1^2 + K_1x_1x_2 + K_1K_2x_2^2} \quad (5)$$

In addition, since $F_{WW}$ and $F_{WM} + F_{MM} = 1$, the corresponding result for $F_{WW}$ is obvious.

The weighted average for this 2-step case is, by analogy with eqn. (2), as shown in eqn. (6).

$$E_T(x_2) = F_{WW}E_T(WW) + F_{WM}E_T(WM) + F_{MM}E_T(MM) \quad (6)$$

At this point we are required to introduce an assumption about the quantity $E_T(WM)$, which is not susceptible to direct measurement. We provisionally postulate that $E_T(WM) = [E_T(WW) + E_T(MM)]/2$, and proceed as before, obtaining eqn. (7).

$$\Gamma = \frac{E_T(x_2) - E_T(WW)}{E_T(MM) - E_T(WW)} = \frac{K_1x_1x_2/2 + K_1K_2x_2^2}{x_1^2 + K_1x_1x_2 + K_1K_2x_2^2} \quad (7)$$

Notice that $\Gamma$ for the 1-step model [eqn. (3)] is equal to $F_M$, whereas $\Gamma$ for the 2-step model [eqn. (7)] is equal to $F_{WM}/2 + F_{MM}$. [$E_T(W)$ in eqn. (3) and $E_T(WW)$ in eqn. (7) are identical quantities, of course, as are $E_T(M)$ and $E_T(MM)$].

## Experimental

*Materials.*—The Dimroth–Reichardt dye [2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate] was purchased from Aldrich Chemical Co. and used directly. Water was purified with a Sybron/Barnstead PCS System consisting of a prefilter and organic, ion-exchange and microfilter cartridges. The organic cosolvents were of analytical or HPLC grades.

*Apparatus.*—Spectrophotometric measurements were made with an On Line Instruments Systems (OLIS)-modified Cary 14 spectrophotometer interfaced to an IBM PC AT computer. The cell compartments were thermostatted at 25.0 °C.

*Procedures.*—Binary aqueous–organic solvent mixtures were prepared gravimetrically. The concentration of dye was 0.10 mmol dm$^{-3}$ in each system except for pure water, which was saturated with the solute. Each solution was scanned four times; absorbance readings were collected at 1.0 nm intervals. From the spectrum, $\lambda_{max}$ for the solvatochromic $\pi \rightarrow \pi^*$ absorption band was determined. The transition energy was calculated with eqn. (8)

$$E_T/\text{kcal mol}^{-1} = \frac{28\,591.5}{\lambda_{max}/\text{nm}} \quad (8)$$

## Results

Table 1 gives measured $E_T$ values for nine aqueous–organic solvent mixtures over the full composition range from $x_2 = 0$ to $x_2 = 1$. Some of these systems have been studied by other workers; we repeated the work because we wanted a large number of data points so as to test our model equations. We did use literature data for several other solvent systems; data on 1,4-dioxane and tetrahydrofuran are from Krygowski *et al.*;[12]

