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Characterization of solvent mixtures: preferential solvation of chemical probes in binary solvent mixtures of polar hydrogen-bond acceptor solvents with polychlorinated co-solvents

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ABSTRACT: The use of chemical probes for the characterization of chemical properties is explored for aprotic binary solvent mixtures. The solvatochromic indicators *N*,*N*-diethyl-4-nitroaniline, 4-nitroanisole, 4-nitroaniline and 4-nitrophenol were used to characterize binary solvent mixtures of a polar aprotic hydrogen-bond acceptor solvent (ethyl acetate, acetonitrile and dimethyl sulfoxide) with a polychlorinated hydrogen-bond donor solvent (chloroform or dichloromethane). The solvent parameters π^*, α and β of the binary mixtures were calculated from the solvatochromic shifts of the indicators. In each case the degree of convergence for a solvent property values obtained from different probes was analyzed. Data obtained by using the non-polar solvatochromic indicator β-carotene are additionally presented. The behavior of the solvent systems was analyzed according to their deviation from ideality due to preferential solvation of the solutes and the complicated intermolecular interactions of the two components of the solvent mixture. 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. Theoretical equations (preferential solvation models) were used to compute the solvatochromic data. The results were analyzed and related to the solvent effects on some aromatic nucleophilic substitution reactions, comparing the application of single- and multiparametric treatments of solvent effects. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: solvent mixtures; solvation; hydrogen-bond acceptor solvents; polychlorinated co-solvents; solvent parameters; solvatochromic shifts

INTRODUCTION

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.[1] In this connection, numerous reports on solvent polarity scales have been published in the last few decades.[2–5] More recently, Abraham *et al.*[6] proposed scales of solute hydrogen-bond acidity and solute hydrogen-bond basicity and devised a general solvation equation.

Negative and positive 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 capabilities.

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 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 the preferential solvation of the solute. 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 has recently been discussed.[7]

In a first attempt to understand the nature of the

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molecular–microscopic properties of mixed solvents, we analyzed the preferential solvation of the Dimroth–Reichardt $E_T(30)$ dye 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (**I**) for some binary solvent mixtures of the aprotic solvent + cosolvent (toluene or methanol) type. We also related the results to the solvent effects on the kinetics of a simple model of aromatic nucleophilic substitution reactions (S_NAr).[8a,b]

In the same direction, we have studied the preferential solvation of the $E_T(30)$ dye for several binary solvent mixtures of the type polar aprotic hydrogen-bond acceptor (PAHBA) solvent + chloroform or dichloromethane (both taken as hydrogen-bond donor solvents).[8c] Most of these mixtures presented synergetic effects for the $E_T(30)$ parameter: the indicator can be preferentially solvated by the hydrogen-bonded complexes yielding $E_T(30)$ values higher than those of the pure solvents mixed. The solvent effects shown by some of these synergetic mixtures for the $E_T(30)$ on simple models of S_NAr reactions with different characteristics (base-catalyzed and non-base-catalyzed reactions) were studied. It was shown that the chemical probe under consideration is not generally valid to interpret the solvation effects produced by these kinds of solvent mixtures on the explored reactions.

Taking into account the preceding results, it was of interest to explore other empirical parameters to describe the solvent features in the molecular–microscopic environments of the solutes. Particularly attractive are multiparameter approaches, with one parameter for each solvent property.

At this point, in order to understand better the nature of the molecular–microscopic properties of binary solvent mixtures and to perform a quantitative evaluation of the solvent effects on different solvent-dependent reference processes, we determined separate solvent parameters that are associated with different solute–solvent interaction mechanisms for mixtures of the PAHBA solvent + chloroform or dichloromethane type as previously characterized by the $E_T(30)$ dye.

This work had several purposes: (i) measuring a set of empirical solvatochromic parameters for the above type of binary mixtures with the intention of obtaining numerical values of the solvent properties for their use as 'predictors or descriptors' of the solvent effects on the behavior of diverse kinds of solutes and transition states; here, the Kamlet, Abboud and Taft scales were selected as microscopic solvent descriptors; the data obtained from β-carotene as a non-polar molecule probe, proposed by Abe, are additionally reported; (ii) analyzing the convergence or divergence in property values obtained from different reference solutes for a given mixture, and discussing the validity of the concept 'property of a mixed solvent; (iii) comparing the preferential solvation response models of different chemical probes in binary solvent mixtures, focusing on the extent and nature of the solute–solvent and solvent–solvent interactions, leading to an understanding of solvation effects; (iv) applying theoretical equations allowing us to correlate the experimental values with the solvent compositions (preferential solvation models), evaluating the parameters of solvation (that assist in the interpretation of solvent effects); and (v) exploring the correspondence between the kinetic properties of some S_NAr reactions (in which base catalysis is not operative) and the molecular–microscopic solvent properties, and comparing the results obtained from the application of uniparametric and multiparametric treatments of solvent effects.

RESULTS AND DISCUSSION

Characterization of binary solvent mixtures by using solvatochromic indicators

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/Vis absorption spectra.[2–5] The $E_T(30)$ scale of Dimroth and Reichardt[3] and the π^*, β and α scales constructed by Kamlet, Abboud and Taft from the solvatochromic comparison method[9] are the most widely used in the uniparametric and multiparametric approaches, respectively. They are calculated from the wavenumbers of the maximum of absorbance of different chemical probes. The $E_T(30)$ values are available for several binary solvent mixtures, but corresponding data for π^*, β and α parameters are still scarce. These latter 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.[10] Recently, new molecules probe (structurally different) have been reported.[11] Abe proposed some solutes of reference having no dipole moments or only small ones such as naphthalene, anthracene or β-carotene (from which the π^*_2 scale is derived).[12]

The PAHBA solvents selected in this work [which take a part in the set of binary mixtures previously characterized by the solvent 'polarity' $E_T(30)$[8c]] were ethyl acetate (EAc), acetonitrile (AcN) and dimethyl sulfoxide (DMSO). The co-solvents $CHCl_3$ and CH_2Cl_2 are dipolar and highly polarizable polychlorinated HBD species, $CHCl_3$ being the strongest. In both cases, the hydrogen atoms can form complexes via hydrogen bonding with the PAHBA solvents. The properties of the pure solvents used to prepare the studied mixtures are given in Table 1. For each system explored, the solvatochromic parameters were systematically deter-

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

Parameter	EAc	AcN	DMSO	$CHCl_3$	CH_2Cl_2
$E_T(30)$	38.1	45.6	45.1	39.1	40.7
π^*	0.55[a]	0.75[a]	1.00[a]	0.58[a]	0.82[a]
π^*(II)	0.55[c]	0.79[c]	1.00[c]	0.81[c]	0.79[c]
π^*(III)	0.57[c]	0.73[c]	1.00[c]	0.75[c]	0.77[c]
β	0.45[a]	0.40[a]	0.76[a]	0.10[a]	0.10[a]
β(IV)	0.49[c]	0.41[c]	0.78[c]	(0.00)[c]	(0.00)[c]
β(V)	0.42[c]	0.48[c]	0.64[c]	(0.48)[c]	0.13[c]
α	0.00[a]	0.19[a]	0.00[c]	0.20[a,b]	0.13[a,b]
α(II,IV)	0.00[c]	0.32[c]	0.02[c]	(0.00)[c]	0.13[c]
α(III,V)	0.00[c]	0.37[c]	0.04[c]	(0.00)[c]	0.12[c]

[a] Data from Ref. 10.
[b] Data from Ref. 20.
[c] Values determined by us from the explored indicators.

mined over the full solvent composition range (at nine molar fractions of co-solvent) at 25 °C.

