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Solvatochromism in binary solvent mixtures. Response models to the chemical properties of reference probes

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ABSTRACT: The present work analyzes the solvent effects on the electronic absorption spectra for a set of solvatochromic solutes in several binary mixtures of a polar aprotic hydrogen-bond acceptor solvent with a cosolvent with potential hydrogen-bond donor capability, in terms of preferential solvation models. It compares the response models of the explored mixtures with respect to the chemical properties of the reference probes. It relates the results obtained with the solvatochromic solutes to the solvent effects on an aromatic nucleophilic substitution reaction. It also gives an evaluation of the degree of convergence for the values of a solvent property determined by individual probes, in order to analyze the validity of the solvatochromic indicators for the characterization of mixed solvents. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: solvatochromism; binary solvent mixtures; response models; chemical properties; reference probes

INTRODUCTION

We have recently explored the solvatochromism of a set of solvatochromic indicators [2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (**I**), *N*,*N*-diethyl-4-nitroaniline (**II**), 4-nitroanisole (**III**), 4-nitroaniline (**IV**), 4-nitrophenol (**V**) and *β*-carotene (**VI**)][1a–c] in several binary mixtures of the type with a polar aprotic hydrogen-bond acceptor (PAHBA) solvent and a cosolvent with a potential hydrogen-bond donor (HBD) ability. We have particularly studied the behavior of binary mixtures of ethyl acetate (EAc) with chloroform or dichloromethane by the application of the preferential solvation models (PSM) in terms of the response models described by empirical solvatochromic parameters. These mixtures were selected to apply the theoretical treatment to the solvatochromism of solutes taking into account that they present high synergetic effects for the $E_T(30)$ polarity. Moreover, we applied the PSM when the solutes were the reagents and/or the intermediates of aromatic nucleophilic substitution reactions (S_NAr) carried out in EAc–$CHCl_3$ mixtures in order to compare two different solvent-dependent processes relating the solvatochromic response with the kinetic response.[1d]

It was now of interest to extend the application of the PSM to interpret the response models of the solutes referred to above to other reported binary mixtures in order to understand better the solvation effects of this particular type of mixture. Moreover, with the purpose of comparison and in order to analyze the influence of the acidity of the cosolvent, we explored the solvatochromic behavior of the cited chemical probes in binary mixtures of EAc and a strong HBD cosolvent (a protic cosolvent). The theoretical treatment was also applied to the kinetic results for an S_NAr reaction carried out in EAc–MeOH mixtures.

The PAHBA solvents considered in this work are EAc and dimethyl sulfoxide (DMSO) and the cosolvents with potential HBD ability are chloroform ($CHCl_3$) and dichloromethane ($CHCl_3$ being the strongest). Acetonitrile (AcN) shares both characteristics: it exhibits HBA ability and it also exhibits a potential ability to donate a hydrogen atom. The protic solvent methanol (MeOH) was taken as the cosolvent with strong hydrogen-bond donor properties. The solvatochromic parameters of these pure solvents are given in Table 1.

This work was aimed at (i) applying several equations (PSM which relate the transition energy of a solvatochromic indicator to the composition of binary solvent mixtures) to the description of the experimental solvatochromic data as a function of solvent composition evaluating the calculated parameters of solvation that assist in the interpretation of the solvent effects; (ii) comparing the solvatochromic response models for the same probes in different binary solvent systems and for

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Table 1. Solvatochromic parameters of six pure solvents: polarity $E_T(30)$, dipolarity/polarizability π^*, hydrogen-bond basicity β, hydrogen-bond acidity α and polarity π^*_2

Parameter	EAc	AcN	DMSO	$CHCl_3$	CH_2Cl_2	MeOH
$E_T(30)$	38.1^{ab}	45.6^{ab}	45.1^{ab}	39.1^{ab}	40.7^{ab}	55.4^{a}
π^*	0.55^{ab}	0.75^{ab}	1.00^{ab}	0.58^{ab}	0.82^{ab}	0.60^{a}
β	0.45^{ab}	0.40^{a} 0.31^{b}	0.76^{ab}	0.10^{a} 0.00^{b}	0.10^{a} 0.00^{b}	0.66^{a}
α	0.00^{a}	0.19^{a}	0.00^{a}	0.20^{ac}	0.13^{ac}	0.98^{a}
π^*_2	1.010^{b}	0.899^{b}	1.199^{d}	1.236^{b}	1.155^{b}	0.9050^{e}

[a] Values taken from Ref. 2.
[b] Values taken from Ref. 3.
[c] Values taken from Ref. 4.
[d] This work.
[e] Value calculated from Ref. 13.