**Table 1** $E_T$ Values for aqueous–organic solvent mixtures

| $x_2$ | $\lambda_{max}$/nm | $E_T$/kcal mol$^{-1}$ |
|---|---|---|
| Methanol | | |
| 0.000 | 453 | 63.1 |
| 0.098 | 471 | 60.7 |
| 0.156 | 478 | 59.8 |
| 0.221 | 485 | 59.0 |
| 0.295 | 494 | 57.9 |
| 0.382 | 496 | 57.6 |
| 0.486 | 507 | 56.4 |
| 0.577 | 506 | 56.5 |
| 0.612 | 507 | 56.4 |
| 0.719 | 510 | 56.1 |
| 0.774 | 510 | 56.1 |
| 0.897 | 516 | 55.4 |
| 1.000 | 516 | 55.4 |
| Ethanol | | |
| 0.033 | 463 | 61.8 |
| 0.070 | 476 | 60.1 |
| 0.113 | 492 | 58.1 |
| 0.163 | 509 | 56.2 |
| 0.223 | 515 | 55.5 |
| 0.321 | 527 | 54.3 |
| 0.427 | 530 | 53.9 |
| 0.559 | 535 | 53.4 |
| 0.640 | 541 | 52.8 |
| 0.739 | 545 | 52.5 |
| 0.856 | 546 | 52.4 |
| 0.940 | 550 | 52.0 |
| 1.000 | 553 | 51.7 |
| Propan-1-ol | | |
| 0.026 | 466 | 61.4 |
| 0.040 | 479 | 59.7 |
| 0.055 | 494 | 57.9 |
| 0.072 | 509 | 56.2 |
| 0.091 | 520 | 55.0 |
| 0.134 | 528 | 54.2 |
| 0.200 | 529 | 54.0 |
| 0.270 | 539 | 53.0 |
| 0.366 | 538 | 53.1 |
| 0.425 | 540 | 52.9 |
| 0.494 | 546 | 52.4 |
| 0.581 | 549 | 52.1 |
| 0.687 | 555 | 51.5 |
| 0.818 | 560 | 51.1 |
| 0.925 | 564 | 50.7 |
| 1.000 | 564 | 50.7 |
| Propan-2-ol | | |
| 0.025 | 463 | 61.8 |
| 0.054 | 476 | 60.1 |
| 0.088 | 506 | 56.5 |
| 0.129 | 522 | 54.8 |
| 0.180 | 529 | 54.0 |
| 0.270 | 541 | 52.8 |
| 0.364 | 547 | 52.3 |
| 0.421 | 554 | 51.6 |
| 0.491 | 556 | 51.4 |
| 0.576 | 576 | 49.6 |
| 0.683 | 576 | 49.6 |
| 0.821 | 576 | 49.6 |
| 0.923 | 582 | 49.1 |
| 1.000 | 591 | 48.4 |
| Ethane-1,2-diol | | |
| 0.031 | 463 | 61.8 |
| 0.073 | 467 | 61.2 |
| 0.115 | 472 | 60.6 |
| 0.168 | 480 | 59.6 |
| 0.247 | 480 | 59.6 |
| 0.329 | 486 | 58.8 |
| 0.433 | 494 | 57.9 |
| 0.494 | 499 | 57.3 |

