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The Use of Solvent E_T-values in High Pressure Kinetics

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The solvatochromic shift and its pressure dependence of the charge transfer band of 2,4,6-triphenyl-pyridinium-*N*-(3,5-diphenyl-)phenol betaine (E_T-values) have been measured together with partial molar volumes of the betaine in a number of solvents.

Despite the relative success of the Kirkwood theory, considerable effort[1] has been made to replace it by a more general description of the influence of various solvents on chemical equilibria and rate constants. Since the physical forces that govern solute-solvent interactions differ widely in strength and range it seems most unlikely that a comparatively simple theory will exceed the Kirkwood theory. An alternative is to try and replace the theoretical description by an empirical approach. Among the latter, the scale of E_T values, which was originally derived by Dimroth and coworkers[2,3] from the solvatochromic effect on the charge transfer band of 2,4,6-triphenyl-pyridinium-*N*-(3,5-diphenyl-)phenol betaine, has deserved the most interest.[4]

The present study was undertaken in order to investigate whether: 1. the effect of pressure on E_T might be a useful parameter to describe the overall variation of solvent properties with applied pressure; 2. the zwitterionic ground state of the betaine could prove to be a good model for ionic transition states as may be demonstrated by studying the solvent dependence of the partial molar volume of the betaine itself. In view of some recent publications[5-8] the limitations and the reliability of the parameters E_T, dE_T/dp and $\bar{V}$ will be critically discussed.

Experimental

The synthesis of the 2,4,6-triphenyl-pyridinium-*N*-(3,5-diphenyl-)phenol betaine was conducted according to literature procedures[2] and yielded a product with one mole of water of crystallization (formula $C_{41}H_{24}NO \cdot H_2O$, mol wt 563.71). A determination of its molecular weight in solution by the vapor pressure depression method indicated that, even at the highest concentrations (*ca.* 10^{-2} M in CH_2Cl_2), no detectable dimerization takes place. All solvents were purified according to standard procedures.

Precision density measurements of the betaine solutions were carried out using a DMA 02C instrument (Anton Paar K.G.) at 25 °C. The temperature was controlled to within ±0.001 °C and monitored by a Hewlett-Packard 280 A quartz thermometer. Spectrophotometric studies were made with a Zeiss DMR 10 instrument equipped with a high pressure attachment which is described elsewhere.[9]

Results and Discussion

Solvatochromic Shifts. The band maximum, λ_{max}, of the intramolecular charge transfer transition of the betaine shows the most remarkable solvatochromic shift so far known. The values of λ_{max} given in Table 1 agree with the results of a number of previous investigations.[2-4] As has been already discussed by Dimroth[2] and Reichardt,[4] generally the more polar the solvent, the more λ_{max} is blue-shifted. Two distinct classes of solvents have emerged: protic and aprotic.

There are many examples[7,10] in which linear free energy relationships satisfactorily hold for the solvent dependence of rate constants of reactions with polar routes and the E_T values of the pure solvents. The concept to use the E_T values of the betaine as a microprobe monitoring local polarities within a solvent might be of even more interest in mixed solvents than in pure ones. The rate constants of the Menschutkin reaction: 3,5-lutidine+ethyl iodide, have been shown to perfectly follow a ln *k vs.* E_T relationship in benzene–nitrobenzene mixtures.[7] The E_T values of two mixed systems with widely differing dielectric constants have been measured during this study: water–dioxane and methanol–dichloromethane (Fig. 1). For the system water–dioxane the shape of the $E_T(x)$ (x=mole fraction) function is very different from that of the $q(x)=(D(x)-1)/(2D(x)+1)$ parameter. Kinetic data on the hydrolysis of the 1-chloro-2-nitroethane, chlorodiphenyl-