On the other hand, the relationships between the transition energy, the wavenumber of maximum absorption or even a solvatochromic parameter dependent on only a single indicator [$E_T(30)$, E_T^N or π^*] and the composition of binary solvent mixtures were studied by Bosch and co-workers.[13] The proposed theoretical equations (based on solvent exchange models[14]), which take into account the solute–solvent and solvent–solvent interactions, are applied here to the experimental data.

Determination of π^* values and exploration of β-carotene as a non-polar indicator

The solvatochromic dipolarity/polarizability parameter π^* was determined employing the solvatochromic indicators *N*,*N*-diethyl-4-nitroaniline (**II**) and 4-nitroanisole (**III**) that belong to the selected probe solutes set proposed by Kamlet, Abboud and Taft.[9] These probes are dipolar aromatic molecules of the A–C_6H_4–D type, where A and D stand for electron-acceptor (NO_2) and electron-donor (NEt_2 and OMe) groups, respectively.

Table 2. Experimental wavenumbers (in kK) and solvatochromic parameters for the binary solvent mixtures PAHBA solvent + $CHCl_3$

PAHBA solvent	X_{CoS}	$\tilde{\nu}$(II)	$\tilde{\nu}$(III)	$\tilde{\nu}$(VI)	π^*(II)	π^*(III)	π^*(avg)
EAc	0.1	25.54	32.97	22.03	0.62	0.49	0.56
	0.2	25.48	32.92	21.93	0.64	0.51	0.58
	0.3	25.45	32.90	21.93	0.65	0.52	0.59
	0.4	25.45	32.83	21.90	0.65	0.55	0.60
	0.5	25.39	32.81	21.86	0.67	0.56	0.62
	0.6	25.35	32.78	21.83	0.68	0.57	0.66
	0.7	25.32	32.78	21.74	0.69	0.57	0.63
	0.8	25.26	32.69	21.69	0.71	0.61	0.66
	0.9	25.04	32.62	21.60	0.78	0.64	0.71
AcN	0.1	24.88	32.41	22.03	0.83	0.73	0.78
	0.2	24.88	32.36	21.93	0.83	0.75	0.79
	0.3	24.81	32.32	21.83	0.85	0.77	0.81
	0.4	24.81	32.32	21.81	0.85	0.77	0.81
	0.5	24.81	32.27	21.74	0.85	0.79	0.82
	0.6	24.75	32.27	21.74	0.87	0.79	0.83
	0.7	24.75	32.27	21.74	0.87	0.79	0.83
	0.8	24.81	32.27	21.67	0.85	0.79	0.82
	0.9	24.88	32.27	21.62	0.83	0.79	0.81
DMSO	0.1	24.68	31.89	21.37	0.89	0.95	0.92
	0.2	24.68	32.15	21.41	0.89	0.84	0.87
	0.3	24.68	32.15	21.46	0.89	0.84	0.87
	0.4	24.68	32.27	21.50	0.89	0.79	0.84
	0.5	24.82	32.36	21.53	0.85	0.75	0.80
	0.6	24.91	32.48	21.55	0.82	0.70	0.76
	0.7	24.94	32.53	21.55	0.81	0.68	0.75
	0.8	24.94	32.57	21.57	0.81	0.66	0.74
	0.9	24.94	32.57	21.60	0.81	0.66	0.74

Table 3. Experimental wavenumbers (in kK) and solvatochromic parameters for the binary solvent mixtures PAHBA solvent + CH_2Cl_2

PAHBA solvent	X_{CoS}	$\tilde{\nu}$(II)	$\tilde{\nu}$(III)	$\tilde{\nu}$(VI)	π^*(II)	π^*(III)	π^*(avg)
EAc	0.1	25.64	32.85	22.03	0.59	0.54	0.57
	0.2	25.61	32.83	22.00	0.60	0.55	0.58
	0.3	25.58	32.81	21.98	0.61	0.56	0.59
	0.4	25.48	32.78	21.98	0.64	0.57	0.61
	0.5	25.45	32.69	21.91	0.65	0.61	0.63
	0.6	25.45	32.67	21.88	0.65	0.62	0.64
	0.7	25.32	32.62	21.83	0.69	0.64	0.67
	0.8	25.23	32.53	21.81	0.72	0.68	0.70
	0.9	25.13	32.41	21.74	0.75	0.73	0.74
AcN	0.1	25.00	32.41	22.05	0.79	0.73	0.76
	0.2	25.00	32.36	21.98	0.79	0.75	0.77
	0.3	24.97	32.36	21.93	0.80	0.75	0.78
	0.4	24.94	32.32	21.93	0.81	0.77	0.79
	0.5	24.91	32.27	21.83	0.82	0.79	0.81
	0.6	24.91	32.27	21.83	0.82	0.79	0.81
	0.7	24.94	32.27	21.74	0.81	0.79	0.80
	0.8	24.97	32.27	21.74	0.80	0.79	0.80
	0.9	25.00	32.32	21.74	0.79	0.77	0.78
DMSO	0.1	24.40	31.78	21.37	0.98	1.00	0.99
	0.2	24.43	31.80	21.46	0.97	0.99	0.98
	0.3	24.53	31.85	21.48	0.94	0.97	0.96
	0.4	24.56	31.89	21.53	0.93	0.95	0.94
	0.5	24.62	31.94	21.53	0.91	0.93	0.92
	0.6	24.65	32.00	21.60	0.90	0.91	0.91
	0.7	24.75	32.10	21.60	0.87	0.86	0.87
	0.8	24.81	32.13	21.62	0.85	0.85	0.85
	0.9	24.91	32.15	21.64	0.82	0.84	0.83

