JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 207–220 (1999)

Characterization of solvent mixtures. Part 8 — Preferential solvation of chemical probes in binary solvent systems of a polar aprotic hydrogen-bond acceptor solvent with acetonitrile or nitromethane. Solvent effects on aromatic nucleophilic substitution reactions

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Received 2 April 1998; revised 29 May 1998; accepted 5 June 1998

ABSTRACT: The use of chemical probes for the characterization of chemical properties was explored for completely non-aqueous aprotic binary solvent mixtures. The Dimroth–Reichardt $E_T(30)$ betaine dye, 4-nitrophenol, 4-nitroanisole, 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline were used to study preferential solvation in binary mixtures of a polar aprotic hydrogen bond-acceptor solvent (DMSO, DMF, acetone, butanone and ethyl acetate) with acetonitrile or nitromethane at 25 °C over the whole range of solvent composition. The indicators were employed to determine $E_T(30)$, π^*, α and β solvatochromic parameters of the mixtures. Each solvent system was analysed according to its deviation from ideal behaviour due to the preferential solvation of the indicators and also from the complicated intermolecular interactions of the mixed solvent. The validity of the concept of an intrinsic, absolute property of a solvent mixture and whether such a property can be defined by means of chemical probes is discussed. These results were related to the solvent effects on some aromatic nucleophilic substitution reactions. The kinetics of the reactions between 1-fluoro-2,4-dinitrobenzene and primary or secondary amines were studied in ethyl acetate–acetonitrile and *N*,*N*-dimethylformamide–acetonitrile mixtures, respectively, taken as representatives of two clearly different solvation models. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: binary solvents; solvation; aromatic nucleophilic substitution reactions

INTRODUCTION

Solvents play a major role in many chemical processes. Organic liquids are characterized by several properties that make them suitable for dissolving and for providing reaction media for various types of solutes.[1] These properties include physical and chemical quantities.

Solvent effects are closely related to the nature and extent of solute–solvent interactions locally developed in the immediate vicinity of the solutes. Chemists have usually attempted to understand this in terms of *polarity*, defined as the overall solvation capabilities that depend on all possible (specific and non-specific) intermolecular interactions. In this connection, numerous reports on solvent polarity scales have been published in the last few decades.[2–5] More recently, Abraham[6] has proposed scales of solute hydrogen-bond acidity and solute hydrogen-bond basicity and has devised a general solvation equation.

Negatively and positively solvatochromic dyes are particularly suitable as standard substances for studying solute–solvent interactions, since the transition energy of the indicator depends on the solvation's sphere composition and properties. This method also provides information on some solvent properties such as polarity and hydrogen-bonding capability.

The chemical characteristics of solvent mixtures are customarily determined in the same manner as those of neat solvents by means of solvatochromic indicators. However, solute–solvent interactions are much more complex in mixed solvents than in pure solvents owing to the possibility of preferential solvation by any of the solvents present in the mixture. Moreover, the solvent–solvent interactions produced in solvent mixtures can affect solute–solvent interactions and therefore preferential solvation. The validity of the concept of an intrinsic, absolute property of a solvent mixture and

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Contract/grant sponsor: Science and Technology Secretariat, UNL, CAI+D Program; *Contract/grant number:* 94-0858-007-054.

CCC 0894–3230/99/030207–14 $17.50

Table 1. Solvatochromic parameters of pure solvents at 25 °C

Parameter	EAc	BUT	AC	DMF	DMSO	NM	AcN
$E_T(30)$	38.1	41.3	42.2	43.8	45.1	46.3	45.6
π^*	0.55^{a}	0.67^{a}	0.71^{a}	0.88^{a}	1.00^{b}	0.85^{a}	0.75^{a}
	0.45^{c}	0.60^{c}	0.62^{c}	0.88^{c}		0.75^{c}	0.66^{c}
	0.49^{d}		0.66^{d}	0.87^{d}			0.71^{d}
	(0.56)	(0.66)	(0.70)	(0.89)		(0.88)	(0.76)
α	0.00^{a}	0.06^{a}	0.08^{a}	0.00^{a}	0.00^{a}	0.22^{a}	0.19^{a}
	(0.00)	(0.09)	(0.13)	$(0.04)_{IV}$	$(0.00)_{IV}$	(0.29)	(0.32)
				$(0.05)_{V}$	$(0.06)_{V}$		
β	0.45^{a}	0.48^{a}	0.48^{b}	0.69^{a}	0.76^{a}	0.06^{a}	0.31^{b}
	(0.45)	(0.58)	0.43^{a}	$(0.71)_{IV}$	$(0.77)_{IV}$	0.37^{e}	0.40^{a}
			(0.53)	$(0.67)_{V}$	$(0.43)_{V}$	(0.20)	(0.44)

Data from ^{a} Ref. 11, ^{b} Ref. 14, ^{c} Ref. 15, ^{d} Ref. 16 and ^{e} Ref. 17. Values in parentheses were determined in this work.

whether such a property can be defined by means of chemical probes has been discussed recently.[7]

We have previously studied the preferential solvation of $E_T(30)$ dye for several completely non-aqueous binary solvent mixtures of the type polar aprotic hydrogen-bond acceptor (PAHBA) solvent–chloroform or dichloromethane, both taken as hydrogen-bond donor solvents.[8] Most of these mixtures presented synergetic effects for the $E_T(30)$ polarity parameter, which is revealed in the PAHBA solvent zone. We have also discussed the influence on the kinetics of some aromatic nucleophilic substitution reactions (ANS) of those solvent mixtures in which the two solvents interact to form a hydrogen-bonded complex with $E_T(30)$ polarity higher than those of the two pure solvents. This ‘improved polarity’ was not ‘reflected’ by the critical states of the ANS reaction analysed. Among the PAHBA solvents, acetonitrile (AcN) and nitromethane (NM) exhibit a lower HBA ability and also exhibit a potential ability to donate a hydrogen atom towards the formation of a hydrogen bond. In order to contribute to a more comprehensive analysis of the microscopic properties of binary aprotic solvent mixtures, it was of interest to discuss the behaviour of solvent mixtures of the type PAHBA solvent − AcN or NM.

In the present study, the solvatochromic parameters [$E_T(30)$, π^*, β, and α] of completely non-aqueous binary mixtures of several dipolar aprotic hydrogen-bond acceptor solvents with acetonitrile and nitromethane were determined and interpreted. Additionally, it was of interest to evaluate the influence of these solvent mixtures on the kinetics of some aromatic nucleophilic substitution reactions.

This work was aimed at (i) studying the preferential solvation of different chemical probes in binary solvent mixtures, analysing the solute–solvent and solvent–solvent interactions; (ii) exploring whether different indicators produce convergent values for a property in a given solvent mixture; (iii) measuring the microscopic properties of binary solvent mixtures with the purpose of obtaining numerical values for solvent properties for their use as a ‘predictor’ or ‘descriptor’ of the solvent effect on the behaviour of diverse kinds of solutes and transition states; and (iv) relating the extent of the preferential solvation of different chemical probes to the kinetic properties of ANS reactions development in the same binary solvent systems.

RESULTS AND DISCUSSION

Microscopic properties of binary solvent mixtures

Different single and multiparametric empirical scales of molecular microscopic properties of solvents have been developed from reference solutes that behave as a probe reflecting changes in the solvation shell through variations in their UV–visible absorption spectra.

The $E_T(30)$ scale of Dimroth and Reichardt[9] and the π^*, β and α scales constructed by Kamlet and co-workers by the solvatochromic comparison method[10] are the parameters most used in the uniparametric and multiparametric approaches, respectively. The $E_T(30)$ ‘polarity’ reflects a combination of polarity and hydrogen-bond donor capability of solvents and is defined as the molar transition energy (in kcal mol^{-1}) of a betaine dye dissolved in the solvent under study. The π^*, β and α parameters (resorting to more specific probes) reflect the dipolarity/polarizability, the hydrogen-bond acceptor (HBA) basicity and the hydrogen-bond donor (HBD) acidity of the solvents, respectively. Different procedures for the calculation of π^*, β and α values have been collected by Marcus.[11] Recently, new probe molecules (structurally different) have been proposed.[12]

$E_T(30)$ values are available for several binary solvent mixtures, but data for π^*, β and α parameters are still scarce.