**Table 1** (*continued*)

| $x_2$ | $\lambda_{max}$/nm | $E_T$/kcal mol$^{-1}$ |
|---|---|---|
| Ethane-1,2-diol | | |
| 0.566 | 498 | 57.4 |
| 0.648 | 498 | 57.4 |
| 0.746 | 503 | 56.8 |
| 0.861 | 510 | 56.1 |
| 0.940 | 510 | 56.1 |
| 1.000 | 510 | 56.1 |
| Dimethyl sulfoxide | | |
| 0.027 | 470 | 60.8 |
| 0.059 | 476 | 60.1 |
| 0.096 | 489 | 58.5 |
| 0.142 | 499 | 57.3 |
| 0.205 | 514 | 55.6 |
| 0.279 | 527 | 54.3 |
| 0.375 | 554 | 51.6 |
| 0.505 | 577 | 49.6 |
| 0.590 | 603 | 47.4 |
| 0.696 | 605 | 47.3 |
| 0.829 | 614 | 46.6 |
| 0.925 | 628 | 45.5 |
| 1.000 | 639 | 44.7 |
| Acetone | | |
| 0.025 | 469 | 61.0 |
| 0.056 | 483 | 59.2 |
| 0.092 | 492 | 58.1 |
| 0.134 | 504 | 56.7 |
| 0.204 | 519 | 55.1 |
| 0.279 | 531 | 53.8 |
| 0.375 | 545 | 52.5 |
| 0.435 | 550 | 52.0 |
| 0.504 | 552 | 51.8 |
| 0.587 | 563 | 50.8 |
| 0.693 | 570 | 50.2 |
| 0.769 | 586 | 48.8 |
| 0.825 | 595 | 48.1 |
| 0.890 | 604 | 47.3 |
| 0.924 | 636 | 45.0 |
| 0.963 | 644 | 44.4 |
| 1.000 | 679 | 42.1 |
| Acetonitrile | | |
| 0.017 | 468 | 61.1 |
| 0.036 | 477 | 59.9 |
| 0.056 | 477 | 59.9 |
| 0.077 | 477 | 59.9 |
| 0.100 | 487 | 58.7 |
| 0.124 | 489 | 58.5 |
| 0.151 | 497 | 57.5 |
| 0.179 | 502 | 57.0 |
| 0.210 | 504 | 56.7 |
| 0.244 | 509 | 56.2 |
| 0.283 | 510 | 56.1 |
| 0.324 | 514 | 55.6 |
| 0.370 | 513 | 55.7 |
| 0.422 | 517 | 55.3 |
| 0.481 | 517 | 55.3 |
| 0.547 | 521 | 54.9 |
| 0.627 | 529 | 54.0 |
| 0.719 | 532 | 53.7 |
| 0.823 | 544 | 52.6 |
| 0.837 | 545 | 52.5 |
| 0.893 | 559 | 51.1 |
| 0.918 | 565 | 50.6 |
| 0.945 | 576 | 49.6 |
| 0.973 | 592 | 48.3 |
| 1.000 | 640 | 44.7 |
| *N*,*N*-Dimethylformamide | | |
| 0.025 | 467 | 61.2 |
| 0.055 | 480 | 59.6 |
| 0.090 | 490 | 58.3 |
| 0.132 | 503 | 56.8 |
| 0.184 | 507 | 56.4 |
| 0.265 | 532 | 53.7 |
| 0.359 | 544 | 52.6 |
| 0.417 | 557 | 51.3 |
| 0.487 | 562 | 50.9 |
| 0.572 | 588 | 48.6 |
| 0.680 | 600 | 47.7 |
| 0.819 | 622 | 46.0 |
| 0.921 | 642 | 44.5 |
| 1.000 | 653 | 43.8 |

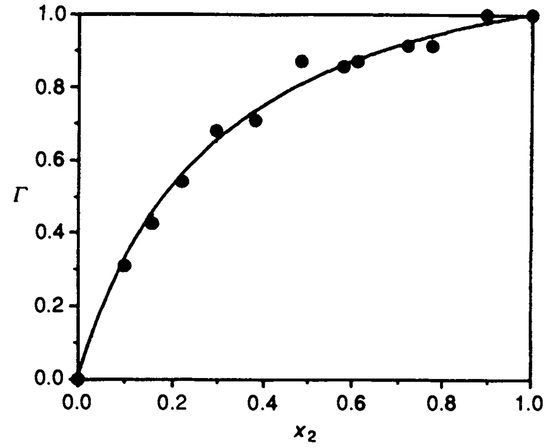

**Fig. 1** Plot of the experimental variable $\Gamma$ against mole fraction of organic component $x_2$ for the methanol–water system. The points are experimental (calculated from Table 1) and the line is drawn with eqn. (3) and the parameter value in Table 2.

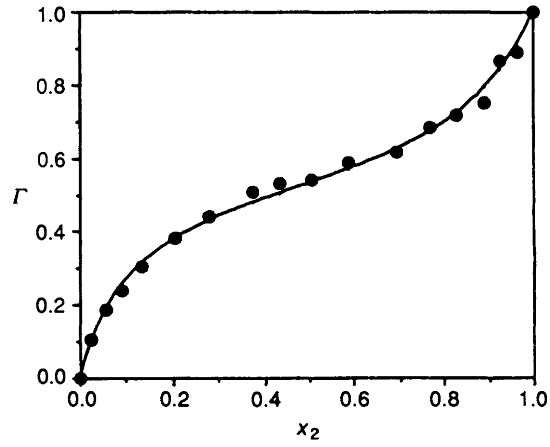

**Fig. 2** Plot of $\Gamma$ against $x_2$ for the acetone–water system. The points are experimental and the line is drawn with eqn. (7)

propane-1,2-diol and propane-1,3-diol data are from Kosower *et al.*;[13] and the amine results are from Dimroth and Reichardt.[14] In all, we have analysed 17 cosolvent systems.