The electronic transition is connected with an intramolecular charge transfer from the electron-donor part to the acceptor part through the aromatic system. The structures of the aromatic nitro compounds used as indicators are basically similar, although the diethylamino and methoxy groups appear to be rather different. 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, and to measure the exoergic effects of solute/solvent dipole–dipole and dipole–induced dipole interactions. Therefore, π^* values mainly represent a blend of dipolarity and polarizability of the solvents and it has been shown that, in the absence of HB interactions, the main physical difference between π^* and the $E_T(30)$ values lies in different responses to solvent polarizability effects.[15]

The π^* value was calculated from the wavenumbers of the UV/Vis absorption maxima of indicators **II** [$\tilde{\nu}$ (II)] and **III** [$\tilde{\nu}$ (III)] according to the conversion expressions reported by Marcus:[10]

$$\pi^*(\mathrm{II}) = 0.314[27.52 - \tilde{\nu}(\mathrm{II})] \quad (1)$$

$$\pi^*(\mathrm{III}) = 0.427[34.12 - \tilde{\nu}(\mathrm{III})] \quad (2)$$

Tables 2 and 3 present the experimental wavenumbers of the maximum of the longest-wavelength electronic absorption band of indicators **II** and **III** and the calculated π^* values for binary solvent mixtures with $CHCl_3$ and CH_2Cl_2, respectively. The data obtained using β-carotene as reference solute are additionally presented. From the comparison of the data obtained with indicators **II** and **III** in a given binary mixture, it can be seen that the dipolarity/polarizability determined with indicator **II** is higher than that determined with **III** except for some DMSO + CH_2Cl_2 mixtures, in which they are very similar. This observation agrees with different studies suggesting that these reference solutes provide contaminated polarity values because they are capable of accepting hydrogen bonds [the preferred site for hydrogen bonding (the nitro group) is a better hydrogen-bond acceptor center in **II** than in **III**].[16] According to Marcus and in order to establish whether the different solutes explored produce convergent values for the property, the degree of convergence is set as already 5% of the total range of values encountered for the property in a large set of diverse solvents. In this direction, disparity in the values obtained from both solutes is observed for the solvent systems in which the co-solvent is $CHCl_3$, showing that the property values for these systems are indicator dependent. On the other hand, convergent values for the property are observed for the systems with cosolvent CH_2Cl_2. The divergence between π^*(II) and π^*(III) values observed for the mixtures with $CHCl_3$ and

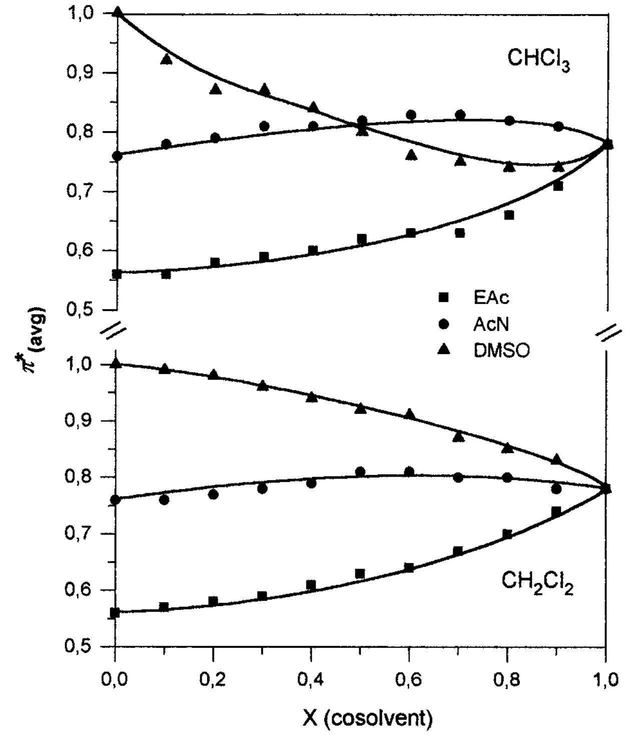

Figure 1. Plots of π*(avg) vs co-solvent mole fraction for PAHBA solvent (EAc or AcN or DMSO) + $CHCl_3$ or CH_2Cl_2 solvent systems

Table 4. Experimental wavenumbers (in kK) and solvatochromic parameters for the binary solvent mixtures PAHBA solvent + $CHCl_3$

PAHBA solvent	X_{CoS}	$\tilde{\nu}$(IV)	$\tilde{\nu}$(V)	β(IV)	β(V)	β(avg)
EAc	0.10	28.17	32.84	0.35	0.48	0.41
	0.20	28.13	32.79	0.34	0.48	0.41
	0.30	28.13	32.68	0.33	0.50	0.42
	0.40	28.13	32.68	0.33	0.48	0.41
	0.50	28.13	32.62	0.31	0.49	0.40
	0.60	28.10	32.52	0.31	0.51	0.41
	0.70	28.13	32.41	0.29	0.54	0.42
	0.80	28.29	32.36	0.21	0.53	0.37
	0.90	28.45	32.21	0.07	0.56	0.32
AcN	0.10	27.43	32.36	0.38	0.51	0.44
	0.20	27.43	32.36	0.38	0.49	0.43
	0.30	27.43	32.21	0.36	0.53	0.44
	0.40	27.43	32.21	0.36	0.52	0.44
	0.50	27.43	32.15	0.36	0.52	0.44
	0.60	27.51	32.10	0.31	0.53	0.42
	0.70	27.62	32.05	0.27	0.54	0.40
	0.80	27.66	32.05	0.27	0.54	0.40
	0.90	28.17	32.10	0.12	0.51	0.31
DMSO	0.10	25.97	31.25	0.83	0.77	0.80
	0.20	26.35	31.45	0.70	0.75	0.73
	0.30	26.39	31.55	0.69	0.71	0.70
	0.40	26.39	31.50	0.69	0.75	0.72
	0.50	26.39	31.45	0.73	0.79	0.76
	0.60	26.88	31.70	0.59	0.72	0.65
	0.70	27.03	31.75	0.55	0.71	0.63
	0.80	27.40	31.80	0.41	0.70	0.56
	0.90	27.66	31.65	0.32	0.75	0.53

the convergence observed for the mixtures with CH_2Cl_2 reflect the different solvation models of the indicators, which not only depend on solute–solvent interactions but also depend on both specific and non-specific solvent–solvent interactions. Moreover, the polarizability/hyperpolarizability characteristics can play a major role in the solvatochromic behavior of polar solutes for these highly polarizable co-solvent species.^{17} The plots of the averaged π* values which, in our opinion, measure the property in a more useful manner for its application to any other similar solute as functions of the solvent composition, are presented in Fig. 1 for co-solvents $CHCl_3$ and CH_2Cl_2 (including the values for the pure solvents determined from the same indicators). The shape of the curves indicates that the property under study is lower than that corresponding to ideal solvent mixtures for EAc + $CHCl_3$ or CH_2Cl_2 mixtures, whereas it is higher and shows a positive deviation from additivity for AcN + $CHCl_3$ or CH_2Cl_2 systems. It can be noticed that, in general, these last mixtures exhibit a small synergetic effect for the property. On the other hand, two different behaviors are seen for DMSO + $CHCl_3$ or CH_2Cl_2 systems: the mixtures with CH_2Cl_2 show positive deviations from linearity but the mixtures with $CHCl_3$ exhibit high negative deviations.