Bosch and co-workers[13] proposed different theoretical equations which take into account the solute–solvent and solvent–solvent interactions in binary mixtures and relate the $E_T(30)$, π^*, β and α solvatochromic parameters with the solvent composition.

Table 2. $E_T(30)$ values (kcal mol^{-1}) for PAHBA solvent–co-solvent systems at 25 °C

PAHBA		Co-solvent mole fraction								
solvent	Co-solvent	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
EAc	NM	40.8	41.6	42.6	43.2	44.2	44.7	45.2	45.8	46.4
	AcN	40.8	41.6	42.6	43.3	44.0	44.5	44.8	45.2	45.5
BUT	NM	42.1	42.8	43.5	44.1	44.4	45.0	45.5	46.0	46.3
	AcN	42.4	43.0	43.5	44.0	44.5	45.0	45.2	45.5	45.6
AC	NM	42.8	43.6	44.0	44.5	44.8	45.4	45.7	46.0	46.3
	AcN	42.7	43.3	43.7	44.2	44.6	45.1	45.2	45.4	45.5
DMF	NM	43.8	43.9	44.3	44.6	44.7	45.2	45.3	45.8	46.1
	AcN	43.9	44.3	44.5	44.6	45.0	45.2	45.4	45.5	45.6
DMSO	NM	45.0	45.1	45.2	45.3	45.4	45.6	45.6	45.8	46.0
	AcN[a]	45.0	45.0	45.1	45.1	45.2	45.3	45.3	45.4	45.6

[a] From Ref. 18.

The two selected co-solvents (NM and AcN) have analogous general properties. Taking into account that for NM the HBA capability values are controversial in the literature, and considering the possibility of experimental difficulties in the determination of the solvatochromic shifts due to overlapping absorptions, the $E_T(30)$ parameter was determined for PAHBA solvent–AcN or NM) and π^*, β and α only for PAHBA solvent–AcN. The PAHBA selected were ethyl acetate (EAc), acetone (AC), butanone (BUT), *N*,*N*-dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). The properties of the pure solvents used to prepare the binary solvent mixtures studied are given in Table 1.

For each system explored, the solvatochromic parameters were systematically determined over the full solvent composition range (at nine molar fractions of co-solvent) at 25 °C.

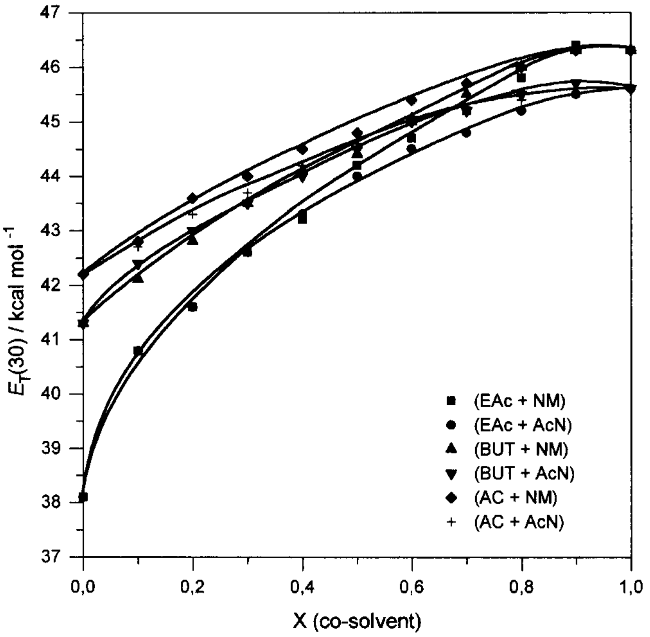


Figure 1. Plot of $E_T(30)$ *vs* co-solvent mole fraction for PAHBA solvent (EAc, BUT, AC) –NM or AcN solvent systems

Determination of $E_T(30)$ values

The $E_T(30)$ solvatochromic parameter is defined as the molar transition energy derived from the longest wavelength solvatochromic UV–visible absorption band of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate (**I**), proposed by Dimroth and Reichardt for empirically measuring the 'polarity' of solvents, and is calculated according to the equation

$$E_T(30)(\text{kcal mol}^{-1}) = hc\bar{\nu}N = 2.859 \times 10^{-3}\bar{\nu}(\text{cm}^{-1}) \qquad (1)$$

The calculated $E_T(30)$ values for the PAHBA solvent–AcN or NM systems are presented in Table 2 (the binary system DMSO–AcN has been reported previously). The corresponding plots of $E_T(30)$ *vs* X_{CoS} are shown in Figs 1 and 2, including the pure solvents.

In order to analyse the data obtained, the binary mixtures were divided into two general groups according to the solvation models reflected in the plots: (a) mixtures that exhibit positive deviations from linearity in the relationship between the solvatochromic parameter values and the solvent composition; and (b) mixtures with negative deviations from linearity.

The different solvation models of indicator **I** can be interpreted from its solute properties. The Dimroth–Reichardt betaine dye exhibits a significant permanent dipole moment (suitable for dipole–dipole and dipole–induced dipole interactions), a large polarizable π-electron system (suitable for dispersion interactions), a substantial negative charge on the phenoxide oxygen [highly basic electron-pair donor centre suitable for interactions with weak Brønsted acids (H-bonding) and Lewis acids (EPD/EPA bonding)] and a positive charge on the pyridinium nitrogen (sterically shielded). Therefore, indicator **I** is sensitive to the dipolarity/polarizability and hydrogen-bond donor capability of the solvents.

Figure 1 presents the plots for mixtures of EAc, BUT

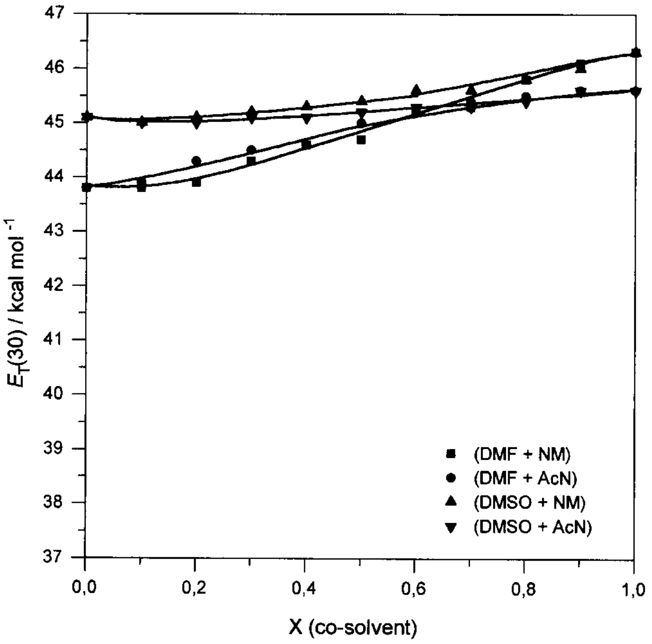


Figure 2. Plot of E_T(30) *vs* co-solvent mole fraction for PAHBA solvent (DMF, DMSO)–NM or AcN solvent systems

and AC with both co-solvents, showing a striking behaviour with positive deviations from linear relationships between the E_T(30) values and the solvent composition. It should be pointed out that the difference between the property values of the co-solvents and the pure solvents is $3.5 \leq \Delta E_T(30) \leq 8.2$ kcal mol^{-1} (1 kcal = 4.184 kJ). The binary systems with EAc as one component of the mixtures exhibit a large increases in the E_T(30) value with small increases in co-solvent concentration and large deviations from linearity, particularly in the EAc-rich region. It can be observed that the EAc–NM system presents a negligible synergistic effect for the solvent property at $X_{NM} = 0.9$. The binary mixtures with BUT and AC exhibit continuous non-linear increases in the E_T(30) value, showing that the curvature in the region rich in these PAHBA solvents is less defined, and the deviations from linearity are smaller than those for mixtures with EAc. All these results indicate that the betaine dye tends to be preferentially solvated by the co-solvent. The shape of the curves denotes enrichment of the solvation shell of the chemical probe in the polar solvent with a potential capability to establish solute–solvent interactions by hydrogen bonding, leading to an additional stabilization of the strong negative charge on the phenoxide oxygen in the electronic ground state of **I**, resulting in increased E_T(30) values.