Table 2. Polynomial dependence of the wavenumber of the absorption maxima $\tilde{\nu}$ of six solvatochromic solutes **I–VI** as a function of the cosolvent mole fraction (X_{CoS}), calculated according to the regression equation: $\tilde{\nu} = A + B(X_{CoS}) + C(X_{CoS})^2 + D(X_{CoS})^3 + E(X_{CoS})^4 + F(X_{CoS})^5$

Solvent	Solute	*A*	*B*	*C*	*D*	*E*	*F*	SD
EAc –$CHCl_3$	**I**	13.5	6.50	−12.3	6.06			0.119
	II	25.7	−1.78	3.40	−2.45			0.040
	III	32.8	2.25	−10.3	15.6	−7.98		0.026
	IV	28.0	1.69	−6.33	7.72	−2.44		0.031
	V	32.9	−0.511	−0.102	−0.141			0.029
	VI	22.0	−0.213	−0.306	0.067			0.028
EAc –CH_2Cl_2	**I**	13.4	3.79	−5.16	2.34			0.043
	II	25.8	−0.920	1.17	−1.00			0.028
	III	32.8	0.310	−1.05	0.25			0.023
	IV	28.0	−0.66	1.49	6.35	−23.7	17.2	0.326
	V	32.9	−6.55	49.0	−139	161	−63.6	0.189
	VI	22.0	−0.132	−0.081	−0.161			0.016
AcN –$CHCl_3$	**I**	16.1	0.504	−3.28	0.412			0.082
	II	25.0	−1.99	10.22	−25.3	27.2	−10.2	0.022
	III	32.4	0.371	−5.25	14.6	−16.5	6.76	0.013
	IV	27.4	0.701	−3.48	3.97			0.066
	V	32.5	−0.590	−0.492	0.781			0.030
	VI	22.1	−1.07	1.13	−0.564			0.027
AcN –CH_2Cl_2	**I**	16.1	−1.25	0.673	−1.18			0.025
	II	25.0	0.520	−3.56	5.75	−2.69		0.009
	III	32.4	0.011	−1.66	2.79	−1.24		0.013
	IV	27.4	0.410	−1.94	2.70			0.047
	V	32.4	1.14	−18.5	67.5	−94.1	44.7	0.087
	VI	22.1	−0.451	5.83	0.042			0.029
DMSO –$CHCl_3$	**I**	15.8	−0.161	1.25	−3.14			0.067
	II	24.3	5.86	−33.4	81.4	−84.3	31.1	0.026
	III	31.8	1.09	0.951	−1.43			0.057
	IV	25.7	6.33	−31.0	75.4	−80.1	32.3	0.147
	V	31.5	−1.17	5.53	1.24	−13.9	−9.38	0.143
	VI	21.0	−9.54	49.3	−105	99.8	−35.0	0.043
DMSO –CH_2Cl_2	**I**	15.8	0.481	−2.10	0.201			0.035
	II	24.3	0.662	−0.401	0.412			0.014
	III	31.8	0.123	0.502	−0.101			0.030
	IV	25.8	2.49	−20.5	67.3	−90.1	43.6	0.072
	V	31.5	4.25	−49.3	153	−196	48.6	0.275
	VI	21.9	−5.93	20.9	−26.8	11.49		0.088
EAc –AcN	**I**	13.4	9.23	−18.8	20.9	−8.76		0.076
	II	25.8	−1.26	1.53	−1.02			0.029
	III	32.8	−0.151	−0.542	0.301			0.031
	IV	28.0	−1.78	2.47	−1.22			0.031
	V	32.9	−1.67	2.83	−1.62			0.045
	VI[a]	22.0	0.011	−0.091	0.130			0.005

[a] Experimental data determined for this work.

Table 3. Experimental wavenumbers (in *kK*) and solvatochromic parameters for nine EAc–MeOH solvent mixtures, measured at 25 °C

	Cosolvent molar fraction								
Property	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
$\tilde{\nu}$(**II**)	25.77	25.71	25.64	25.64	25.57	25.54	25.51	25.44	25.32
π^*(**II**)	0.55	0.57	0.59	0.59	0.61	0.62	0.63	0.65	0.69
$\tilde{\nu}$ (**III**)	32.89	32.84	32.73	32.73	32.79	32.79	32.79	32.73	32.68
π^*(**III**)	0.53	0.55	0.59	0.59	0.57	0.57	0.57	0.59	0.61
π^*(av.)	0.54	0.56	0.59	0.59	0.59	0.59	0.59	0.62	0.65
$\tilde{\nu}$ (**IV**)	27.85	27.70	27.55	27.51	27.40	27.36	27.32	27.25	27.14
β (**IV**)	0.54	0.58	0.61	0.62	0.64	0.64	0.64	0.64	0.64
α (**II,IV**)	0.59	0.75	0.83	0.85	0.89	0.91	0.95	0.97	0.98
$\tilde{\nu}$ (**I**)	16.46	17.39	17.90	18.02	18.30	18.48	18.73	18.90	19.14
E_T^N	0.51	0.59	0.63	0.64	0.67	0.68	0.70	0.72	0.74
$\tilde{\nu}$(**VI**)	22.15	22.15	22.15	22.20	22.20	22.22	22.22	22.25	22.27
π^*_2	0.96	0.96	0.96	0.94	0.94	0.93	0.93	0.91	0.90