Taking into account the shortcoming that the π* scale cannot be applied to non-polar and less polarized molecules, Abe introduced chemical probes with small or zero dipole moments in either the ground or the excited states, or in both such as naphthalene, anthracene or β-carotene. In order to go further into the characterization of the explored binary mixtures by analyzing the behavior of this type of solute with regard to the properties of the solvents, we determined the solvent spectral shifts for β-carotene (**VI**), which can be useful for correlation purposes. This chemical probe is a polyene with a strongly allowed π → π* transition polarized approximately along the long axis of the molecule.^{12} The experimental data for the explored mixtures are given in Tables 2 and 3 for co-solvents $CHCl_3$ and CH_2Cl_2, respectively.

Determination of β values

The solvatochromic HBA-ability parameter β was determined by the magnitudes of 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:^{10}

$$\beta = 0.358[31.10 - \tilde{\nu}(\text{IV})] - 1.125\pi^*(\text{II}) \quad (3)$$

$$\beta = 0.346[35.045 - \tilde{\nu}(\text{V})] - 0.57\pi^*(\text{III}) - 0.12\delta \quad (4)$$

Table 5. Experimental wavenumbers (in kK) and solvatochromic parameters for the binary solvent mixtures PAHBA solvent + CH_2Cl_2

PAHBA solvent	X_{CoS}	$\tilde{\nu}$(IV)	$\tilde{\nu}$(V)	β(IV)	β(V)	β(avg)
EAc	0.10	28.01	32.68	0.44	0.50	0.47
	0.20	27.97	32.68	0.44	0.49	0.47
	0.30	27.97	32.68	0.43	0.48	0.46
	0.40	27.93	32.63	0.41	0.49	0.45
	0.50	27.89	32.52	0.42	0.50	0.46
	0.60	27.86	32.47	0.43	0.50	0.46
	0.70	27.97	32.47	0.34	0.49	0.41
	0.80	28.09	32.36	0.27	0.49	0.38
	0.90	28.25	32.31	0.18	0.48	0.33
AcN	0.10	27.43	32.36	0.42	0.51	0.46
	0.20	27.43	32.36	0.42	0.49	0.46
	0.30	27.47	32.36	0.40	0.48	0.44
	0.40	27.47	32.31	0.39	0.48	0.44
	0.50	27.51	32.26	0.36	0.48	0.42
	0.60	27.59	32.31	0.34	0.46	0.40
	0.70	27.74	32.31	0.29	0.45	0.37
	0.80	27.86	32.26	0.26	0.47	0.36
	0.90	28.13	32.26	0.17	0.47	0.32
DMSO	0.10	25.84	31.25	0.78	0.74	0.76
	0.20	25.84	31.85	0.79	0.53	0.66
	0.30	25.91	31.20	0.80	0.76	0.78
	0.40	25.97	31.15	0.79	0.78	0.78
	0.50	25.97	31.35	0.81	0.72	0.77
	0.60	26.11	31.30	0.77	0.74	0.76
	0.70	26.32	31.35	0.73	0.75	0.74
	0.80	26.60	31.35	0.66	0.75	0.70
	0.90	27.06	31.45	0.52	0.71	0.62

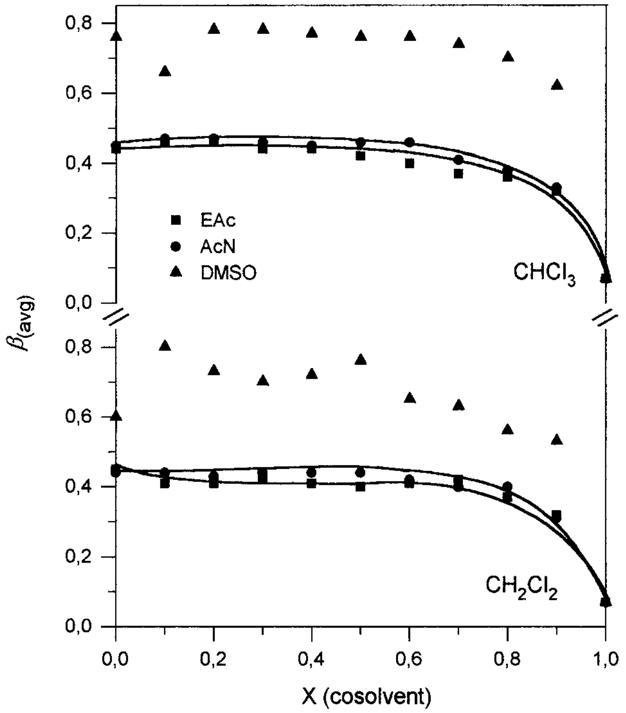

Figure 2. Plots of β(avg) vs co-solvent mole fraction for PAHBA solvent (EAc or AcN or DMSO) + $CHCl_3$ or CH_2Cl_2 solvent systems

The δ parameter is a 'polarizability correction term,' equal to 0.00 for all non-chlorinated aliphatic and dipolar aprotic solvents, 0.50 for polychlorinated aliphatic solvents and 1.00 for aromatic solvents. Tables 4 and 5 present the experimental wavenumbers of the maximum of the longest wavelength electronic absorption band of indicators **IV** and **V** and the calculated β values for the mixtures with $CHCl_3$ and CH_2Cl_2, respectively. It can be seen that the HBA ability calculated from indicator **V** is higher than that calculated from **IV** except for DMSO + $CHCl_3$ or CH_2Cl_2 mixtures at low co-solvent concentrations. This observation can be related to the different nature (NH or OH) of the acid probes used. Moreover, incomplete complexation of the acceptors in weak donor solvents is suggested for 4-nitroaniline.[18] The binary mixtures with both co-solvents exhibit, in general, divergence of values for the β parameter obtained from both indicators. This disparity in the values is higher for co-solvent-rich mixtures than for PAHBA solvent-rich mixtures, indicating that it is mainly dependent on the co-solvent. The plots of β(avg) as a function of the solvent composition are presented in Fig. 2 for co-solvents $CHCl_3$ and CH_2Cl_2. The plots clearly show some synergetic mixtures for the property (with β values higher than those corresponding to the pure solvents). This behavior is observed particularly for the DMSO + $CHCl_3$ solvent system, with π^* values with high negative deviations from linearity. The shape of the curves suggests that there is a contribution from more than one hydrogen-bonded species. These results can be understood in terms of the relative changes in the amounts of 1:1 and 2:1 $CHCl_3$–DMSO complexes (2 chloroforms to 1 DMSO).[19] When more $CHCl_3$ is added to DMSO, the proportion of 1:1 complexes drops and the number of 2:1 complexes increases, leading to the observed enhancements in the property values.