Figure 2 shows the plots for binary mixtures of DMF and DMSO with both co-solvents. The difference between the E_T(30) values of the co-solvents and the pure solvents is $0.6 \leq \Delta E_T(30) \leq 2.5$, lower than those for the mixtures previously analysed. All systems exhibit a similar behaviour, showing nearly linear curves with small negative deviations from linearity. The E_T(30) value increases smoothly in the co-solvent-rich region and flattens out at $X_{CoS} < 0.5$. In these binary mixtures, the solvent–solvent interactions can notably affect the solute–solvent interactions, and therefore preferential solvation. The highly dipolar solvents with strong hydrogen-bond acceptor capability (DMF and DMSO) can interact with AcN and NM (highly dipolar solvents with potential hydrogen-bonding ability) forming associates by means of hydrogen bonds and dipole–dipole interactions. In the solvation shell, DMF and DMSO can compete with indicator **I** to establish interactions by hydrogen bonding with the co-solvent. Some mixtures with DMSO show an E_T(30) value slightly lower than those for the pure solvents.

The results obtained indicate that a similar behaviour is

Table 3. π^* Values for PAHBA solvent–acetonitrile systems at 25 °C

PAHBA solvent		Acetonitrile mole fraction								
		0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
EAc	π^* (II)	0.59	0.63	0.64	0.65	0.66	0.69	0.71	0.74	0.75
	π^* (III)	0.57	0.59	0.61	0.61	0.66	0.66	0.66	0.71	0.73
	π^* (avg)	0.58	0.61	0.625	0.63	0.66	0.675	0.685	0.725	0.74
BUT	π^* (II)	0.69	0.69	0.71	0.72	0.74	0.74	0.74	0.74	0.75
	π^* (III)^a	0.66	0.66	0.68	0.69	0.71	0.71	0.71	0.71	0.72
	π^* (avg)	0.675	0.675	0.695	0.705	0.725	0.725	0.725	0.725	0.735
AC	π^* (II)	0.71	0.71	0.71	0.73	0.75	0.75	0.75	0.75	0.75
	π^* (III)^a	0.68	0.68	0.68	0.70	0.72	0.72	0.72	0.72	0.72
	π^* (avg)	0.695	0.695	0.695	0.715	0.735	0.735	0.735	0.735	0.735
DMF	π^* (II)	0.88	0.88	0.87	0.87	0.87	0.87	0.86	0.85	0.83
	π^* (III)	0.88	0.84	0.82	0.80	0.79	0.77	0.77	0.75	0.75
	π^* (avg)	0.88	0.86	0.845	0.835	0.825	0.82	0.815	0.80	0.79
DMSO	π^* (II)	0.98	0.97	0.96	0.94	0.92	0.89	0.87	0.86	0.83
	π^* (III)	1.00	1.00	0.97	0.93	0.88	0.86	0.84	0.79	0.79
	π^* (avg)	0.99	0.985	0.965	0.935	0.90	0.875	0.855	0.825	0.81

[a] Values estimated from Eqn (4).

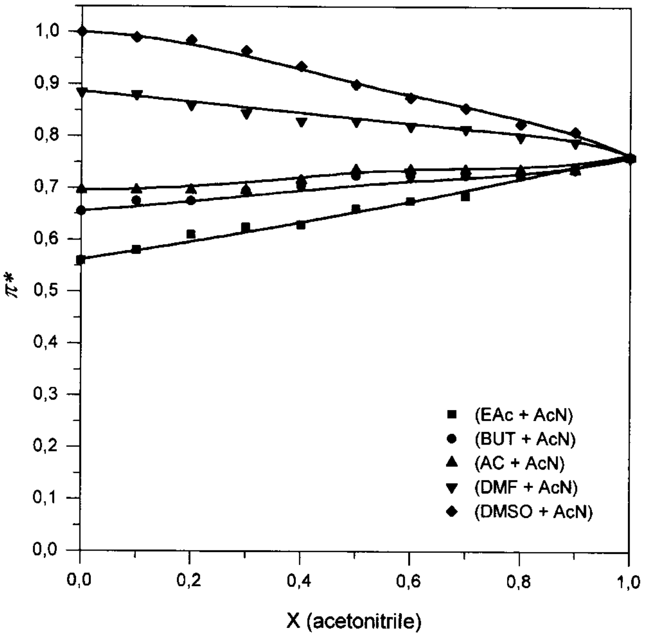


Figure 3. Plot of π^* *vs* co-solvent mole fraction for PAHBA solvent–AcN solvent systems

exhibited when the co-solvent is NM or AcN. For mixtures with EAc, BUT and AC (solvents that do not interact appreciably with NM and AcN), the co-solvent manifests its properties even at low concentrations. For mixtures with DMF and DMSO, the association interferes with the property.

Determination of π^* values

The solvatochromic dipolarity/polarizability parameter π^* was determined employing the solvatochromic indicators *N*,*N*-diethyl-4-nitroaniline (**II**) and 4-nitroanisole (**III**), which belong to the selected probe solutes set proposed by Kamlet and co-workers.[10]

These probes are aromatic molecules of the A–C_6H_4–D type where A and D are electron-acceptor (NO_2) and electron-donor (*N*,*N*-Et_2 and OMe) groups, respectively. The structures of the aromatic nitro compounds used as indicators are basically similar, although the diethylamine and methoxy groups appear to be different. The electronic transition is connected with an intramolecular charge transfer from the electron donor part to the acceptor part through the aromatic system. These indicators present positive solvatochromism owing to their more dipolar first excited state relative to their less dipolar ground state. According to the chemical structure of the probes, they are supposed to be insensitive to specific HBD and HBA interactions with solvents.

The π^* solvatochromic parameter measures the exoergic effects of solute–solvent, dipole–dipole and dipole–induced dipole interactions. That is, it measures the ability of solvents to stabilize a neighbouring charge or dipole by virtue of non-specific dielectric interactions. Therefore, π^* values represent a blend of dipolarity and polarizability of the solvents.

The π^* solvatochromic parameter was calculated from the wavenumbers of the UV–visible absorption maxima of indicators **II** [$\bar{\nu}$(**II**)] and III [$\bar{\nu}$(**III**)] according to the conversion expressions reported by Marcus:[11]

$$\pi^* = 0.314[27.52 - \bar{\nu}\,(\mathbf{II})] \tag{2}$$

$$\pi^* = 0.427[34.12 - \bar{\nu}\,(\mathbf{III})] \tag{3}$$

For all the binary systems explored, the values of $\bar{\nu}$(**II**) were obtained experimentally and the π^* calculated parameters are presented in Table 3. However, the values of $\bar{\nu}$(**III**) could not be obtained directly in all cases because of overlapping absorptions. The values of $\bar{\nu}$(**III**) were determined experimentally for the EAc–AcN, DMF–AcN and DMSO–AcN systems. For BUT–AcN and AC–AcN binary mixtures the $\bar{\nu}$(**III**) value was estimated from the correspondent experimental $\bar{\nu}$(**II**) values and the correlation between the wavenumber of the absorption maxima of both indicators in the EAc–AcN, DMF–AcN and DMSO–AcN systems, in agreement with the equation $\bar{\nu}(\mathbf{III}) = 14.26 + 0.72$, $\bar{\nu}$(**II**) ($n = 31$, $r = 0.9594$, SD = 0.085). The standard deviation of this regression equation compares well with the 0.100 kK (1 kK = 1000 cm^{-1}) precision limit of the solvatochromic comparison method. The calculated π^* (**III**) values are presented in Table 3 and also given are the averaged π^* (avg) values.

The dipolarity/polarizability determined with **II** is, in general, slightly higher than those calculated with **III.** The $\Delta\pi^*$ difference between the experimentally determined values from the indicators **II** and **III** for the pure solventes is $\Delta\pi^*$ (AcN) = 0.06, $\Delta\pi^*$ (EAc) = 0.02, $\Delta\pi^*$ (DMF) = 0.01 and $\Delta\pi^*$ (DMSO) = 0.00 units. The same difference for the solvent mixtures explored is $\Delta\pi^* \leq 0.05$ for the EAc–AcN system, $\Delta\pi^* \leq 0.10$ for the DMF–AcN system and $\Delta\pi^* \leq 0.07$ for the DMSO–AcN system. Therefore, for these solvent systems, the average values should give an acceptable estimation of the microscopic property under study.

The plots of π^* (avg) *vs* X_{AcN}, corresponding to the data shown in Table 3, including the values of π^* (avg) for the pure solvents measured for this work, are presented in Fig. 3.