The solvents appear to fall into two classes. Solvents whose behaviour can be described by eqn. (3) we will call 1-step solvents; those described by eqn. (7) we call 2-step solvents. (Of course it is always possible to achieve better curve-fits by increasing the number of parameters in the model equation, but we have adopted the parsimony principle and have used the minimum number of parameters required to give curve-fits commensurate with the experimental uncertainties.)

Figs. 1, 2 and 3 show several solvents and the curve-fits achieved with this treatment. Fig. 1 is of the methanol system, a

Table 2 Model parameter values for the dependence of $E_T(30)$ on solvent composition in aqueous–organic mixtures[a]

| No. | Organic solvent | Class | $K_1$ | $K_2$ | $E_T(30)$[b] | log $P$[c] |
|---|---|---|---|---|---|---|
| 2 | Methanol | 1-step | 4.4(0.2) | — | 55.4 | −0.74 |
| 5 | Ethanol | | 6.1(0.4) | — | 51.7 | −0.32 |
| 6 | Propan-1-ol | | 12.2(1.1) | — | 50.7 | +0.34 |
| 7 | Propan-2-ol | | 6.4(0.5) | — | 48.4 | 0.00 |
| 1 | Ethane-1,2-diol | | 3.9(0.3) | — | 56.1 | −1.93 |
| 4 | Propane-1,2-diol | | 7.1(0.5) | — | 54.0 | −1.35 |
| 3 | Propane-1,3-diol | | 7.3(0.2) | — | 54.9 | −1.64 |
| 8 | Dimethyl sulfoxide | | 2.8(0.1) | — | 44.7 | −2.03 |
| 11 | Acetone | 2-step | 10.1(0.7) | 0.18(0.01) | 42.1 | −0.24 |
| 9 | Acetonitrile | | 7.9(0.5) | 0.05(0.01) | 44.7 | −0.34 |
| 16 | Dioxane | | 8.8(0.7) | 0.28(0.02) | 36.0 | −0.42 |
| 14 | Tetrahydrofuran | | 22.3(1.2) | 0.17(0.01) | 37.4 | +0.22[d] |
| 10 | Dimethylformamide | | 8.8(0.9) | 0.74(0.07) | 43.8 | −0.73 |
| 17 | Piperidine | | 20.1(1.0) | 0.44(0.03) | 35.5 | +0.85 |
| 15 | 2,6-Lutidine | | 49.6(6.4) | 0.34(0.04) | 36.7 | +2.30 |
| 13 | 2-Picoline | | 31.0(3.3) | 0.42(0.04) | 38.3 | +1.06 |
| 12 | Pyridine | | 18.5(1.7) | 0.42(0.04) | 40.3 | +0.65 |

[a] Quantities in parentheses are standard deviations. [b] Of the pure solvent. [c] From ref. (15) except as noted. [d] From ref. (16).

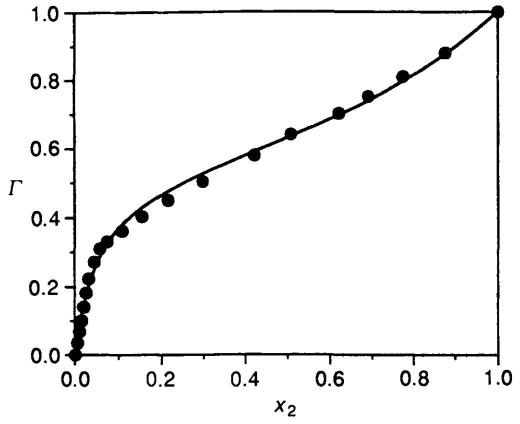

Fig. 3 Plot of $\Gamma$ against $x_2$ for the piperidine–water system. The points are experimental and the line is drawn with eqn. (7)

