DETERMINATION OF THE EMPIRICAL POLARITY PARAMETER $E_T(30)$ FOR BINARY SOLVENT MIXTURES[*]

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Empirical solvent polarity parameters $E_T(30)$ were determined by UV–visible spectrophotometry using Dimroth– Reichardt's betaine dye, as a function of composition, for (aprotic + aprotic) and (aprotic + protic) binary solvent mixtures. For (aprotic + aprotic) solvent systems the cosolvent was toluene, and the other solvents used were selected with different structural characteristics and an extensive range of polarity: chloroform, 1,4-dioxane, ethyl acetate, tetrahydrofuran, acetone, nitromethane and N,N-dimethylformamide. For (aprotic + protic) solvent systems, the protic cosolvent used was methanol, and the aprotic solvents selected were toluene, chloroform, 1,1,1-trichloroethane, tetrahydrofuran, acetone, N,N-dimethylformamide, and dimethyl sulphoxide. Each system was analysed according to its deviations from additivity due to selective solvation of the betaine. A preliminary application of these empirical solvent polarity parameters was related to the solvent effects in a simple example of a nucleophilic aromatic substitution reaction.

INTRODUCTION

The strong influence of solvents in chemical and physical processes (reaction rates, mechanisms, selectivity, chemical equilibrium, position and intensity of spectral absorption bands, liquid chromatographic separations) has been well established. The effects are explained in terms of 'solvent polarity', defined as the overall solvation capability that depends on all possible (specific and non-specific) intermolecular interactions between solute and solvent molecules.[2a]

In the last 30 years, numerous polarity scales have been proposed. The scales based on the single-parameter approach include Dimroth–Reichardt's E_T30,[3a] Brooker's χ_R,[3b] Walter's ε_K,[3c] Brownstein's S,[3d] Kosower's Z,[3e] Dubois–-Bienvenue's Φ,[3f] Allerhand and Schleyer's G,[3g] Knauer and Napier's $\mathscr{A}_N$,[3h] Gutmann's AN and DN[3i] and Kamlet and Taft's π^*.[3j] These scales are based on the spectral absorption of a single indicator dye. In addition, some multiparametric correlation equations using singular empirical parameters were described by Koppel and Palm (Y, P, B and E

parameters),[4a] Krygowski and Fawcett ($E_T(30)$, DN parameters),[4b] Dougherty (IP, EA parameters),[4c] Fowler *et al.* (E_T, ε parameters),[4d] Swain *et al.* (A, B parameters)[4e] and Kamlet *et al.* (π^*, α, β parameters).[4f] The π^* scale focuses on the average UV–visible spectral data for a set of solvatochromic solutes. More recently, Buncel and Rajagopal's π^*_{azo} polarity scale[5] (based on the UV–visible spectral behaviour of a set of merocyanine azo dyes) was reported as an alternative to the π^* scale. Later, Drago's unified polarity scale[6a] and the extended model[6b] were also presented.

In this connection, most of the work reported was concerned with empirical polarity parameters for pure solvents, and considerable effort has been made to elucidate the extent to which various parameters for pure solvents are correlated. This work was aimed at reporting empirical solvent polarity parameters $E_T(30)$ for several binary solvent systems to facilitate multiple applications of this solvent polarity scale to chemical reactivity, analytical chemistry and physical processes.[7]

RESULTS AND DISCUSSION

The empirical solvent polarity parameter $E_T(30)$ was determined for (aprotic + aprotic) binary solvent system (cosolvent toluene) and (aprotic + protic) binary solvent systems (cosolvent methanol). $E_T(30)$ is defined as the molar transition energy (kcal mol^{-1}) derived from the longest-wavelength solvatochromic absorption band of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye)[2a] (1). $E_T(30)$ values have been reported for more than 300 pure solvents and some binary solvent mixtures.[2b,2d]

The betaine dye presents a strongly negative solvatochromism owing to its highly dipolar electronic ground state relative to its less dipolar excited state. It exhibits a significant permanent dipole moment (suitable for dipole–dipole and dipole–induced dipole interactions), a large polarizable π-electron system (π-systems and dispersion interactions), a substantial negative charge on the phenoxide oxygen [highly basic electron-pair donor centre suitable for hydrogen-bonding donor (HBD) and electron-pair donor (EPD) electron-pair acceptor (EPA) bonding] and a positive charge on the pyridinium nitrogen (sterically shielded). Therefore, the solvation effect of the betaine is more important for HBD and EPA solvents than for EPD solvents.[2b,2c]

The longest-wavelength UV–visible absorption band of 1 was determined by varying the solvent composition systematically. Each binary system was studied at nine molar fractions of cosolvent and $E_T(30)$ values were plotted against composition of the solvent mixtures. The mixed solvent systems were examined for deviations from additivity, and the results were interpreted through selective solvation of 1 in terms of intermolecular betaine–solvent interactions.