Calculation of α values

For each binary system analyzed, the α parameter was calculated from $E_T(30)$, π^* and β according to the conversion expression proposed by Marcus:[10,20]

$$\alpha = 0.0692E_T(30) - 2.090 - 0.900\pi^* - 0.147\beta + 0.190\delta \qquad (5)$$

The calculated α values are presented in Tables 6 and 7 for the co-solvents $CHCl_3$ and CH_2Cl_2, respectively [it must be pointed out that the HBD strengths determined here for the co-solvents might show differences from the values encountered in dilute solutions of CCl_4 (as monomer)].[21] It can be noted that the β parameter has little influence on the accuracy of the resulting α values.

Table 6. Solvatochromic parameters α(II,IV), α(III,V) and α(avg) for the binary solvent mixtures PAHBA solvent + $CHCl_3$

PAHBA solvent	X_{CoS}	α(II,IV)	α(III,V)	α(avg)
EAc	0.1	0.13	0.22	0.18
	0.2	0.14	0.24	0.19
	0.3	0.16	0.25	0.21
	0.4	0.17	0.23	0.20
	0.5	0.15	0.22	0.18
	0.6	0.13	0.20	0.16
	0.7	0.10	0.17	0.14
	0.8	0.08	0.13	0.11
	0.9	0.02	0.07	0.04
AcN	0.1	0.31	0.39	0.35
	0.2	0.33	0.39	0.36
	0.3	0.30	0.34	0.32
	0.4	0.25	0.30	0.28
	0.5	0.21	0.24	0.23
	0.6	0.17	0.21	0.19
	0.7	0.12	0.15	0.14
	0.8	0.09	0.10	0.09
	0.9	0.07	0.05	0.06
DMSO	0.1	0.13	0.09	0.11
	0.2	0.16	0.20	0.18
	0.3	0.16	0.20	0.18
	0.4	0.15	0.23	0.19
	0.5	0.17	0.25	0.21
	0.6	0.19	0.28	0.24
	0.7	0.18	0.27	0.22
	0.8	0.14	0.24	0.19
	0.9	0.08	0.16	0.12

Table 7. Solvatochromic parameters α(II,IV), α(III,V) and α(avg) for the binary solvent mixtures PAHBA solvent + CH_2Cl_2

PAHBA solvent	X_{CoS}	α(II,IV)	α(III,V)	α(avg)
EAc	0.1	0.04	0.08	0.06
	0.2	0.09	0.13	0.11
	0.3	0.11	0.15	0.13
	0.4	0.11	0.17	0.14
	0.5	0.13	0.15	0.14
	0.6	0.14	0.16	0.15
	0.7	0.14	0.16	0.15
	0.8	0.14	0.14	0.14
	0.9	0.12	0.10	0.11
AcN	0.1	0.31	0.35	0.33
	0.2	0.30	0.32	0.31
	0.3	0.27	0.31	0.29
	0.4	0.26	0.28	0.27
	0.5	0.23	0.24	0.24
	0.6	0.21	0.22	0.22
	0.7	0.19	0.19	0.19
	0.8	0.18	0.16	0.17
	0.9	0.17	0.14	0.15
DMSO	0.1	0.05	0.04	0.04
	0.2	0.07	0.09	0.08
	0.3	0.08	0.06	0.07
	0.4	0.09	0.07	0.08
	0.5	0.08	0.08	0.08
	0.6	0.07	0.07	0.07
	0.7	0.08	0.08	0.08
	0.8	0.08	0.07	0.07
	0.9	0.09	0.04	0.06

Figure 3 presents the plots of α (avg) vs X_{CoS} for both solvent systems. It can be observed that all the EAc or DMSO + $CHCl_3$ solvent mixtures have a higher ability to donate a hydrogen atom toward the formation of a hydrogen bond than the expected ability derived from the average of the quantities characterizing the two neat solvents mixed, exhibiting high synergetic effects. Some AcN + $CHCl_3$ and EAc + CH_2Cl_2 mixtures present weak synergism for the property.

Preferential solvation of solvatochromic indicators: application of preferential solvation models

In order to understand better the influence of solute–solvent and solvent–solvent interactions on the preferential solvation of the explored chemical probes, we applied reported preferential solvation models[13] to the description of the data obtained from indicators **I**–**VI** in EAc + $CHCl_3$ or CH_2Cl_2 mixtures. These types of mixtures were selected for this analysis taking into account that they present high synergetic effects for the $E_T(30)$ polarity (the highest synergism was observed for co-solvent $CHCl_3$) and, in contrast, we have reported that EAc + $CHCl_3$ mixtures do not produce kinetic synergism on simple models of S_NAr (non-base-catalyzed reactions of halonitrobenzenes with primary or secondary amines).[8c]

As is known, in solvent mixtures the solutes can interact to different degrees with the components of the mixture, and this difference in the interactions is reflected in the composition of the microsphere of solvation. Several equations based on solvent exchange models that relate the transition energy of the Dimroth–Reichardt $E_T(30)$ indicator to the solvent composition have been derived and compared.[13,14] Moreover, a more general model based on a two-step solvent exchange process can be effectively applied to synergetic mixtures for $E_T(30)$.[22] In this connection, Eqns (6) and (7) were used to relate a solvatochromic property (Y) of each solvatochromic indicator to the solvent composition:

$$Y = Y_1 + \frac{a(x_2^0)^2 + c(1 - x_2^0)x_2^0}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_2^0} \qquad (6)$$

$$Y = Y_1 + \frac{a(x_2^0)}{(1 - x_2^0) + f_{2/1}(x_2^0)} \qquad (7)$$

where $a = f_{2/1}(Y_2 - Y_1)$ and $c = f_{12/1}(Y_{12} - Y_1)$.