1-step solvent; such a solvent shows a hyperbolic concentration dependence characteristic of a simple 1 : 1 stoichiometric binding relationship. Figs. 2 and 3 show 2-step solvents, the acetone curve being 'classical' in its sigmoid appearance, evidence of a 3-state process; the piperidine curve shows the inflection point characteristic of 2-step behaviour, but the curve is less symmetrical than the acetone curve. The quality of the curve-fits in these figures is typical; as a curve-fit criterion we define $s$, the percentage standard deviation of the experimental points about the fitted line, by eqn. (9) where $n$ is the number of

$$s = 100\left[\frac{\Sigma(\Gamma_{\text{calc}} - \Gamma_{\text{obs}})^2}{n - 2}\right]^{\frac{1}{2}} \qquad (9)$$

data points in a study, including the two pure solvents. The measure $s$ had an average value of 2.9% for the 17 solvent systems; for methanol (Fig. 1), $s$ = 2.7%, for acetone (Fig. 2), $s$ = 1.8% and for piperidine (Fig. 3), $s$ = 1.7%.

The model parameter values were determined by fitting experimental data to either eqns. (3) or (7), as appropriate, by nonlinear regression with the program Systat®. Table 2 gives the parameter values and their uncertainties. [The table also lists values of $E_T(30)$ and log $P$ of the pure solvents for later convenience; $P$ is the octan-1-ol–water partition coefficient.]

## Discussion

*Classification of Solvents.*—There is a connection between the class assignment of the organic cosolvent and the $E_T$ value of the pure cosolvent, as revealed by the listing in Table 2. If $E_T$ is greater than about 48, the solvent is a 1-step solvent, and if $E_T$ is less than about 42, it is a 2-step solvent. Within the range $42 \leqslant E_T \leqslant 48$ a solvent may belong to either class. Inspection of the experimental curve of measured $E_T$ against $x_2$ usually allows the assignment to be made; 1-step solvents show a simple hyperbolic binding isotherm, whereas 2-step solvents show an inflection point. (It is possible that the application of two criteria to classification may be unambiguous; thus on the basis of the 17 solvents studied we can say that a solvent is a 1-step solvent if its $E_T$ is greater than 47 *or* its log $P$ is less than −1.)

It might be questioned whether classification into two groups is needed, inasmuch as the 'simpler' 1-step solvents could be analysed as 2-step solvents. This is certainly possible, but it does not seem to be justified. When this treatment is applied, the values of $K_1/K_2$ (for 1-step solvents) turn out to be about 4 (within a factor of 2). This means, at least approximately, that if these are 2-step solvents, the putative binding sites are identical and independent, and a single parameter, $K_1$, suffices to describe the results. Thus to attribute additional meaning to a second parameter would be unjustified. In such cases, the $K_1$ evaluated from a 2-step treatment is about twice that found from a 1-step treatment [as is expected from substituting $K_2 = K_1/4$ into eqn. (7)]. This phenomenon, in which a 2-step treatment sometimes yields the result $K_1/K_2 \approx 4$, arises also in the analysis of surface tension data.[4]

The characteristic shape of 2-step solvent systems arises from the parameter behaviour in which $K_1 > 1$ and $K_2 < 1$. Chemically this implies that the first organic cosolvent molecule preferentially displaces a water molecule from the solvation shell ($K_1 > 1$), whereas the last water molecule is difficult to dislodge. (We have elsewhere[6] noted that a 2-step, 3-state treatment may function as a widely applicable description because the intermediate state may actually represent an assemblage of partially hydrated, partially cosolvated states.) A species distribution diagram for acetone is shown in Fig. 4, which displays the dominance of the partially cosolvated species over a very wide composition range. Langhals[17] has proposed a method using the Dimroth–Reichardt dye as a probe for determining the water content of organic solvents; clearly this method will have a higher sensitivity for 2-step