(Aprotic + toluene) solvent systems

The aprotic cosolvent selected was the aromatic solvent toluene [$\varepsilon_{25} = 2\cdot34$, $\mu = 0\cdot36$ D, $E_T(30) = 33\cdot9$ kcal mol^{-1} (1 kcal = 4·184 kJ)] since it possesses a small permanent dipole moment and a π-electron system
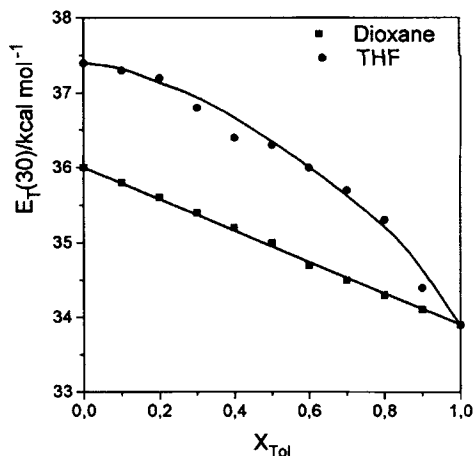

Figure 1. Plot of $E_T(30)$ vs cosolvent mole fraction for (dioxane + toluene) and (THF + toluene) solvent systems

which contains neither electron-pair donor center nor an electron-pair acceptor center, so it does not compete with the betaine dye for EPD/EPA and HBD solvents. Molecular interactions in the pure solvent are weak and the solvation effect of the betaine dye is poor, owing to π-electron interactions. The results are given in Table 1.

Figure 1 shows the shifts in molecular transition energy $E_T(30)$ with increase in toluene concentration for (1,4-dioxane + toluene) and (THF + toluene) solvent systems. 1,4-Dioxane [$\varepsilon_{25} = 2\cdot21$, $\mu = 0$ D, $E_T(30) = 36\cdot0$ kcal mol^{-1}] has a cyclic structure with two electron-pair donor centers and without a permanent dipole moment, so that molecular interactions in the pure solvent and in the 1,4-dioxane–cosolvent are weak. The (1,4-dioxane + toluene) system exhibits a decrease of $E_T(30)$ values as a linear function of cosolvent mole fraction, suggesting additivity.[8,9] THF [$\varepsilon_{25} = 7\cdot58$, $\mu = 1\cdot63$ D, $E_T(30) = 37\cdot4$ kcal mol^{-1}] has a cyclic structure, one electron-pair donor centre and a permanent dipole moment. The (THF + toluene) system shows a continuous non-linear decrease in $E_T(30)$ values with

Table 1. $E_T(30)$ values (kcal mol^{-1}) for (aprotic + toluene) binary solvent systems

| Solvent | Toluene | mole | fraction | | | | | | |
	0·10	0·20	0·30	0·40	0·50	0·60	0·70	0·80	0·90
Dioxane	35·8	35·6	35·4	35·2	35·0	34·7	34·5	34·3	34·1
Tetrahydrofuran	37·3	37·2	36·8	36·4	36·3	36·0	35·7	35·3	34·4
Ethyl acetate	37·9	37·6	37·4	37·1	36·8	36·6	36·3	36·0	35·7
Chloroform	39·0	39·1	38·9	38·6	38·2	37·8	37·4	36·9	36·4
Acetone	41·8	41·3	40·7	40·0	39·6	39·1	38·5	38·1	37·6
N,N-Dimethylformamide	43·5	43·3	42·9	42·5	42·0	41·6	41·1	39·9	37·5
Nitromethane	45·3	44·3	43·4	42·7	42·2	41·6	41·0	40·3	38·7

increase in cosolvent concentration, exhibiting a positive deviation from additivity due to selective solvation of the betaine dye with THF.