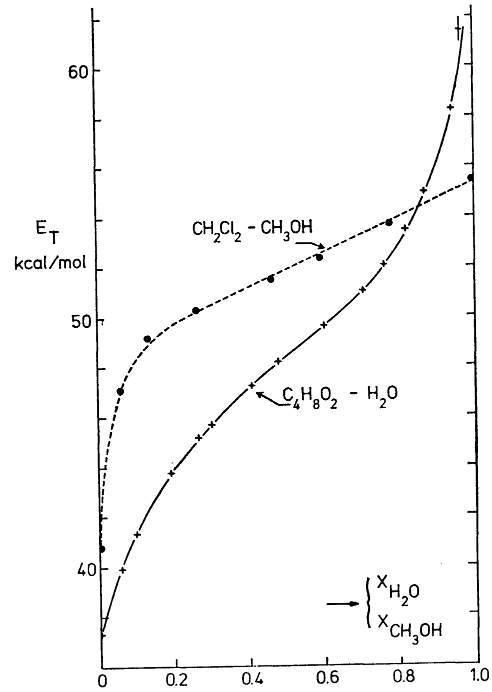

Fig. 1. Variation of solvent E_T parameters in mixed solvents.
——: Dioxane–water, ------: dichloromethane–methanol.

methane, and benzoylchloride[11] show that in water–dioxane mixtures (excluding very high and very low mole fractions) a linear dependence $\ln k \approx E_T$ is found only in the latter case. For the former reactions no preference of E_T above q can be established. In the inorganic field, data of Burgess *et al.*[12,13] show that in water–dioxane either E_T, or Y (Winstein-Grunwald parameter) or q correlate with $\ln k$. The rate constants for the isomerization of *trans*-diaquobis(oxalato)-chromate(III) anions in water–dioxane mixtures[14] closely obey a linear free energy relationship with E_T. Thus the choice of the proper parameter depends crucially on the reacting system in question.

A close inspection of the E_T values in water–dioxane mixtures reveals that E_T is influenced by several effects. The sharp decline of E_T when small amounts of dioxane are added in the water rich region ($1 > x_{H_2O} > 0.8$) is similar to the decline of the dielectric constant, but *not* of q. Thus E_T seems to be sensitive to the rupture of the water structure. The hydrophobic interactions between the phenyl substituents of the betaine and the solvent obviously play a major part in determining E_T. In the dioxane rich region ($x_{\text{dioxane}} \geqq 0.8$) the functions $q(x)$ and $E_T(x)$ are very similar. Thus lowering the ground state of the betaine by dipolar interactions is dominant when the dielectric constant of the mixture is increased by adding water. How far specific solvation interactions between the positions of very high charge density within the betaine molecule and the polar water molecules are reflected in E_T is not known. The existance of such a type of interaction can be concluded from the fact that the betaine contains water of crystallization, but is insoluble in pure water. An attempt to gain further insight into these interactions failed because the betaine has no triplet ESR spectrum which could give information about the distribution of electron density within the molecule. Furthermore, the experimental dipole moment of 12 Debye[3] does not agree with a simple $N^+—O^-$ dipole. However, the existence of some preferential solvation by the polar component of a mixture is also evident from the E_T values in dichloromethane–methanol mixtures. Minor amounts of methanol in dichloromethane drastically increase E_T as is shown in Fig. 1.

Table 1. Absorption maximum of charge transfer band, λ_{max}, blue-shift of λ_{max} under pressure and partial molar volumes, $\bar{V}$, of 2,4,6-triphenylpyridinium-*N*-(3,5-diphenyl)phenol betaine in different solvents

Solvent	$D^{a)}$	q	λ_{max} nm	$d\lambda/dP \cdot 10^3$ nm/atm	$\bar{V}$ ml/mol
$CHCl_3$	4.70	0.356	732	8	455.1±2.7
CH_2Cl_2	8.9	0.420	700	7	451.2±1.4
$(CH_3)_2CO$	20.5	0.464	684	6	417.0±3.6
$(CH_3)_2NCHO$	36.7	0.480	653	4	445.7±2.4
$(CH_3)_2SO$	48.9	0.485	634	4	462.6±3.8
CH_3CN	37.5	0.480	625	5	440.4±3.4
C_2H_5OH	24.3	0.470	550.5	5	426±20
CH_3OH	32.6	0.477	515	6	421±10

a) Ref. 4 and the references quoted therein.