According to the shape of the curves, two patterns of behaviour are seen for the solvent systems under study. For the EAc–AcN, BUT–AcN and AC–AcN solvent systems, in general, the values of the property are very close to the average of the properties of the pure solvents (nearly ideal behaviour), indicating additivity of the properties. In these mixtures the solute–solvent interactions do not affect the auto- and mutual solvent–solvent interactions. For the DMF–AcN and DMSO–AcN

Table 4. β Values for PAHBA solvent–acetonitrile systems at 25 °C

PAHBA solvent	β	Acetonitrile mole fraction 0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
EAc	β (**IV**)	0.51	0.51	0.50	0.51	0.53	0.50	0.47	0.44	0.45
	β (**V**)	0.49	0.52	0.51	0.51	0.48	0.48	0.51	0.49	0.48
	β (avg)	0.50	0.515	0.505	0.51	0.50	0.49	0.49	0.46	0.465
BUT	β (**IV**)	0.58	0.58	0.57	0.57	0.52	0.51	0.49	0.48	0.47
AC	β (**IV**)	0.54	0.54	0.53	0.52	0.48	0.48	0.48	0.48	0.46
DMF	β (**IV**)	0.75	0.74	0.71	0.72	0.62	0.61	0.55	0.53	0.47
	β (**V**)	0.67	0.70	0.71	0.74	0.71	0.74	0.77	0.71	0.66
DMSO	β (**IV**)	0.78	0.77	0.76	0.78	0.77	0.72	0.69	0.62	0.55
	β (**V**)	0.61	0.57	0.55	0.70	0.71	0.74	0.68	0.73	0.73

systems, the components of the mixtures with the highest value of the dipolarity/polarizability manifest their properties (already in dilute solutions in the case of DMSO), indicating moderate preferential solvation of the indicator by the component of the mixture with the highest value of π^*.

Determination of β values

The solvatochromic HBA ability parameter β was determined from the magnitudes of the enhanced solvatochromic shifts for 4-nitroaniline (**IV**) relative to *N*,*N*-diethyl-4-nitroaniline (**II**) and for 4-nitrophenol (**V**) relative to 4-nitroanisole (**III**), according to the conversion expression proposed by Marcus:[11]

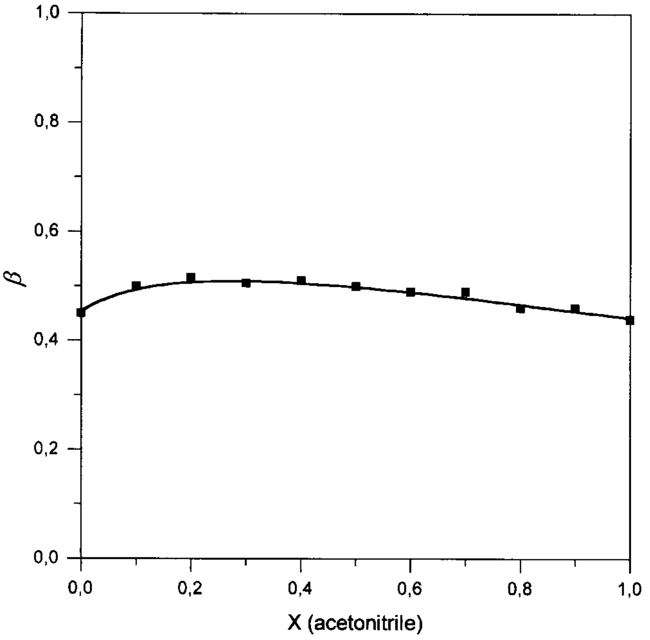


Figure 4. Plot of β *vs* co-solvent mole fraction for EAc–AcN solvent system

$$\beta = 0.358[31.10 - \bar{\nu}\ (\mathbf{IV})] - 1.125\pi^*\ (\mathbf{II}) \qquad (5)$$

$$\beta = 0.346[35.045 - \bar{\nu}\ (\mathbf{V})] - 0.57\pi^*\ (\mathbf{III}) - 0.12\delta \qquad (6)$$

The parameter δ is a 'polarizability correction term,' equal to 0.00 for all non-chlorinated aliphatic and dipolar aprotic solvents, 0.5 for polychlorinated aliphatic, solvents and 1.00 for aromatic solvents.

In this case, Eqn 6 reduces to a

$$\beta = 0.346[35.045 - \bar{\nu}(\mathbf{V})] - 0.57\pi^*(\mathbf{III}) \qquad (6a)$$

The shifts in the binary mixtures with EAc, DMF and DMSO were determined for indicators **IV** and **V** and the calculated β (**IV**), β (**V**) and β (avg) values are presented in Table 4. For the binary mixtures with AC and BUT, the β parameter was obtained from just one probe, **IV**, because of overlapping absorptions. These results are also presented in Table 4.

In order to make a comparison with indicators **II** and **III**, it is of interest to point out that the correlation between the wavenumber of the maximum absorption of indicators **IV** and **V** is poor ($n = 31$, $r = 0.840$, $\mathrm{SD} = 0.249$).

The $\Delta\beta$ difference between the experimentally determined β values with indicators **IV** and **V** for the pure solvents are $\Delta\beta$ (AcN) = 0.065, $\Delta\beta$(EAc) = 0.07, $\Delta\beta$(DMF) = 0.04 and $\Delta\beta$(DMSO) = 0.13 units. For the mixtures with EAc, the value $\Delta\beta \leq 0.05$ units suggests that the averaged values give an appropriate estimate of the properties of the mixtures. These values are presented in Fig. 4, showing that the HBA ability of the mixtures is slightly higher than that of the pure solvents. On the other hand, the corresponding differences are $\Delta\beta \leq 0.22$ and $\Delta\beta \leq 0.21$ units for the DMF–AcN and DMSO–AcN systems, respectively, notably higher than those observed for the EAc–AcN system. It is also remarkable that the β (**IV**) parameters from DMSO–AcN are in agreement with the values reported by Marcus[7] with the same indicator. The disparity of the values for the β parameter from **IV** and **V** reflects the different sensitivities (different responses) of the probes, indicating different solute–solvent interactions, that also depend on the solvent–

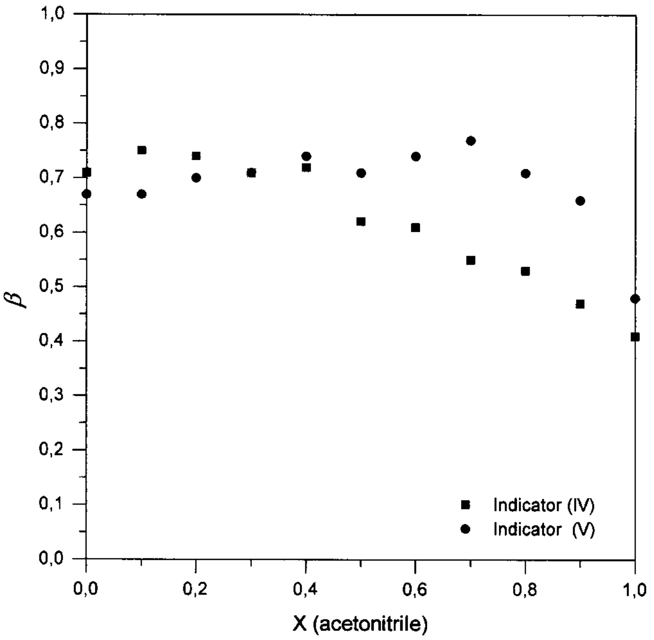


Figure 5. Plot of β *vs* co-solvent mole fraction for DMF–AcN solvent system

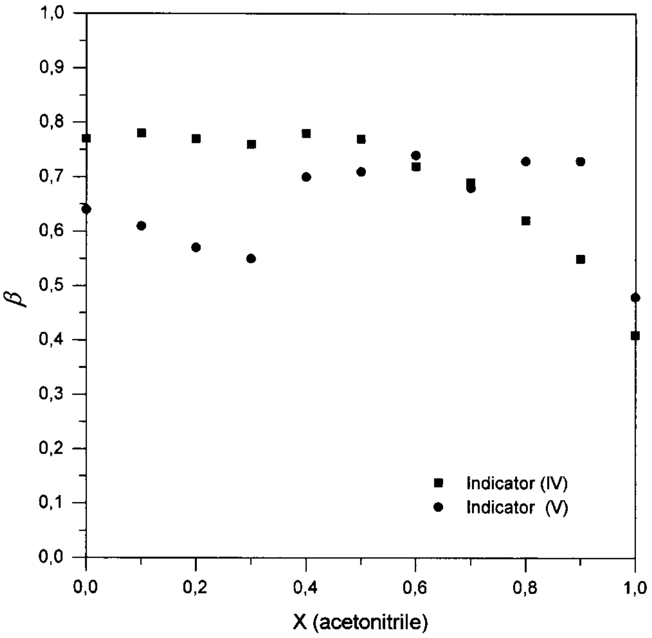


Figure 6. Plot of β *vs* co-solvent mole fraction for DMSO–AcN solvent system

solvent interactions. The β (**IV**) and β (**V**) values are presented in Figs 5 and 6 as a function of solvent composition for the DMF–AcN and DMSO–AcN systems, respectively.