Figure 2 shows the shifts in molecular transition energy $E_T(30)$ with increase in toluene concentration for (ethyl acetate + toluene) and (acetone + toluene) solvent systems. Ethyl acetate [$\varepsilon_{25} = 6\cdot02$, $\mu = 1\cdot78$ D, $E_T(30) = 38\cdot1$ kcal mol^{-1}] and acetone [$\varepsilon_{25} = 20\cdot7$, $\mu = 2\cdot88$ D, $E_T(30) = 42\cdot2$ kcal mol^{-1}] are polar solvents, typical representatives of donor–acceptor interactions. These solvents interact weakly with the cosolvent and act as acceptors towards the phenoxide oxygen of the betaine dye, forming 1 : 1 complexes that indeed may characterize these systems. Both solvent systems exhibit a region with a gradual linear decrease in $E_T(30)$ values with increase in toluene concentration until $X_{cosolv} \approx 0\cdot85$, owing to a diminishing solvation effect of the 1 : 1 complex.[10] They also show an inflection zone with a large deviation from additivity, leading to a region with a large decrease in $E_T(30)$ values for a relatively small increase in cosolvent concentration, indicating a strong solvation effect due to disappearance of the complexed betaine.

Figure 3 shows the shifts in $E_T(30)$ with increase in toluene concentration for (chloroform + toluene) and (nitromethane + toluene) solvent systems. Chloroform [$\varepsilon_{25} = 4\cdot70$, $\mu = 1\cdot0$ D, $E_T(30) = 39\cdot1$ kcal mol^{-1}] is a polychlorinated solvent, whose hydrogen-bond donor ability has been reported.[11] Nitromethane [$\varepsilon_{30} = 35\cdot87$, $\mu = 4\cdot1$ D, $E_T(30) = 46\cdot3$ kcal mol^{-1}] is a very polar solvent that also presents hydrogen-bond donor ability, and Buncel and Rajagopal[5] included both solvents in the secondary solvent set (sss). The strong negative charge on the phenoxide oxygen of 1 in the electronic ground state can acquire additional solvent stabilization by hydrogen bonding, resulting in increased $E_T(30)$ values.

Figure 3. Plot of $E_T(30)$ vs cosolvent mole fraction for (chloroform + toluene) and (nitromethane + toluene) solvent systems

The plots for these binary systems exhibit two inflection zones [unlike all other (aprotic + toluene) binary systems studied] with different characteristics suggesting dissimilar effects of solvation of the betaine dye for each one.

Figure 4 shows the shifts in molecular transition energy $E_T(30)$ with increase in toluene concentration for the (DMF + toluene) solvent system. DMF [$\varepsilon_{25} = 36\cdot71$, $\mu = 3\cdot82$ D, $E_T(30) = 43\cdot8$ kcal mol^{-1}] is a very polar solvent capable of electron-pair acceptor interactions, but the acceptor centre is sterically shielded owing to the N-methyl groups. This solvent system exhibits two regions with non-linear decreases in $E_T(30)$ values versus toluene concentration and an inflection
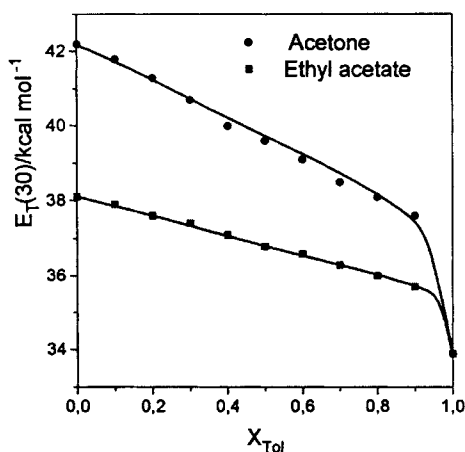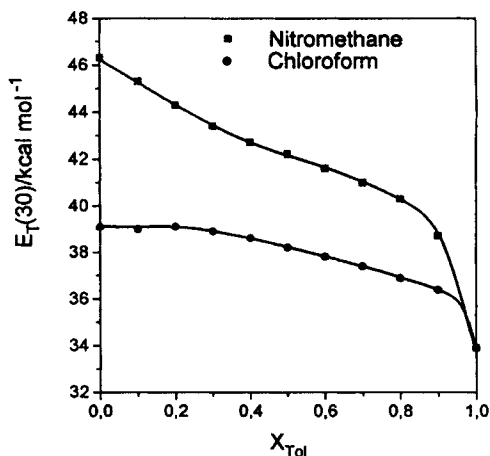