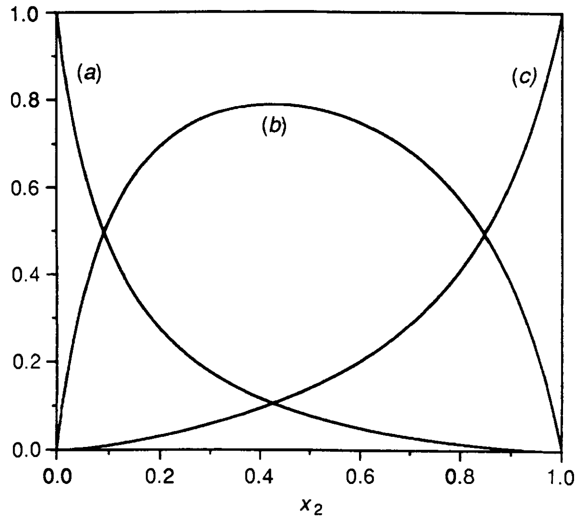

**Fig. 4** Species distribution diagram for the acetone–water system. The quantities $F_{WW}$, $F_{WM}$, and $F_{MM}$ represent fractions of solute in the fully hydrated, partially cosolvated, and fully cosolvated forms, respectively.

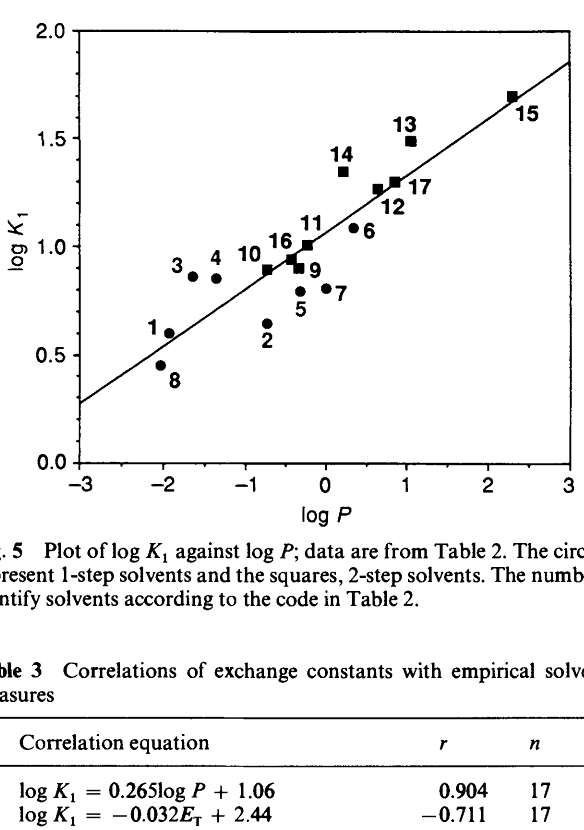

**Fig. 5** Plot of log $K_1$ against log $P$; data are from Table 2. The circles represent 1-step solvents and the squares, 2-step solvents. The numbers identify solvents according to the code in Table 2.

**Table 3** Correlations of exchange constants with empirical solvent measures

| Correlation equation | $r$ | $n$ |
|---|---|---|
| $\log K_1 = 0.265 \log P + 1.06$ | 0.904 | 17 |
| $\log K_1 = -0.032 E_T + 2.44$ | −0.711 | 17 |
| $\log (K_1 \text{ or } K_1K_2)^a = 1.47\beta - 0.37$ | 0.732 | 11 |
| $\log (K_1 \text{ or } K_1K_2)^a = 0.016\Delta H^\circ - 1.06$ | 0.872 | 7 |
| $\log K_2 = 2.30\beta - 1.82$ | 0.826 | 6 |
| $\log K_2 = 0.0131\Delta H^\circ - 1.83$ | 0.794 | 6 |

[a] $K_1$ for 1-step solvents; $K_1K_2$ for 2-step solvents.

solvents because of the $K_2$-determined gradient of the function $\Gamma$ at high values of $x_2$.