The convergent values of the HBA property for the mixtures with EAc (moderate HBA solvent) from indicators **IV** and **V** should reflect that the interactions between the probe solutes with the components of the solvent mixtures are less strong than the auto-and mutual interactions of the solvents. Therefore, for these solvent systems, the average values should give an acceptable estimate of the property under study.

On the other hand, the disparity in the β values produced by the same indicators for the mixtures with DMF and DMSO (strong HBA solvents) indicate that the interactions between the solutes and DMF and DMSO interfere with the auto- and mutual interactions. Therefore, in these cases, the values are not averaged.

Calculation of α values

For each binary systems analysed, the α parameter was calculated from $E_T(30)$, π^*, and β according to the conversion expression proposed by Marcus:[11,19]

$$\alpha = 0.0692E_T(30) - 2.090 - 0.900\pi^* - 0.147\beta + 0.190\delta \quad (7)$$

Since none of the solvents used in this work is aromatic or polychlorinated, Eqn 7 reduces to.

$$\alpha = 0.0692E_T(30) - 2.090 - 0.900\pi^* - 0.147\beta \quad (7a)$$

The calculated α values are presented in Table 5. These values (and those for the net solvents determined for this work) are plotted in Fig. 7 [taking into account that the effect of the estimated value of β on the accuracy of the

Table 5. α Values for PAHBA solvent–acetonitrile systems at 25 °C

PAHBA solvent	α	Acetonitrile mole fraction 0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
EAc	α	0.14	0.16	0.22	0.26	0.29	0.31	0.32	0.32	0.33
BUT	α (**IV**)	0.16	0.19	0.21	0.24	0.26	0.30	0.31	0.34	0.34
AC	α (**IV**)	0.16	0.22	0.23	0.25	0.26	0.30	0.31	0.32	0.33
DMF	α (**IV**)	0.05	0.09	0.12	0.14	0.19	0.21	0.24	0.26	0.29
	α (**V**)	0.06	0.10	0.12	0.14	0.18	0.19	0.20	0.23	0.26
DMSO	α (**IV**)	0.02	0.02	0.05	0.07	0.12	0.15	0.17	0.22	0.26
	α (**V**)	0.04	0.05	0.08	0.09	0.12	0.15	0.18	0.20	0.23

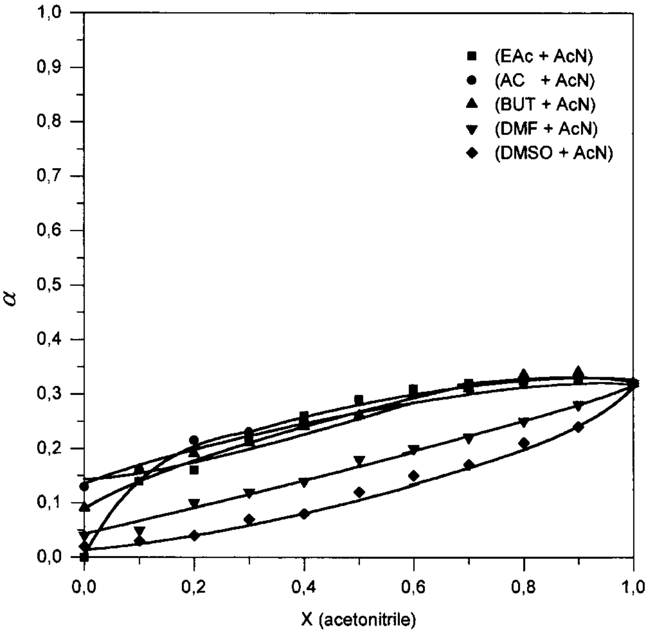


Figure 7. Plot of α *vs* co-solvent mole fraction for PAHBA solvent–AcN solvent systems

resulting α values is much lower than other terms in Eqn 7a, the α averaged values are plotted for DMF and DMSO mixtures].

As can be observed from the shapes of the curves of α *vs* X_{CoS}, all the solvent systems analysed seem to present similar models to those reflected in the $E_T(30)$ *vs* X_{CoS} curves. In fact, this behaviour may be expected, taking into account that $E_T(30)$ is a combined measure of solvent dipolarity/polarizability and hydrogen-bond donor ability.

The binary mixtures with EAc, BUT and AC have a higher ability to donate a hydrogen atom towards the formation of a hydrogen bond than the expected ability derived from the weighted mean of the quantities characterizing the two neat solvents mixed. The calculated α values for some binary mixtures in the co-solvent-rich region are higher than those for the pure solvents.

The binary mixtures with DMF and DMSO have reduced hydrogen-bond donor ability with respect to ideal behaviours. This could be explained by the strong solvent–solvent interactions via hydrogen bonding (mainly in the DMF rich-region). It should be pointed out that almost ideal behaviour is observed for the DMF–AcN solvent system.

Solvent effects on aromatic nucleophilic substitution

The rate of aromatic nucleophilic substitution (ANS) reactions is notably affected by the solvent properties. Since the first pioneering studies,[20] different contributions have reported the influence of solvent effects on ANS reactions which showed how extensive and complex the interactions of the substrate and/or the intermediates with the solvent molecules can be.[21] Nevertheless, few systematic studies have been reported about the effects of the solvents, particularly mixed solvents.[22]

The gross mechanism of ANS reactions when primary or secondary amines are the nucleophiles is now well established[21,23] (Scheme 1).

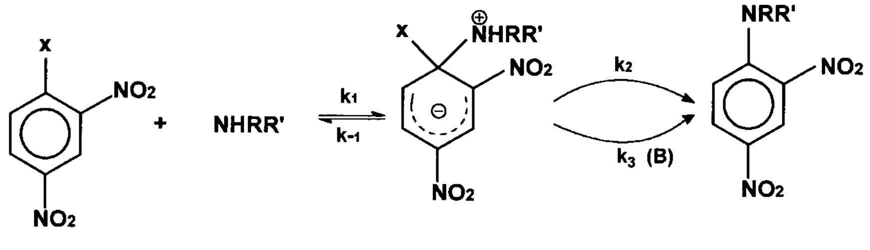
Application of the steady-state approximation derives in Eqn 8, where k_A is the observed second-order rate constant and B can be either a second molecule of the nucleophile or an added base.

$$k_A = \frac{k_1(k_2 + k_3^B[B])}{k_{-1} + k_2 + k_3^B[B]} \tag{8}$$

The main situations of interest with respect to the reaction shown in Scheme 1 are as follows with respect to Eqn 8:

(a) $k_2 + k_3{}^B\,[B] \gg k_{-1}$. In this case, no base catalysis is possible: Eqn 8 simplifies to $k_A = k_1$ and the formation of the intermediate is rate-limiting.