Figure 2. Plot of $E_T(30)$ vs cosolvent mole fraction for (ethyl acetate + toluene) and (acetone + toluene) solvent systems
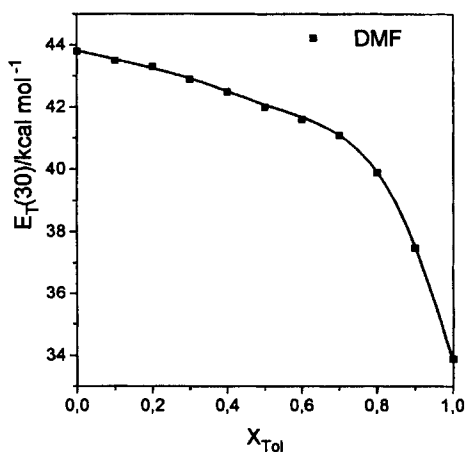

Figure 4. Plot of $E_T(30)$ vs cosolvent mole fraction for (acetone + toluene) solvent system

region that exhibits a large deviation from additivity [corresponding to toluene concentrations smaller than for the other (aprotic + toluene) solvent systems]. This behaviour suggests that betaine–DMF intermolecular interactions compete with interactions between DMF molecules and that the selective solvation effect of the betaine dye by DMF is less important.

(Aprotic + methanol) solvent systems

The cosolvent selected was methanol [$E_T(30)$ = $55\cdot5$ kcal mol^{-1}], a hydroxylic, polar, protic solvent, known to form strong hydrogen bonds and able to act both as a donor and as an acceptor. Since alcohols can play dual roles, as HBD–HBA, they are classified as amphiprotic solvents and extensive self-association in the pure solvents is well known.[12] Methanol exhibits high values of HBD acidity ($\alpha = 0\cdot98$) and self-association energy ($\delta_{SA} = 3\cdot0$),[13] with an excellent correlation between the extent of oligomerization and HBD ability. The results are given in Table 2. It was suggested by Reichardt and Eschner[14] that the betaine dye 1 takes part in hydrogen bond formation with alcohols via the phenoxide oxygen and the hydroxylic proton, forming 1 : 1 intermolecular complexes.

Figure 5 shows the shifts in $E_T(30)$ with increase in methanol concentration for the (toluene + methanol) solvent system. This system exhibits the conditions required to apply the analysis that leads to a separation of solute solvation into non-specific and specific components, as described by Drago et al.[6b] because toluene does not compete with the betaine dye to establish specific hydrogen-bonding interactions with methanol. The plot shows a region with large increases in $E_T(30)$ at low methanol concentrations and for relatively small increases in cosolvent concentration, attributed to the specific hydrogen-bonding interactions of methanol with the phenoxide oxygen of 1 ($X_{MeOH} < 0\cdot10$). It also shows an inflection zone that exhibits a large deviation from additivity caused by both specific and non-specific solvation effects. At high concentrations of cosolvent, the plot exhibits a region
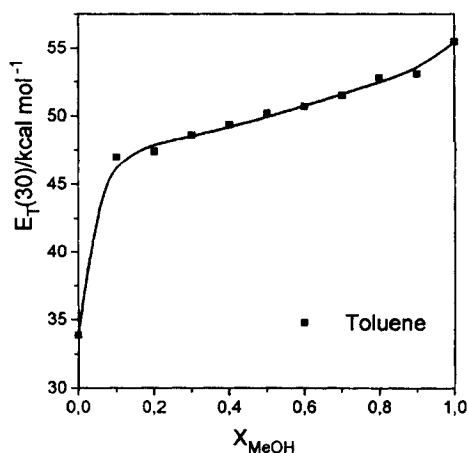

Figure 5. Plot of $E_T(30)$ vs cosolvent mole fraction for (toluene + methanol) solvent system

where the hydrogen-bonded adduct is fully formed and the changes observed in $E_T(30)$ values are due to non-specific solvation of the adduct (the positive slope indicates that the solvation of the adduct is larger in methanol than in toluene). For cosolvent concentrations higher than $X_{MeOH} \approx 0\cdot90$ this system exhibits a tendency to additivity.