Piezo-Solvatochromic Shifts. Generally, when hydrostatic pressure is applied on a solution of the betaine the charge transfer band is blue-shifted. The total effect at 1000 bar, however, reaches only 4 to 8 nm (Table 1). Considering that the charge transfer band is very broad (width at $\varepsilon_{max}/2$ *ca.* 170 nm in $CHCl_3$ at 25 °C) and unsymmetrical, the accuracy in determining λ_{max} may be expected to be *ca.* ±1 nm at best. Thus within our experimental conditions no definite trend between $\Delta\lambda_{max}/\Delta P$ and the nature of the various solvents could be established. This is despite the varied nature of the solvents employed. Therefore we are convinced that the effect of pressure on the betaine charge transfer band is not a suitable indicator of the sum of all the pressure dependent solvent-solute interactions. In particular, no useful empirical parameter could be derived from $\Delta\lambda_{max}/\Delta P$ of the betaine describing the rearrangement of solvent structure in the vicinity of a dipolar species under various external pressures. The linear dependence of $\ln k(P)$ *vs.* $\Delta\lambda_{max}/\Delta P$ reported for two Menschutkin reactions in two solvents[5,8] seems to be more or less accidental in view of the limited range and accuracy of the $\Delta\lambda_{max}/\Delta P$ parameter. On the contrary, the values of $\Delta\lambda_{max}/\Delta P$ can be explained satisfactorily on the basis of the simple Kirkwood theory taking into account the pressure dependence of the macroscopic dielectric constant (q_P-parameter). Therefore we conclude that under pressure mainly the ground state of the betaine is lowered by dipolar solvent-solute interactions. How far the less polar excited state of the betaine, which according to the Franck Condon principle is not in thermodynamic equilibrium with its solvation shell, is influenced by pressure is not known. An attempt to determine the effect of pressure on the excited state failed because no fluorescence spectrum of the betaine could be found. It is most probable that the solvent structure around an excited nonpolar betaine molecule is very similar to that around the very polar ground state.[8] Only the induced dipole moments of the solvent molecules can follow the optical transition of the betaine. However, interaction with induced dipole moments is known to be comparatively small.

Partial Molar Volumes. The apparent molar volumes, φ_i, were determined according to the equation

$$\varphi_i = M/d_0 - (d_i - d_0)\cdot 1000/c_i \cdot d_0,$$

where M is the molecular weight of the betaine and c_i is its molar concentration, while d_i and d_0 are the densities of the solution and the pure solvent, respectively. Within experimental errors, no concentration dependence of φ_i was observed, which may be expected considering the relatively low concentration range studied, *i.e.*, $c \leqq 0.02$ M. Thus the partial molar volumes $\bar{V}$, of the betaine were merely taken from the average values of φ_i over the entire concentration range.

These values, which are listed in Table 1, certainly show no distinctive trend with solvent polarity parameters such as D, q, or E_T. Thus the effects that govern the solvent dependence of $\bar{V}$ are not solely of a dipolar origin (electrostriction). Therefore, we conclude that with respect to partial molar volumes the dipolar ground state of the betaine is not a suitable model for ionic transition states in chemical kinetics, *e.g.* in Menschutkin reactions. Of all possible solvent parameters the $\bar{V}$ values of the betaine correlate best with the compressibilities and internal pressures of the different solvents. Following Dack's arguments,[15] such a behaviour is caused by the sum of all solvent-solute interactions as well as "the ability of the solvent to create cavities absorbing the intrinsic volume" of the betaine. Unfortunately, the individual contributions to $\bar{V}$ such as: electrostriction due to charge-dipole and dipole-dipole interactions; hydrogen bonding; hydrophobic and van der Waals interactions, *etc.* cannot be separated. Despite the severe limitations of the Kirkwood theory, so far the $q_P=\frac{\partial}{\partial P}\left(\frac{D-1}{2D+1}\right)$-parameter seems to best describe the large electrostriction effects found when the solvent dependence of activation volumes in polar reactions is studied.

It is obvious from the above arguments that a lot of questions on solute-solvent interactions, which were hoped to be "solved" by introducing empirical parameters, are still open. In view of the many exceptions that exist, both when the Kirkwood theory or the scale of E_T values is used, the choice of a proper description of solvent effects depends on the system studied and perhaps on personal judgement as to whether one prefers an oversimplified but theoretically based physicochemical treatment, or a more overall empirical approach.

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