(b) $k_2 + k_3{}^B\,[B] \ll k_{-1}$. This situation corresponds to the rapid formation of the intermediate (ZH), followed by its rate-determining decomposition. In this case, Eqn 8 reduces to Equation 9, which predicts base catalysis with a linear dependence of k_A on [*B*]:



ZH

Scheme 1

Table 6. Second-order rate coefficients, k_A (1 mol^{-1} s^{-1}), for the reaction of 5×10^{-5} M FDNB with primary and secondary amines

			[Amine] (M)							
Solvent	X_{AcN}	Amine	0.002	0.004	0.008	0.010	0.016	0.020	0.040	0.080
EAc–AcN	0	*n*-Butylamine		4.49	4.82	4.66	4.74	5.32	5.76	
	0.10		4.19	5.13	5.22	5.88	5.75	5.78	5.45	
	0.30		4.77	5.89	6.04	6.18	6.60	6.71	6.99	
	0.50		5.86	6.44	6.04	6.39	6.93	7.05	7.10	
	0.70		6.66	7.20	6.61	5.84	6.09	7.01	7.35	
	0.90		5.96	7.03	7.40	7.43	7.41	7.49	7.53	
	1.00		7.54	7.79	7.87	7.72	7.48	6.95	7.86	
DMF–AcN	0		35.7	37.3	39.1	41.0	41.4			
	0.10		37.0	37.4	40.0	38.8	39.4	37.3	38.5	
	0.30		32.0	33.3	33.0	33.7	33.4	34.4	35.8	33.0
	0.50		18.7	23.0	20.7	25.2	18.9	23.2	23.5	22.7
	0.70		18.4	19.3	17.0	17.8	16.3	15.9	16.4	16.0
	0.90		9.80	10.0	10.4	10.6	10.5	10.3	10.6	10.8
EAc–AcN	0	Morpholine	0.11	0.20	0.33	0.39	0.47	0.63	1.33	2.52
	0.10		0.18	0.29	0.46	0.56	0.64	1.17	1.82	3.59
	0.30		0.33	0.43	0.67	0.75	1.14	1.35	2.3	3.45
	0.50		0.37	0.53	0.93	1.08	1.34	1.64	2.74	4.61
	0.70		0.55	0.68	0.98	1.19	1.37	1.42	3.09	4.69
	0.90		0.63	0.67	0.89	1.32	1.89	2.19	3.05	5.60
	1.00		0.80	1.11	1.40	1.74	2.10	2.72	4.05	5.53
DMF–AcN	0		3.70	4.98	5.47	5.94	7.57	8.55	12.6	
	0.10		2.91	3.49	4.55	5.07	5.95	6.76	11.7	19.8
	0.30		2.59	2.90	4.02	4.38	6.00	6.83	10.1	15.8
	0.50		2.54	3.00	3.59	4.58	5.13	6.17	8.44	11.8
	0.70		1.54	1.74	2.75	3.23	3.98	4.45	5.95	9.72
	0.90		1.27	1.37	1.86	1.95	2.61	2.99	4.86	7.56
EAc–AcN	0	Piperidine	10.0	16.8	27.0	31.4	35.0	47.5		
	0.10		16.5	23.5	34.5	40.7	53.2	63.7		
	0.30		41.1	52.4	75.1	77.8	120	143		
	0.50		56.5	67.2	90.4	91.8	135	158		
	0.70		65.5	77.1	96.5	105	135	162		
	0.90		87.3	101	131	140	165			
	1.00		135	155	169	174				

$$k_A = \frac{k_1 k_2}{k_{-1}} + \frac{k_1 k_3^B}{k_{-1}}[B] \tag{9}$$

(c) $k_2 + k_3{}^B\,[B] \approx k_{-1}$. In this intermediate situation, Eqn 8 indicates that base catalysis should be observed with a curvilinear dependence of k_A on [*B*]. At low [*B*], the plot of k_A vs [*B*] should be a straight line which will change to a plateau at high [*B*], where the formation of the intermediate becomes rate-limiting. Numerous kinetic studies devoted to the reactions shown in Eqn 8 have demonstrated the validity of Eqns 8 and 9.

A new situation has recently been discovered for several systems for which an upward curvature has been found in the plot of k_A *vs* [*B*], which corresponds to a parabolic dependence of k_A *vs* [*B*] and a fourth-order kinetic law. Several alternative mechanisms have been proposed to account for this new kinetic finding.

Several kinetic studies devoted to ANS reactions with amines indicate that the occurrence and efficiency of base catalysis depend on the identities of the amine, the nucleofuge, the base and the solvent. In general, base catalysis is more often observed with secondary than with primary amines, with poor leaving groups, and in less polar solvents; one of the three described kinetic situations is observed.

The ANS reactions were extensively investigated in both polar and apolar solvents with different structural characteristics. In aprotic polar solvents, the ANS reactions followed second-order kinetics (first order in both reagents), whereas in apolar solvents the order in amine was in the 1–3 range, depending on the nature of the solvent and the nature of the amine.[24] The evidence for mechanisms proposed for ANS reactions by primary or secondary amines in aprotic solvents of low relative permittivity has recently been reviewed.[25]

In previous studies,[26] we have shown that solvent effects on the second-order rate coefficients, k_A, for the reactions of 1-chloro-2,4-dinitrobenzene (CDNB) with piperidine (PIP) in several aprotic solvents are well correlated by the Dimroth–Reichardt solvent polarity scale $E_T(30)$. The correlation is remarkably good if HBD solvents are excluded. However, the studies of the reaction in methanol and in other alkanols are not well

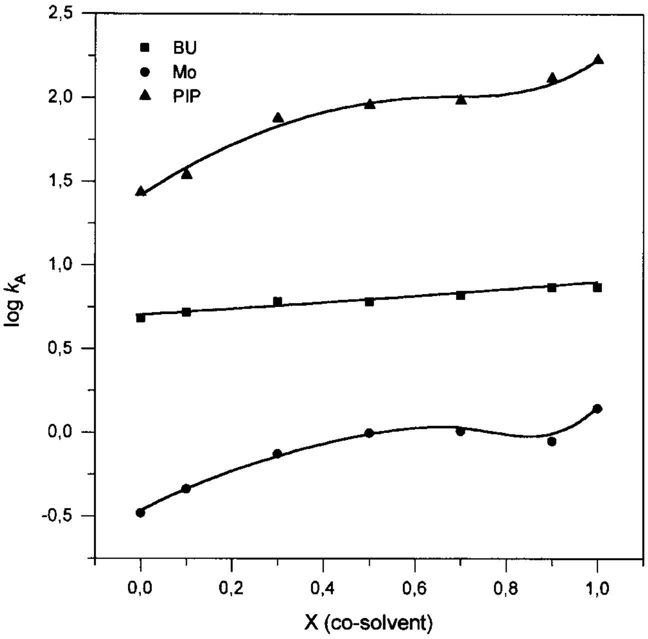


Figure 8. Plot of log k_A *vs* co-solvent mole fraction for the reaction of FDNB with primary or secondary amines in EAc–AcN solvent system at 25 °C

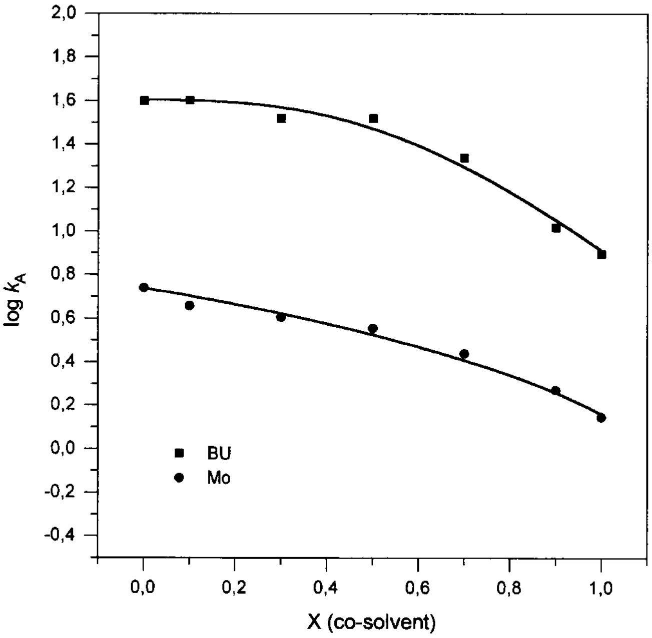


Figure 9. Plot of log k_A *vs* co-solvent mole fraction for the reaction of FDNB with primary or secondary amines in DMF–AcN solvent system at 25 °C

correlated by $E_T(30)$ parameters and the reactivity in hydroxylic solvents is inversely proportional to the HBD ability of the solvents.

More recently,[27] we have studied the CDNB + PIP reaction in two different systems of completely non-aqueous binary mixtures in which preferential solvation is the rule, but without synergetic effects for the $E_T(30)$ parameter.