The constants of these processes are defined by the preferential solvation parameters ($f_{2/1}$ and $f_{12/1}$) that relate the ratio of the mole fractions of the solvents S1, S2, and

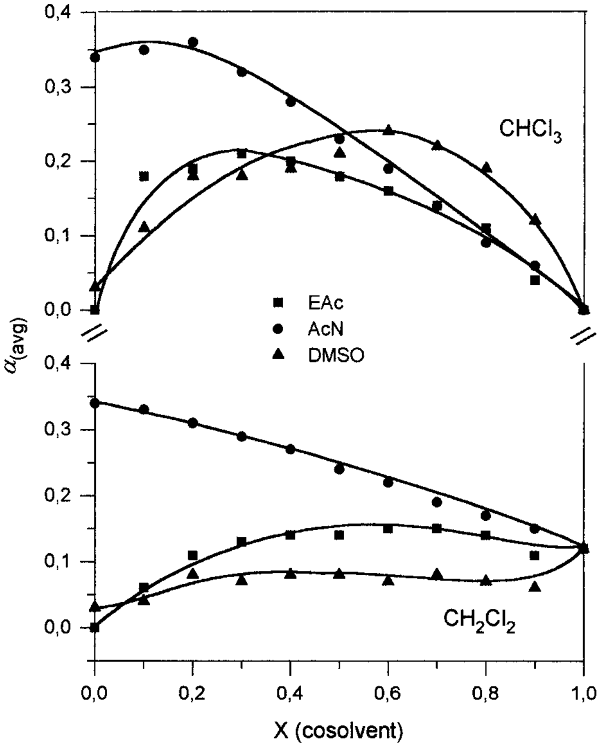

Figure 3. Plots of α(avg) vs co-solvent mole fraction for PAHBA solvent (EAc or AcN or DMSO) + CHCl$_3$ or CH$_2$Cl$_2$ solvent systems

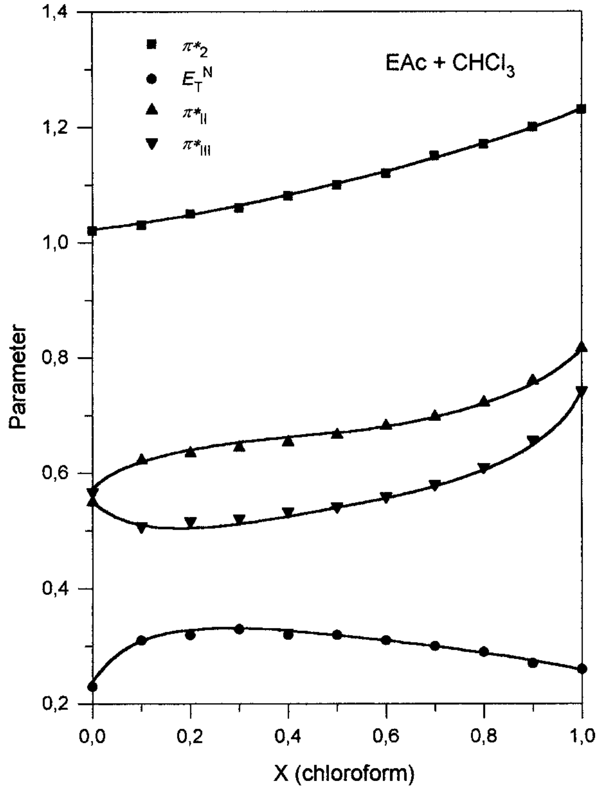

Figure 4. Plots of computed solvatochromic parameters π*(II), π*(III), π*$_2$ and E_T^N vs co-solvent mole fraction for EAc + CHCl$_3$ solvent system

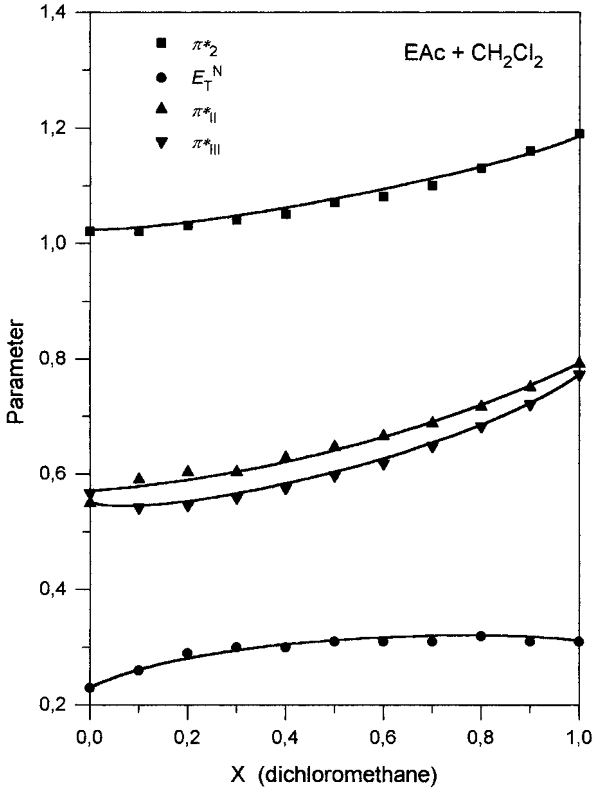

Figure 5. Plots of computed solvatochromic parameters π*(II), π*(III), π*$_2$ and E_T^N vs co-solvent mole fraction for EAc + CH$_2$Cl$_2$ solvent system

S12 (which represents a solvent formed by the interactions of solvents S1 and S2) solvating the indicator (x^s_1, x^s_2 and x^s_{12}, respectively) with the ratio of the mole fractions of the two solvents in the bulk mixed solvent (x^0_1 and x^0_2, respectively). The constants $f_{2/1}$ and $f_{12/1}$ measure the tendency of the indicator to be solvated with S2 and S12, respectively, with reference to S1.

The fits obtained in the application of the two-step model to the experimental data for EAc + CHCl$_3$ or CH$_2$Cl$_2$ solvent systems [and additionally to the E_T^N values which were calculated from $E_T(30)$ values[8c]] are very good [sum square residual (ssr) <0.008] and Eqn. (6) can be successfully applied to all indicators in all explored mixtures, except for **IV** and **V** in mixtures with cosolvent CH$_2$Cl$_2$ (ssr >0.5). The ssr values obtained in the application of the simplified Eqn. (7) (ssr values ca 0.1 or less) are three times higher than those obtained from the general Eqn. (6). Therefore, in general, the behavior of the indicators studied in the solvent systems selected for this analysis is better described by the general than by the simplified model, except for **VI**, where the two equations can be well fitted without a significant increase in the ssr values. Moreover, in the latter case, the $f_{2/1}$ values are close to unity and the system can be considered ideal and described by the most simplified equation, $Y = x^0_1 y_1 + x^0_2 y_2$.