Figure 6 shows the shifts in $E_T(30)$ with increase in methanol concentration for (chloroform + methanol) and (1,1,1-TClE + methanol) solvent systems. Chloroform and 1,1,1-TClE [$\varepsilon_{20} = 7\cdot53$, $\mu = 1\cdot78$ D, $E_T(30) = 36\cdot2$ kcal mol^{-1}] are polychlorinated solvents with three potential hydrogen-bonding acceptor centres on each. Chloroform exhibits hydrogen-bond donor ability but 1,1,1-TClE does not exhibit this property. Both systems show large increases in $E_T(30)$ values for small changes in cosolvent concentration, but this increment is much stronger for the (1,1,1-TClE + methanol) system than for the (chloroform + methanol) system, because methanol must compete with chloroform to interact with the phenoxide oxygen as the latter

Table 2. $E_T(30)$ values (kcal mol^{-1}) for (aprotic + methanol) binary solvent systems

Solvent	Methanol	mole	fraction						
	0·10	0·20	0·30	0·40	0·50	0·60	0·70	0·80	0·90
Toluene	47·0	47·4	48·6	49·4	50·2	50·9	51·5	52·8	53·1
1,1,1-Trichloroethane	47·6	48·5	49·7	50·2	50·9	51·3	52·1	53·0	53·8
Tetrahydrofuran	45·7	48·1	49·3	50·6	51·3	52·3	52·9	53·3	53·7
Chloroform	46·1	47·7	48·5	49·4	50·2	51·1	52·0	52·9	54·1
Acetone	47·8	50·6	51·7	52·7	53·0	53·6	54·1	54·4	54·8
N,N-Dimethylformamide	47·2	48·8	50·1	51·5	52·5	53·2	53·8	54·5	54·9
Dimethyl sulphoxide	47·0	48·5	49·6	51·1	51·9	52·9	53·6	54·5	54·9

Figure 6. Plot of $E_T(30)$ vs cosolvent mole fraction for (chloroform + methanol) and (TClE + methanol) solvent systems

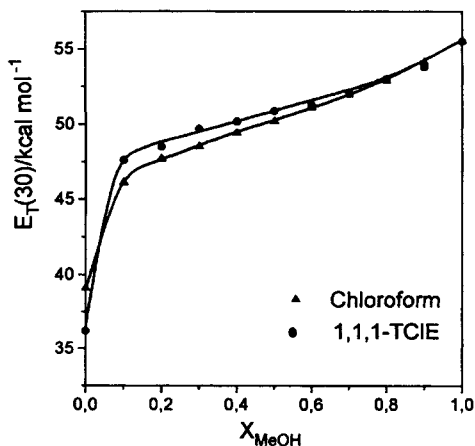Figure 8. Plot of $E_T(30)$ vs cosolvent mole fraction for (DMF + methanol) and (DMSO + methanol) solvent systems

can form a hydrogen bond with the betaine dye. They also show an inflection zone from which the betaine–methanol complex is fully formed, and a region where changes in $E_T(30)$ values are a linear function of cosolvent concentration owing to the effect of selective solvation of the complex with methanol.

Figure 7 shows the shifts in $E_T(30)$ with increase in methanol concentration for (THF + methanol) and (acetone + methanol) solvent systems. THF and acetone are suitable as acceptors to establish hydrogen-bonding with the cosolvent and to compete effectively with the betaine dye for hydroxylic hydrogens. Both systems exhibit a similar behaviour: the change in $E_T(30)$ is a
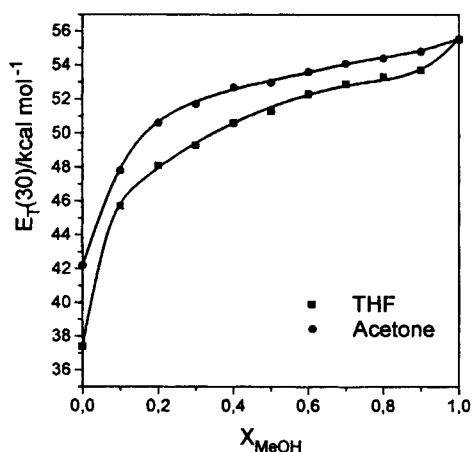
continuous non-linear function of the cosolvent concentration. The increase in $E_T(30)$ values is stronger for $X_{MeOH} < 0 \cdot 50$ than for higher cosolvent concentrations, and the plot shows an undefined inflection zone. The system (THF + methanol) exhibits an inflection zone near to $X_{MeOH} \approx 0 \cdot 90$.

Figure 8 shows the shifts in $E_T(30)$ with increase in methanol concentration for (DMF + methanol) and (DMSO + methanol) solvent systems. DMF and DMSO $[\varepsilon_{25} = 46 \cdot 68, \mu = 3 \cdot 96$ D, $E_T(30) = 45 \cdot 0$ kcal mol$^{-1}]$ are highly polar aprotic, EPD/EPA and HBA solvents. These systems are very similar, with a continuous non-linear increase in $E_T(30)$ and small deviations from additivity, principally in the case of DMSO (ca $1 \cdot 7$ kcal mol^{-1}). Both solvents compete effectively with the betaine dye to establish hydrogen bonding with methanol.