Kinetic determinations

In the first part of this work, we characterized several completely non-aqueous binary solvent mixtures of the PAHBA solvent–AcN or NM type. In this connection, the kinetics of FDNB–*n*-butylamine and FDNB–morpholine reactions were studied at 25 °C in two of those mixtures: EAc–AcN and DMF–AcN. These mixtures presented different microscopic properties, the former providing convergent results for a given property if different probes are used for its determination, whereas in the latter this convergence is not observed. We also determined the kinetics of the FDNB–piperidine reaction in EAc–AcN at 25 °C.

The reactions were explored at different solvent compositions and in each case the influence of amine concentration was studied. The reactions were carried out under pseudo-first-order conditions. They yielded the expected product in quantitative yield [*N*-(2,4-dinitrophenyl)butylamine, *N*-(2,4-dinitrophenyl)morpholine and *N*-(2,4-dinitrophenyl)piperidine, respectively], and proved to be first order in the corresponding substrate. The second-order rate coefficients, k_A, calculated from the experimental pseudo-first-order rate coefficients, k_ρ, are listed in Table 6. The k_A values for the development of the reactions in the corresponding pure solvents are additionally presented.

The variation of the rate constant with the change in amine in all solvent systems follows the usual pattern found in ANS reactions. The rate constants decrease from PIP through BU to Mo. It should be pointed out that the rate values decrease with decrease in the basicity of the amine and, when comparing amines of approximately the same basicity, PIP is more nucleophilic than BU.

For the three kinds of ANS reactions explored, the kinetic data show a general tendency in agreement with the overall solvation capability of the solvent mixtures. The rate constant values decrease from DMF–AcN to EAc–AcN binary mixtures. On the other hand, for the EAc–AcN system the k_A values increase with increase in co-solvent concentration, whereas in the DMF–AcN system the opposite behaviour was observed.

Figure 8 presents the plots of log k_A as a function of co-solvent mole fraction for the reaction analysed in the EAc–AcN system at [amine] = 0.008 M. For the secondary amines, the shapes of the curves are similar, exhibiting continuous increases in log k_A with increase in co-solvent concentration and an inflection point in the AcN-rich zone (clearly marked for Mo). For the primary amine, a linear increase can be observed with increase in co-solvent concentration.

Figure 9 presents the plots of log k_A as a function of co-solvent mole fraction for the reaction in the DMF–AcN

Table 7. Partial rate coefficients for the reaction of FDNB with secondary amines in EAc–AcN

X_{AcN}	Amine	$k_1\ k_2/k_{-1}$	$k_1\ k_3/k_{-1}$	k_3/k_2	n	r	SD
0.0	Mo	0.053	30.87	582	8	0.999	0.043
	PIP	8.625	2045	237	6	0.989	2.299
0.1	Mo	0.110	43.67	397	7	0.996	0.112
	PIP	13.09	2559	195	6	0.997	1.494
0.3	Mo	0.391	40.51	103	8	0.988	0.177
	PIP	28.37	5652	199	6	0.996	3.891
0.5	Mo	0.454	53.4	117	7	0.996	0.137
	PIP	47.5	5418	114	6	0.996	3.891
0.7	Mo	0.533	53.93	101	8	0.991	0.203
	PIP	54.75	5210	95	6	0.998	2.489
0.9	Mo	0.715	54.44	101	8	0.994	0.282
	PIP	81.19	5506	69	5	0.989	5.149

system at [amine] = 0.008 M. For both primary and secondary amines, the shapes of the curves show a general tendency for curvilinear decreases in k_A values with increase in co-solvent concentration.

As can be observed, no acceleration in rate is produced for an increasing amount of amine for the FDNB –BU reaction in the two solvent systems.

On the other hand, an acceleration in rate is produced for the reaction with Mo and PIP in EAc–AcN. Table 7 presents the partial rate coefficients. For both amines, the $k_3/k_2 \geq 100$ ratio in the co-solvent-poor zone increases with increase in PAHBA solvent, indicating base catalysis. At high co-solvent concentration, $k_3/k_2 \approx 50$–100, which can be considered a border condition in the evaluation of base catalysis. For the reaction with the nucleophile Mo, the plot of k_A *vs* amine concentration exhibits a curvilinear tendency. In this case, the amine concentration range was extended and the standard methods of analysis were applied to the results in AcN, giving values of $k_1 = 16.14$ $\mathrm{l\,mol^{-1}\ s^{-1}}$, $k_2/k_{-1} = 0.056$, $k_3/k_{-1} = 6.04$ $\mathrm{l\,mol^{-1}}$ and $k_3/k_2 = 108$ $\mathrm{l\,mol^{-1}}$. For this situation $k_2 + k_3{}^B\ [B] \approx k_{-1}$, and the formation of the intermediate becomes rate-limiting. Presumably the same behaviour would occur with PIP.

Table 8. Values of $k_A{}^{Cl}$ and $k_A{}^F/k_A{}^{Cl}$ for the reactions of FDNB and CDNB with Mo

Solvent	X_{AcN}	$k_A{}^{Cl}$	$k_A{}^F/k_A{}^{Cl}$
EAc–AcN	0	0.0355	37
	0.1	0.036	50
	0.3	0.0390	59
	0.5	0.381	72
	0.7	0.381	81
	0.9	0.335	91
	1	0.04	101
DMF–AcN	0	0.164	77
	0.1	0.145	81
	0.3	0.121	83
	0.5	0.0851	99
	0.7	0.0750	79
	0.9	0.0489	99

For the DMF –AcN system, an intermediate situation between the conditions $k_2 + k_3{}^B\ [B] \approx k_{-1}$ and $k_2 + k_3{}^B\ [B] \ll k_{-1}$ can be seen, the rate-limiting step corresponding to the formation and the decomposition of the intermediate, respectively. The value $k_3/k_2 \approx 50$ and a curvilinear tendency are observed in the plots of k_A *vs* [B] at high co-solvent concentration.

A useful alternative criterion for base catalysis can be applied when the nucleofuges are halogens. If the rate-constant sequence $F \gg$ other halogens is observed, then cleavage of the carbon–fluorine bond is not involved in the rate-determining step. In this direction, the values of the second-order rate constant were determined for the reaction of 1-chloro-2,4-dinitrobenzene (CDNB) with Mo in EAc–AcN and DMF–AcN solvent systems at 25 °C (no significant acceleration in rate occurs with increasing amount of amine). The experimental data are reported in Table 8. Additionally, the calculation of $k_A{}^F/k_A{}^{Cl}$ coefficient ratios is presented.

For the solvent systems explored, the values $k_A{}^F/k_A{}^{Cl} \approx 50$–100 for the title reaction are considered as indirect evidence confirming a situation of a border condition in the evaluation of base catalysis.

Correlation analysis

The often linear correlation between empirical solvent parameters and other solvent-dependent properties (*e.g.* logarithms of rate and equilibrium constants, absorption energies) can be considered as manifestations of general free-energy relationships (LFERs).[9,28] It is possible to interpret the solvent effects with the aid of model processes that yield the same or similar effects. Although polarity parameters for many pure solvents have been thoroughly correlated with each other and with other solvent-dependent properties, the extent to which such parameters for binary solvent mixtures are likewise correlated is still not significant.

Table 9. Correlation coefficient (*r*), standard deviation (SD), slope (*B*) and intercept (*A*) [and their standard errors (s_B, s_A)] and the number of data points (*n*) for the linear regression $\log k_A = A + B\,[E_T(30)]$ in PAHBA solvent–AcN systems (including pure solvents)

Amine	PAHBA solvent	*r*	SD	*B*	s_B	*A*	s_A	*n*
BU	EAc	0.944	0.028	0.026	0.004	−0.329	0.175	7
	DMF	0.939	0.105	0.341	0.056	16.609	2.504	7
Mo	EAc	0.962	0.064	0.074	0.009	−3.328	0.408	7
	DMF	0.907	0.099	−0.253	0.052	11.842	2.350	7
PIP	EAc	0.969	0.079	0.102	0.011	−0.516	0.500	7

In earlier papers,[8,26,27] we described the correlation analysis between $E_T(30)$ and another solvent-dependent model process, *i.e.* the ANS reaction of halonitrobenzenes with primary and secondary amines in pure solvents and in several completely non-aqueous binary solvent mixtures with different microscopic characteristics.