The $f_{2/1}$ parameters are in general higher than unity for **II** in all mixtures, indicating the large solvation of this solute by the EAc–$CHCl_3$ or EAc–CH_2Cl_2 complex (high $f_{12/1}$ values). For all mixtures and all reference solutes (except the previously mentioned **IV** and **V** in mixtures with CH_2Cl_2) $f_{12/1} > f_{2/1}$, indicating that the order of preferential solvation is complex > co-solvent > EAc.

By means of the computed parameters obtained by the fitted equations, the solvatochromic properties for any solvent composition of the binary solvent–indicator systems can easily be calculated. In this direction, plots of the recalculated properties E_T^N, π^*(II) and π^*(III) as a function of the solvent composition are presented in Figs 4 and 5 for co-solvent $CHCl_3$ and CH_2Cl_2, respectively. Additionally, for the purpose of comparison, these figures show the π^*_2 values estimated by applying Eqn. (8) (which correlates parameter π^*_2 with six solvent spectral shift data of β-carotene[23]):

$$\tilde{\nu}(\mathrm{VI}) = 24213\mathrm{cm}^{-1} - 2145\mathrm{cm}^{-1} \times \pi^*_2 \quad (r = 0.994) \qquad (8)$$

where $\tilde{\nu}$(VI) is the solvatochromic property value obtained by the application of the fitted equations to the data presented in Tables 2 and 3. It should be pointed out that, as a first approximation, we extended the reported procedures for pure solvents to mixed solvents. Moreover, the π^*_2 scale could be modified or redefined when the database is enlarged.[23b]

The shape of the independent parameter vs solvent composition (for both co-solvents) plots shows two different response models for the chemical probes in the explored strongly complexing mixtures.[24] Solutes **II, III** and **VI** reflect a similar behavior with values of the measured property for the mixtures between those corresponding to the pure solvents, exhibiting negative deviations from linearity (in particular, nearly ideal behavior is observed for π^*_2). In these cases, the probes interact with the mixed solvent less strongly than the solvent–solvent interactions. On the other hand, a maximum in the curves is observed for indicator **I**: the property values for the pure solvents are very similar, and the solute has strong interactions with the mixed solvent magnifying the measured property. In this case, the increased 'polarity' values could be assumed to be due mainly to an increased acidity and/or polarity of the mixed solvent [it is known that the $E_T(30)$ betaine dye is practically independent of the polarizability].

The plots of the dependent parameters calculated by the fitted data vs solvent composition (for both co-solvents) are additionally presented in Fig. 6. It can be observed that the β values measured with the pair **II**–**IV** increase with increasing co-solvent content, showing synergism for the property. In contrast, the values obtained with **III**–**V** decrease with increase in co-solvent concentration, exhibiting two inflection points. On the other hand, the changes in the α values indicate a strong synergetic effect for the HBD ability for both systems explored.

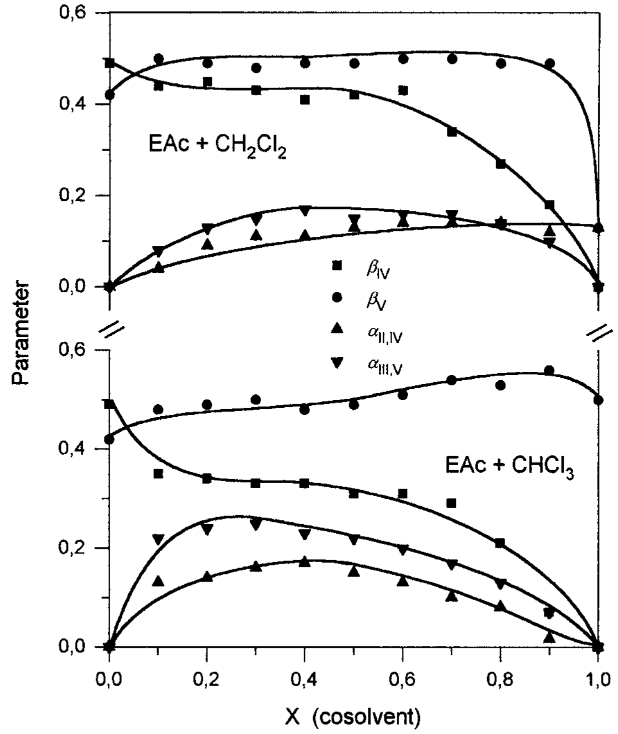

Figure 6. Plots of the dependent parameters (α and β) vs co-solvent mole fraction for EAc + $CHCl_3$ or CH_2Cl_2 solvent system

Application

Correspondence between solvent effects on S_NAr reactions and solvent properties. Correlation analysis of kinetic data with the computed solvent parameters for (EAc + $CHCl_3$) mixtures.

The S_NAr reactions between halonitrobenzenes and primary or secondary amines have long been investigated in both polar and apolar solvents. The rate of these reactions is notably affected by the solvent properties, and different studies have shown how extensive and complex are the interactions of the substrate and/or the intermediate(s) with the solvent molecules.[25] The mechanism of these reactions is well established: the breakdown of the zwitterionic σ intermediate can occur spontaneously or by a base-catalyzed mechanism.

Although solvent property parameters for many pure solvents have been thoroughly correlated with other solvent-dependent processes, the extent to which such parameters for binary solvent mixtures are likewise correlated is still not significant.

Through the analysis of the solvent effects on the non-base-catalyzed S_NAr reaction of 1-chloro-2,4-dinitrobenzene (CDNB) with piperidine (PIP) carried out in several

Table 8. Second-order rate constants, k_A ($l\ mol^{-1}\ s^{-1}$), for the S_NAr reaction between halodintrobenzenes and primary or secondary amines in the binary solvent mixtures EAc + $CHCl_3$, measured at 25 °C

	Reaction			
X_{cos}	CDNB[a] + Mo	CDNB[a] + PIP	CDNB[a] + BUT	FDNB[b] + BUT
0.20	0.0218	0.190	0.870	5.90
0.40	0.0179	0.176	0.660	4.01
0.60	0.0138	0.140	0.481	2.68
0.80	0.00612	0.119	0.279	1.10

[a] [CDNB] = 10^{-4} M.
[b] [FDNB] = 5×10^{-5} M.

aprotic solvent + toluene systems, we have demonstrated that there exists a satisfactory correlation between $E_T(30)$ values and the logarithms of the rate constants.[8a,b] On the other hand, the same correlation analysis to the kinetic data for the non-base-catalyzed reactions of CDNB + PIP or *n*-butylamine (BUT) or morpholine (Mo) and 1-fluoro-2,4-dinitrobenzene (FDNB) + BUT in some PAHBA solvent + $CHCl_3$ mixtures revealed that, in the cases of synergetic mixtures, the parameter–kinetics correspondence is very poor (showing that this situation is more expressive for solvent systems with strong synergism, particularly for EAc + $CHCl_3$ mixtures).[8c]