CONCLUSIONS

Based on the results obtained from each system, the following conclusions can may be drawn.

For (aprotic + toluene) solvent systems, the variation in $E_T(30)$ values as a function of toluene concentration shows that the most important solvation effects of the betaine dye are exhibited at high cosolvent concentration and are produced by selective solvation of the betaine dye by the aprotic solvents that is different from the interactions of the cosolvent. The exception is the (1,4-dioxane + toluene) system, which shows a linear behaviour indicating additivity.

For (aprotic + methanol) solvent systems, the variation of $E_T(30)$ values as a function of methanol concentration shows a sharp enhancement in the solvation effect of the betaine dye by methanol even at low cosolvent concentrations. These changes are less defined

Figure 7. Plot of $E_T(30)$ vs cosolvent mole fraction for (acetone + methanol) and (THF + methanol) solvent systems
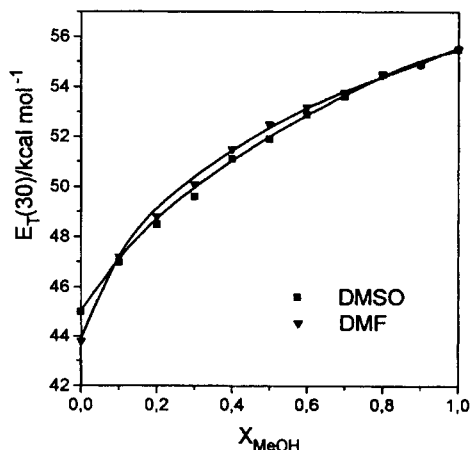
when the aprotic solvents can compete with the betaine dye for hydrogen bonding, indicating that hydrogen bonding is the predominant factor of the betaine dye solvation.

These values of $E_T(30)$ for binary mixtures of solvents can be applied to the selection of a suitable solvent for synthetic or other practical applications and provide useful data for the analysis of solvent effects on reaction rates.

APPLICATIONS

A preliminary application of these empirical parameters of solvent polarity is demonstrated with the aid of two examples related to solvent effects on one of the simplest systems for aromatic, nucleophilic substitution (ANS): the reaction of 1-chloro-2,4-dinitrobenzene with piperidine.[15]

In ANS reactions, interactions of the substrate and/or intermediate(s) with solvent molecules may be extensive and complex. Although the influence of the solvent has long been recognized, there has been little systematic study on the ways in which solvents may affect reaction rates. Previously, we have shown that solvent effects on the second-order rate coefficients, k_A, for the reactions of 1-chloro-2,4-dinitrobenzene with piperidine in 13 aprotic solvents with a 43 units range in dielectric constant are well correlated by Reichardt's solvent parameter $E_T(30)$.[16a,16b] The correlation is remarkably good if HBD solvents are excluded.[16b]

For the reactions of nitroaryl halides with either primary or secondary amines, the two-step mechanism depicted in Scheme 1 is fully established: breakdown of the zwitterionic σ intermediate, ZH, may occur either spontaneously or by a base-catalysed mechanism. The transition state leading to the zwitterionic intermediate, ZH, is expected to be favoured by increasing solvent polarity. This was observed for aprotic solvents. However, the studies of the reaction in methanol[16c] and in other alkanols[16d] showed reaction rates even smaller than those in cyclohexane.

Kinetic determinations

The kinetic studies of the described reaction were carried out using two different models of binary solvent systems: (DMF + toluene) and (1,1,1-TClE + methanol). Both mixtures of solvents were selected from among sets of mixtures such as (aprotic + toluene) and (aprotic + methanol), respectively, for which $E_T(30)$ values were determined, since *a priori* no additional complications were expected in their behaviour as reaction media. In each case kinetic determinations were performed for several binary mixture compositions.

As mentioned previously, base catalysis may assist the breakdown of the intermediate ZH. Although *a priori* no base catalysis is expected for the better nucleofuge chloride, the influence of amine concentration was studied. In all cases the reactions were carried out under pseudo-first-order conditions; they generated the expected N-(2,4-dinitrophenyl)piperidine in quantitative yield, and proved to be first order in the substrate. The second-order rate coefficients, k_A, calculated from the experimental pseudo-first-order rate coefficients, k_ψ, are given in Table 3, for the reactions at 25 °C. As observed, no significant acceleration in the rate occurs with increasing amounts of amine in all the mixtures of solvents studied, absence of base catalysis also being confirmed. The same holds true for reactions previously carried out in pure aprotic and pure protic solvents.