We have now extended the preceding correlation analysis to the kinetic data for the proposed ANS model reaction in PAHBA–AcN systems (k_A values are at [amine] = 0.008 M). The results are summarized in Table 9. The regression equations were assessed by the evaluation of the correlation coefficients (*r*) and the standard deviations (SD). The correlations are relatively good ($r \geq 0.94$, SD ≤ 0.08) for the reactions in EAc–AcN solvent systems but are poor in DMF–AcN systems ($r \leq 0.94$, SD ≥ 0.10). The slopes have opposite signs for mixtures with EAc and mixtures with DMF, indicating different solvation models.

Table 10 presents the correlation analysis for the logarithm of the kinetic data (at [amine] = 0.008 M) with π^*, α and β solvatochromic parameters as measures of the solvent properties, according to the Kamlet–Taft model, $\log k_A = Y + s\pi^* + a\alpha + b\beta$, which is excellent for FDNB–BU in EAc–AcN.

CONCLUSIONS

From the analysis of the solvation models of the different chemical probes using several PAHBA solvent–acetonitrile or nitromethane solvent systems, and from the kinetic determinations in these binary solvent systems, the following conclusions can be drawn.

Preferential solvation phenomena are not operative and ideal behaviour is observed only for solute **II** in mixtures in which the PAHBA solvents are EAc, AC and BUT, and for solute **III** in mixtures with EAc (data for probe **III** in mixtures with AC and BUT were interpolated). For the rest of the cases explored, preferential solvation takes place. All the indicators interact to different extents with the components of the solvent mixtures. The difference in the interactions is reflected in the composition of the microsphere of solvation: each solute has in its environment more of one solvent than the other if compared with the bulk solvent, and this local concentration may vary from one probe to another.

When a particular parameter that measures a microscopic property for a given binary mixture is obtained from different probes, the following behaviour is observed: for the explored cases in which the preferential

Table 10. Correlation coefficients (*r* and r^2), standard deviation (SD), intercept (*Y*) and parameters *s*, *a* and *b* (and their standard errors) and the number of data points (*n*) for $\log k_A = Y + s\pi^* + a\alpha + b\beta$ in PAHBA solvent–AcN systems (including pure solvents)

Amine	PAHBA solvent	r (r^2)	SD	Y (s_Y)	s (s_s)	a (s_a)	b (s_b)	*n*
BU	EAc	0.995 (0.990)	0.011	−1.567 (0.969)	2.424 (0.848)	−0.799 (0.483)	1.985 (1.098)	7
	DMF(**IV**)	0.997 (0.995)	0.029	−1.109 (1.369)	1.843 (1.537)	−0.030 (0.691)	1.489 (0.359)	7
	DMF(**V**)	0.997 (0.995)	0.030	10.81 (3.357)	−10.24 (3.736)	−7.420 (1.718)	0.345 (0.159)	7
Mo	EAc	0.993 (0.986)	0.043	0.000 (0.031)	−1.184 (0.275)	−0.792 (0.216)	3.034 (0.309)	7
	DMF(**IV**)	0.981 (0.963)	0.058	−3.559 (2.798)	4.020 (3.141)	0.839 (1.413)	0.938 (0.734)	7
	DMF(**V**)	0.983 (0.966)	0.056	2.115 (6.373)	−1.722 (7.094)	−2.750 (3.264)	0.393 (0.302)	7
PIP	EAc	0.999 (0.997)	0.058	0.000 (0.041)	2.434 (0.370)	0.897 (0.291)	0.138 (0.417)	7

solvation is not operative, the different indicators produce convergent values of the property at a given composition of the mixture; and for the explored cases in which preferential solvation phenomena are the rule, two different situations can be pointed out:

(a) Convergence of the values of the measured microscopic properties is observed in the cases of indicators **II** and **III** in mixtures with DMF and DMSO, and in the cases of indicators **IV** and **V** in mixtures with EAc. Consequently, the average of the obtained values for the same parameter by the different indicators should give an acceptable estimate of the microscopic property of the mixture.

(b) Disparity in the values for the same parameter obtained from different indicators is observed for **IV** and **V** in mixtures of DMF and DMSO. This behaviour reflects the different sensitivities of the indicators to solute–solvent interactions, which is not only solute dependent but also solvent dependent. In these cases, the strong interactions of the solute with one component of the mixture interfere with the self- and mutual interactions of the solvents.

Apparently, the low HBD character of these mixtures precludes synergistic effects on the explored solvatochromic indicators (in only a few cases can we observe negligible synergistic effects on the chemical probes) and, consequently, the correspondence parameters *vs* kinetics is better than in the case of PAHBA solvent–chloroform or dichloromethane mixtures, in which the synergistic effects on the indicators are relevant. On the other hand, the preferential solvation model, and necessarily the solvent effects produced by these kinds of binary mixtures of solvent on the ANS reactions studied, seem to be dependent on the type of amine.

As observed, the preferential solvation of the probes explored should not obviate their use as ‘stand-ins’ for the general solutes. Therefore, probes which interact with the components of the binary mixed solvent less strongly than with these self- or mutual interactions would have similar environments and provide convergent values of the properties with the expressions employed for neat solvents.

EXPERIMENTAL

Reagents and solvents. 1-Chloro-2,4-dinitrobenzene, 1-fluoro-2,4-dinitrobenzene, piperidine, and *n*-butylamine were purified as described previously.[8] Morpholine (Aldrich, 99%) was distilled under reduced pressure over sodium and was kept under nitrogen. *N*-(2,4-Dinitrophenyl)piperidine, *N*-(2,4-dinitrophenyl)butylamine and *N*-(2,4-dinitrophenyl)morpholine were prepared and purified by methods reported previously.[8] 2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt’s dye; Aldrich, 95%), 4-nitroanisole (Aldrich, 97%) and 4-nitroaniline (Aldrich, 99%) were used without further purification. *N,N*-Diethyl-4-nitroaniline was prepared by nitration of *N,N*-diethylaniline (Carlo Erba, 99.5%).[29a] 4-Nitrophenol was prepared by nitration of phenol (Mallinckrodt, *Ca* 99.5%).[29b] The solvents were purified as previously reported[8] and all of them were kept over 4 Å molecular sieves and stored in special vessels that allow delivery without air contamination. All binary solvent mixtures were prepared prior to use and stored under anhydrous conditions.

Solvatochromic parameters measurements. The pure solvents were mixed in appropriate proportions by weight to give binary solvent mixtures of various compositions. Indicators solutions were prepared just prior to use. Visible spectra of sample solutions in 10 mm cells were recorded at 25 °C by using a Perkin-Elmer Model 124 UV–visible spectrophotometer and a Zeiss PMQ 3 UV–visible spectrophotometer equipped with a data-acquisition system [the accuracy of the measured wavenumbers of the absorption peaks is ≤ 0.1 kK (1 nm in λ); this, of the order of the precision limit of the solvatochromic comparison method, justifies in all cases the statements about deviations from linearity of the solvatochromic parameters of the mixtures] and a thermostated cell holder. Temperatures were measured in the cell and were accurate to within ± 0.1 °C.

Kinetic procedures. The kinetics of the reactions were studied spectrophotometrically.[26a] A Perkin-Elmer Model 124 spectrophotometer was used, with a data-acquisition system based on a microprocessor. This set-up has a 12-bit analogue-to-digital converter which allows absorbance measurements with an error of $<0.1\%$ at a maximum of 12 readings s^{-1}. The microprocessor controls data acquisition and also measures time through a quartz crystal-controller oscillator. Once data acquisition is completed, data can be read in the system display and/or transferred to a computer through an interface. In all cases, pseudo-first-order kinetics were observed.

Standard solutions of 1-halo-2,4-dinitrobenzene and the corresponding primary or secondary amine were prepared in the desired binary solvent mixture at room temperature. The reactions were run by mixing known amounts of each solution in the thermostated cells of the spectrophotometer, recording the absorbances at *ca* 400 nm. The pseudo-first-order (k_ρ), and second-order (k_A), rate coefficients were obtained as described previously. In all cases, the ‘infinity’ value, $A\infty$, was experimentally determined for each run at the working temperature. Within the experimental error, this value agreed with the ‘theoretical’ value calculated from application of Beer’s law to a corresponding solution of *N*-(2,4-dinitrophenyl)amine in the working binary solvent mixture. All the kinetic runs were carried out at least in duplicate; the error in k_A was $\leq$2–3% for all the solvent mixtures examined.

Acknowledgements

We are indebted to the Universidad Nacional del Litoral (UNL), República Argentina. This work received financial support from the Science and Technology Secretariat, UNL, CAI+D Program (Project 94-0858-007-054).

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