the same solvent mixtures with different solutes, focusing on the extent and nature of solute–solvent and solvent–solvent interactions; (iii) extending the analysis to the kinetic response for the S_NAr reaction of 1-fluoro-2,4-dinitrobenzene (FDNB) and morpholine (Mo) carried out in EAc–MeOH mixtures; and (iv) characterizing the properties of the binary solvent mixtures through the convergence criteria applied to a set of solvatochromic indicators.

RESULTS AND DISCUSSION

In order to present the reported experimental results[1a–c] in a useful, abbreviated way, we calculated the polynomial dependence of the spectroscopic data of the solutes in the studied mixtures as a function of the solvent composition. The expressions are depicted in Table 2.

Table 3 presents the measured wavenumbers of the UV–visible absorption maximum of indicators **I**–**IV** and **VI** in mixtures with cosolvent MeOH (the indicator **V** was excluded as consequence of uncertainty in the measurements). The Kamlet, Abboud and Taft solvatochromic parameters π^*, α and β (widely used as molecular–microscopic solvent descriptors) were calculated according to the conversion expressions reported by Marcus[2] and are additionally reported.

Preferential solvation of solutes: application of preferential solvation models

As is known, in mixed solvents the solutes can interact to a different degree 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 the solvent exchange theory[5]) that relate the transition energy of the Dimroth–Reichardt $E_T(30)$ indicator to the solvent composition were derived and compared.[6a,b] In this connection, Eqns (1) and (2) have been used to relate a solvatochromic property (Y) of each solvatochromic indicator with the solvent composition.[6c]

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

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

where

$$a = f_{2/1}(Y_2 - Y_1); \quad c = f_{12/1}(Y_{12} - Y_1)$$

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 solvents S1, S2 [which in this paper is the cosolvent (CoS)] and S12 (which represents a solvent formed by the interactions between solvents S1 and S2) solvating the indicator (x_1^s, x_2^s, and x_{12}^s, respectively) to the ratio of the mole fractions of the two solvents in the bulk mixed solvent (x_1^0 and x_2^0, respectively). The $f_{2/1}$ and $f_{12/1}$ constants measure the tendency of the indicator to be solvated by S2 and S12, respectively, with reference to S1. It should be noted that the one-step systems [Eqn. (2)] are particular cases of the two-step model [Eqn. (1)]. Ideal binary systems are also particular cases of one-step models, and both can be consistently explained from the two-step solvent exchange model (the fit to the one-step model, when feasible, is useful to avoid overparametrization).

The wavenumber of maximum absorption of the cited solvatochromic indicators in the PAHBA solvent–$CHCl_3$ or CH_2Cl_2 mixtures were fitted to Eqns (1) and (2) and the results obtained are presented in Table 4. In general, the

Table 4. Preferential solvation parameters for the solvatochromic solutes **I–VI** in mixtures of EAc or AcN or DMSO with $CHCl_3$ or CH_2Cl_2, calculated from the data in Table 2 and Eqns (1) and (2)