For (DMF + toluene) binary solvent mixtures, the absence of base catalysis allows the inference that hydrogen bonding of the intermediate ZH to a HBA solvent is not relevant. This suggests that specific solvent effects are negligible in this system as in pure aprotic solvents. As expected, according to the two-step mechanism described, the kinetic data show a tendency for decreasing k_A values with increase in toluene concentration owing to the diminution of the overall solvation capability of the binary mixture.

When the reaction was performed in (1,1,1-TClE + methanol) binary solvent mixtures, a slight

ZH
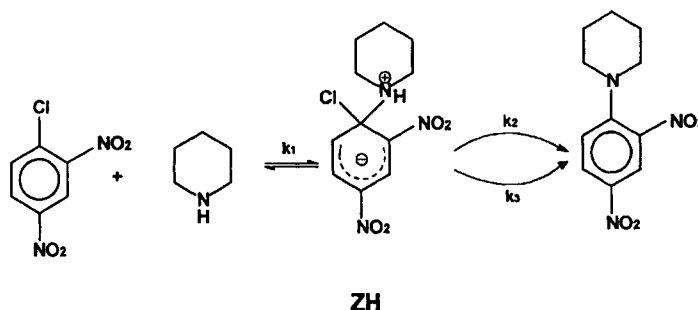
Scheme 1

Table 3. Second-order reaction rate coefficients k_A (10^{-2} l mol^{-1} s^{-1}) for the reaction of 1-chloro-2,4-dinitrobenzene (1×10^{-4} M) with piperidine in (DMF + toluene) and (1,1,1-TClE + methanol) binary solvent mixtures at 25 °C

Solvent	Mole fraction of 2nd solvent	[Piperidine] (M)				
		0·050	0·080	0·160	0·250	
DMF + toluene	0·10	105	109	108	111	108
	0·20	101	105	107	106	106
	0·30	100	98·6	99·1	102	99·9
	0·50	86·3	84·4	87·8	86·0	86·0
	0·70	71·3	66·9	69·4	69·3	69·2
	0·80	52·5	51·2	52·5	53·2	52·4
	0·90	31·5	30·9	31·2	32·6	31·6
1,1,1-TClE + methanol	0·05		8·88	9·75	10·7	9·78
	0·10		4·38	5·41	6·94	5·58
	0·20		3·17	3·54	4·52	3·67
	0·50		2·53	2·49	2·55	2·52
	0·70		2·66	2·99	2·85	2·83
	0·80		1·82	1·90	1·84	1·83

acceleration in reaction rates with increase in piperidine concentration mixtures was observed. According to Bunnett and Garst,[17] this phenomenon cannot be considered as base catalysis because in all cases the relation $k_3/k_2 < 5$ holds. The strikingly low reactivity previously observed for the reactions in hydroxylic solvents appeared once again in this system of solvents. The reactions in protic solvents have a highly organized initial state and exhibit strong solvation of the piperidine molecules, as this kind of solvent is responsible for the observed rate decrease. In addition, the kinetic data exhibit a substantial decrease in k_A values for small increments in methanol concentrations in the mixture of solvents. This sensitivity of the reaction rates to small amounts of the protic solvent can be explained by a change in the solvation of the intermediate, ZH, due to competition between the built-in solvation and specific solvation from methanol.

Linear solvation energy correlations

Although polarity parameters for many pure solvents have been thoroughly correlated with each other and with other solvent properties, the extent to which such parameters for binary solvent mixtures are likewise correlated is largely unknown.

For the reaction of 1-chloro-2,4-dinitrobenzene with secondary amines, we have mentioned that solvent effects in aprotic pure solvents are satisfactorily correlated by $E_T(30)$ if HBD solvents are excluded. On the other hand, the rate diminution observed for the reactions performed in alkanols must be associated with a specific hydroxylic solvent effect, which is not recognized by the $E_T(30)$ parameters. In this connection, it was of interest to assess if the empirical polarity parameters

$E_T(30)$ determined as a function of the composition for (DMF + toluene) and (1,1,1-TClE + methanol) binary solvent systems are suitable to reflect the solvent effect of these mixtures on one of the simplest ANS reaction. Figures 9 and 10 show plots of log k_A vs $E_T(30)$ for each binary solvent system analyzed.