*Parameter Correlations.*—The parameter values given in Table 2 can be correlated with several empirical measures. Perhaps the most useful, as the most general, of these is shown in Fig. 5 as a plot of log $K_1$ against log $P$. This quite convincing trend of log $K_1$ with log $P$ permits log $K_1$ to be predicted for a cosolvent to within 0.3 unit in log $K_1$. Table 3 gives the equation of the line in Fig. 5, and it also lists some other correlations that have been found. In this table, log $P$ and $E_T(30)$ for the pure solvents are given in Table 2; $\beta$ is the Taft-Kamlet solvatochromic measure of solvent hydrogen bond basicity;[18] and $\Delta H^\circ$ is the enthalpy change for boron trifluoride–solvent Lewis acid–base complex formation in dichloromethane.[19] The premise behind the plots of log $K_1$ (for 1-step solvents) or log $K_1K_2$ (for 2-step solvents) is that these quantities are comparable because each ($K_1$ or $K_1K_2$) is responsible for defining the overall conversion of fully hydrated to fully cosolvated solute in its respective class.

In considering the meaning of these correlations it is helpful to write eqns. (3) and (7) in the form of eqns. (10) and (11).

$$\delta_M E_T = \frac{\Delta E_T K_1 x_2}{x_1 + K_1 x_2} \tag{10}$$

$$\delta_M E_T = \frac{\Delta E_T K_1 x_1 x_2 / 2 + \Delta E_T K_1 K_2 x_2^2}{x_1^2 + K_1 x_1 x_2 + K_1 K_2 x_2^2} \tag{11}$$

In these equations $\delta_M E_T = E_T(x_2) - E_T(W)$ and $\Delta E_T = E_T(M) - E_T(W)$. Thus $\Delta E_T$ gives the maximum amplitude of the dependent variable $\delta_M E_T$, whereas $K_1$ and $K_2$ determine its path. The correlations in Table 3 concern $K_1$ and $K_2$, although, since there is some relationship between $K_1$ and $E_T$, the amplitudes and paths are not fully independent.

We have seen that the exchange constants are correlated with log $P$, $\beta$ and $\Delta H^\circ$. Together, these correlations implicate hydrophobicity (through log $P$) and electron-pair donor ability (through $\beta$ and $\Delta H^\circ$) as dominant solvent characteristics that control $K_1$ and $K_2$.

## Conclusions

(1) The dependence of $E_T(30)$ on solvent composition in binary aqueous–organic solvent mixtures can be quantitatively described over the *entire* composition range by the phenomenological model of solvation effects.

(2) Organic cosolvents are classified as '1-step' solvents if a single solvation equilibrium constant, $K_1$, suffices to describe the $E_T$ behaviour, or as '2-step' solvents if two constants, $K_1$ and $K_2$, are required. 1-step solvents tend to be highly polar or to possess hydroxy groups. The separation of organic solvents into two classes based on polarity has also been noticed in surface tension[4] and solubility[3] analyses.

(3) The solvation parameters are positively correlated with the empirical solvent measures log $P$,[15] $\beta$,[18] and $\Delta H^\circ$,[19] implying that solvent hydrophobicity and electron-pair donor ability are solvent characteristics controlling these parameters.

## Acknowledgements

This work was supported in part by a grant from Glaxo, Inc. R. D. S. was a Fellow of the American Foundation for Pharmaceutical Education and of Bristol-Myers Squibb, Inc.

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*Paper* 3/06277E
*Received* 20*th October* 1993
*Accepted* 6*th December* 1993