We have now extended the preceding analysis to the correlations of the reported kinetic data for the explored CDNB + BUT or Mo or PIP and FDNB + BUT reactions in EAc + chloroform mixtures, with the computed solvent descriptors π^*, α and β (obtained by the application of the preferential solvation models) according to the Kamlet, Abboud and Taft multiparameter model $\log\ k_A = Y + s\pi^* + a\alpha + b\beta$. In this connection and in order to increase the kinetic data set with respect to that previously reported, we determined here the second-order rate constants for the same reactions carried out in the same mixtures but at other co-solvent mole fractions. The results are presented in Table 8. The data derived from the three-parameter correlation equation are presented in Table 9. In order to be able to compare the results, the data derived from the single-parameter model $\log\ k_A = A + B[E_T(30)]$[8c] (for all the available kinetic data) are additionally given. It should be noted that, in all cases, the reactions are not base catalyzed and the values employed in the correlations are the average of the values obtained at the explored amine concentrations. The regression equations were assessed by the evaluation of the correlation coefficient (*r*) and the standard deviation (SD). The results clearly demonstrate that the use of the multiparameter equation instead of the uniparameter equation produces an improvement in the correlation between the solvent-dependent process (reaction rate)

Table 9. Correlation data for log k_A vs E_T^N and log k_A vs (π^*, α, β) in EAc + $CHCl_3$ mixtures (including pure solvents): correlation coefficient (*r* and r^2), standard deviation (SD), slope (*B*), and intercept (*A*) [and their standard errors (s_A, s_B)], intercept (*Y*) and parameters *s*, *a* and *b* (and their standard errors) and the number of data points (*n*), for the reactions between 1-chloro- or 1-fluoro-2,4-dinitrobenzene and morpholine or piperidine or butylamine

	$\log k_A = A + B[E_T^N]$					$\log k_A = Y + s\pi^* + a\alpha + b\beta$						
Reaction	*r*	SD	*A* (s_A)	*B* (s_B)	Indicator	*r* (r^2)	SD	*Y* (s_Y)	*s* (s_s)	*a* (s_a)	*b* (s_b)	*n*
Mo + CDNB	0.390	0.303	−3.08 (0.918)	3.90 (3.08)	(II, IV)	0.976 (0.954)	0.080	2.71 (1.80)	−6.45 (2.21)	1.78 (0.498)	−1.60 (1.21)	11
					(III, V)	0.990 (0.981)	0.052	1.84 (0.265)	−3.04 (0.419)	0.335 (0.317)	−4.15 (0.511)	11
PIP + CDNB	0.180	0.157	−1.07 (0.475)	0.876 (1.60)	(II, IV)	0.983 (0.966)	0.033	2.65 (0.749)	−4.58 (0.918)	0.442 (0.207)	−1.45 (0.503)	11
					(III, V)	0.985 (0.971)	0.031	1.32 (0.158)	−2.10 (0.249)	−0.535 (0.189)	−1.66 (0.304)	11
BUT + CDNB	0.838	0.274	−4.28 (0.829)	12.8 (2.78)	(II, IV)	0.905 (0.820)	0.242	1.00 (5.43)	−2.76 (6.65)	6.23 (1.50)	−0.811 (3.64)	11
					(III, V)	0.992 (0.985)	0.070	0.237 (0.360)	−4.09 (0.568)	2.14 (0.431)	2.63 (0.693)	11
BUT + FDNB	0.378	0.453	−1.29 (1.37)	5.64 (4.60)	(II, IV)	0.990 (0.981)	0.076	6.35 (1.72)	−8.49 (2.11)	2.36 (0.475)	−1.66 (1.15)	11
					(III, V)	0.993 (0.987)	0.064	6.05 (0.329)	−5.17 (0.518)	0.054 (0.393)	−5.44 (0.633)	11

and the solvent properties. In most cases, when the composition of the binary mixtures is modified, the rates of the reactions are mainly affected by the dipolarity/hyperpolarizability and the HBA capability of the mixed solvent.

CONCLUSIONS

The spectroscopic data obtained from the solvatochromic indicators revealed that, in general, preferential solvation phenomena are operative for solutes **I**–**V** in the explored polychlorinated mixtures. In contrast, nearly ideal behavior is observed for **VI** in the same solvent systems.

The analysis of the solvent parameter data demonstrates that the general tendency is disparity in the values for the same parameter obtained from different indicators. The observed divergence is more pronounced for $CHCl_3$ mixtures than for CH_2Cl_2 mixtures. This behavior reflects the different sensitivities of the indicators to solute–solvent interactions, which is not only solute dependent but also solvent dependent.

The application of preferential solvation models to the description of the data for independent parameters [π*(II), π*(III), π^*_2 and E_T^N] in EAc + $CHCl_3$ or CH_2Cl_2 mixtures shows two different response models. Solutes **II**, **III** and **VI** reflect similar solvatochromic behavior, having similar environments. These dipolar and/or polarizable solutes are specially influenced by the polarizability/hyperpolarizability characteristics of the polychlorinated mixed solvent. In contrast, these binary mixtures are synergetic for E_T^N values, which can be explained by the high sensitivity of the Dimroth–Reichardt indicator to hydrogen-bond donation of the mixed solvent.

The reported results indicate that the properties of the explored complex aprotic mixtures seem to be better described by the group of parameters derived from the solvatochromic comparison method.

EXPERIMENTAL

Reagents and solvents. 4-Nitroanisole (Aldrich, 97%) and 4-nitroaniline (Aldrich, 99%) were used without any further purification. *N*,*N*-Diethyl-4-nitroaniline was prepared by nitration of *N*,*N*-diethylaniline (Carlo Erba, 99.5%).[26a] 4-Nitrophenol was prepared by nitration of phenol (Mallinckrodt, ca 99.5%).[26b] β-Carotene (Merck, for biochemistry) was crystallized from benzene and methanol. The solvents were purified as reported previously[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 parameter measurements. The pure solvents were mixed in appropriate proportions by weight to give binary solvent mixtures of various compositions. Indicator solutions were prepared just prior to use. Visible spectra of sample solutions in a 10 mm cell were recorded at 25 °C by using a Perkin-Elmer Model 124 UV/Vis spectrophotometer and a Zeiss PMQ 3 UV/Vis spectrophotometer, equipped with a data-acquisition system [the accuracy of the measured wavenumbers of the absorption peaks is $\leq$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 determined spectrophotometrically by the procedure already described.[8c]

Computation methods. The parameters of solvation which minimize the square residuals of the k_A and the $E_T(30)$ values for the binary solvent system were computed by non-linear regression using the MATLAB 4.2 program (Mathworks).

Acknowledgements

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