The correlations were assessed by evaluation of the correlation coefficient (r) and the standard deviation (s). On the basis of Reichardt's criteria, both correlations are satisfactory: (a) for the (DMF + toluene) system, $r = 0·981$, $s = 0·082$; and (b) for the (1,1,1-TClE + methanol) system, $r = 0·986$, $s = 0·068$.
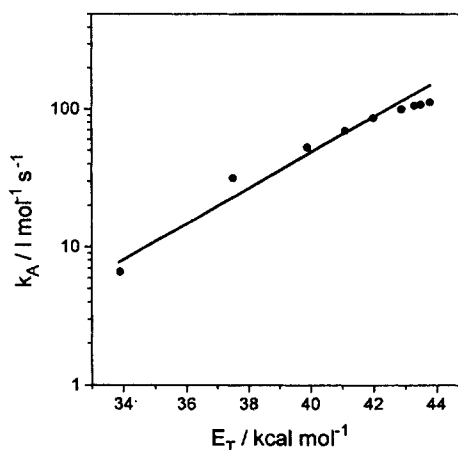

Figure 9. Correlation of log k_A with $E_T(30)$ for the reaction of 1-chloro-2,4-dinitrobenzene with piperidine at 25 °C in (DMF + toluene) solvent mixtures (including the pure solvents[16b])
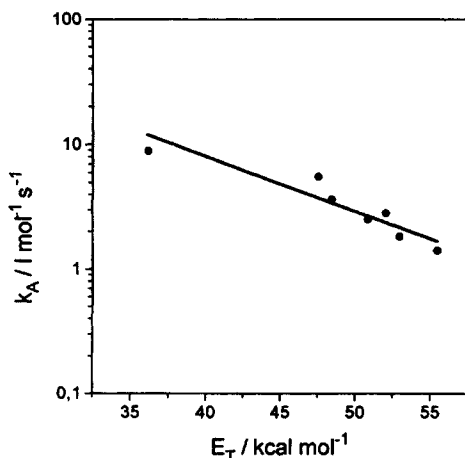
Figure 10. Correlation of log k_A with $E_T(30)$ for the reaction of 1-chloro-2,4-dinitrobenzene with piperidine at 25 °C in (1,1,1-TClE + methanol) solvent mixtures (including the pure solvents[16b,16d])

In conclusion, we have demonstrated that the $E_T(30)$ polarity parameters corresponding to the binary solvent systems explored are appropriate to account for the total medium effects on a simple model of the ANS reaction and it would be expected to be similar for other binary mixtures of solvents.

EXPERIMENTAL

Reagents and solvents. 2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye, Aldrich, 95%, m.p. 271–275 °C) was used without further purification. 1-Chloro-2,4-dinitrobenzene and piperidine were purified as described previously.[16b] *N*-(2,4-Dinitrophenyl)piperidine was prepared as reported previously.[16c] Anhydrous methanol was prepared by Lund and Bjerrum's method and stored over 3 Å molecular sieves. Toluene was kept over sodium wire for several days, refluxed for 72 h and fractionally distilled from sodium (b.p. 110 °C). The other solvents were purified as reported previously[16b] and all of them were kept over 4 Å molecular sieves and stored in special vessels that allow delivery without air contamination. All solvent mixtures were prepared prior to use and stored under anhydrous conditions.

$E_T(30)$ determination. The betaine solution (*ca* 2×10^{-4} mol dm^{-3}) in each binary solvent mixture was prepared just prior to use. Visible spectra of sample solutions were recorded on a Perkin-Elmer Model 124 UV–visible spectrophotometer and a ZEISS PMQ3 UV–visible spectrophotometer equipped with a data acquisition system and a 10 mm thermostated cell

holder (25 ± 0·1 °C), compared with blank solutions (identical in composition with each sample except for the absence of the indicator). The $E_T(30)$ values were determined from the longest wavelength UV-visible absorption band of the betaine and were calculated according to the equation $E_T(30)$ [kcal mol^{-1}] $= hc\nu N = 2 \cdot 859 \times 10^{-3}\nu$ (cm^{-1}).

Kinetic measurements. The kinetics of the reactions were studied spectrophotometrically with a Perkin-Elmer Model 124 UV-visible spectrophotometer essentially by the procedure described previously.[16b] All the kinetic runs were carried out at least in duplicate and the error in k_A was less than 2–3% for the solvent mixtures examined.

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