PAHBA solvent	Indicator	Cos	$f_{2/1}$	$f_{12/1}$	ssr
EAc	**I**	$CHCl_3$	8.97	14.0	4.36×10^{-5}
		CH_2Cl_2	1.08	6.21	1.16×10^{-5}
	II	$CHCl_3$	12.4	49.7	0.0083
		CH_2Cl_2	59.3	133	0.0042
	III	$CHCl_3$	1.62	8.69	0.0085
		CH_2Cl_2	12.7	28.5	0.002
	IV	$CHCl_3$	1.04	9.64	0.0025
		CH_2Cl_2	0.03	0.18	0.5
	V	$CHCl_3$	17.0	27.1	0.058
		CH_2Cl_2	0.16	0.19	0.230
	VI	$CHCl_3$	0.91	1.33	0.0052
			0.63[a]		0.0059
		CH_2Cl_2	0.55	1.28	0.0014
			0.37[a]		0.0018
AcN	**I**	$CHCl_3$	5.8	12.4	2.2×10^{-4}
		CH_2Cl_2	0.0002	0.58	1.02×10^{-5}
	II	$CHCl_3$	0.69	3.5	5.9×10^{-3}
		CH_2Cl_2	0.46	0.00001	2.2×10^{-3}
	III	$CHCl_3$	0.14	1.2	1.7×10^{-3}
		CH_2Cl_2	54.9	1×10^{-4}	9.7×10^{-3}
	IV	$CHCl_3$	0.0028	1×10^{-3}	1.5×10^{-2}
		CH_2Cl_2	0.86	5.0	2×10^{-3}
	V	$CHCl_3$	0.35	1.3	6×10^{-3}
		CH_2Cl_2	0.0005	7.3	6×10^{-3}
	VI	$CHCl_3$	3.8	1.4	5×10^{-3}
			1.92[a]		6×10^{-3}
		CH_2Cl_2	1.59	1.2	55×10^{-3}
			1.13[a]		6×10^{-3}
DMSO	**I**	$CHCl_3$	2.4	10.8	10^{-5}
		CH_2Cl_2	3.8	8.5	3×10^{-5}
	II	$CHCl_3$	1.5	1.2	2×10^{-2}
		CH_2Cl_2	1.1	2.8	10^{-3}
	III	$CHCl_3$	0.088	1.2	10^{-2}
		CH_2Cl_2	2.3	2.9	9×10^{-3}
	IV	$CHCl_3$	1.7	8.9	0.121
		CH_2Cl_2	0.41	4.4	7×10^{-3}
	V	$CHCl_3$	2.2	4.3	0.11
		CH_2Cl_2	0.14	11.2	0.31
	VI	$CHCl_3$	20.9	5.2	4×10^{-4}
			1.45[a]		3×10^{-3}
		CH_2Cl_2	5.6	2.0	2×10^{-3}
			1.59[a]		3×10^{-3}

[a] From Eqn. (2).

data for the analyzed solutes in all mixtures can be well fitted to Eqn. (1) and the general two-step preferential solvation model can be satisfactory applied. Nevertheless, in some cases, the simplified one-step model also gives good fits without a significant variation of the standard deviations.

From the analysis of the results for the mixtures with cosolvent $CHCl_3$, some general trends can be deduced. When the PAHBA solvent is EAc or DMSO, (i) the preferential solvation parameters, $f_{12/1}$ and $f_{2/1}$, are higher than unity, indicating that the solutes are preferentially solvated by the mixed solvent (S12) and the cosolvent in preference to the PAHBA solvent (except **VI** with EAc and **III** with DMSO); (ii) the observed tendency is that $f_{12/1}$ values are higher than $f_{2/1}$ values (except for II and VI in DMSO); then, the preferential solvation order is intersolvent complex $> CHCl_3 >$ EAc or DMSO; and (iii) the $f_{12/1}$ values for mixtures with EAc are higher than those with DMSO (except for **VI**) showing that the preferential solvation effects of the EAc–$CHCl_3$ complex with respect to EAc seem to be higher than those of the DMSO–$CHCl_3$ complex with respect to DMSO. The evaluation of the calculated parameters suggests that these mixtures manifest similar solvation response models. On the other hand, the mixtures with AcN also show $f_{12/1}$ values higher than $f_{2/1}$, but these latter parameters are, in general, lower than unity, indicating that the solutes are preferentially solvated by AcN in

Table 5. Preferential solvation parameters for the solvatochromic solutes **I–VI** in mixtures of EAc with AcN or MeOH, calculated from the data in Tables 2 and 3 and Eqn. (1)

Cosolvent	Indicator	$f_{2/1}$	$f_{12/1}$	ssr
AcN	**I**	0.451	0.177	0.011
MeOH		5.60	15.1	0.018
AcN	**II**	4.71	10.2	0.004
MeOH		1.88	8.13	0.022
AcN	**III**	0.963	1.02	0.006
MeOH		1.21	9.10	0.002
AcN	**IV**	4.45	7.02	0.006
MeOH		1.05	3.03	0.007
AcN	**V**	10.1	18.78	0.007
AcN[a]	**VI**	0.119	0.596	1.1×10^{-4}
MeOH[a]		1.08	1.12	0.001

[a] The data can be also well fitted to the simplified Eqn. (2).

preference to the solvation by $CHCl_3$. The preferential solvation order for these mixtures is intersolvent complex >AcN >$CHCl_3$.

From the analysis of the results for the mixtures with cosolvent CH_2Cl_2, the trend is that there is a marked difference between the preferential solvation response models of EAc or DMSO–CH_2Cl_2 mixtures and AcN–CH_2Cl_2 mixtures. In the first type of mixture the solutes tend to be preferentially solvated by EAc–CH_2Cl_2 and DMSO–CH_2Cl_2 complexes with respect to the pure solvents ($f_{12/1} > 1$). In contrast, the solutes tend to be preferentially solvated by AcN with respect to the intersolvent complexes and CH_2Cl_2 ($f_{12/1}$ and $f_{2/1}$ values are <1).

The different behaviors observed for the mixtures of both cosolvents with EAc or DMSO with respect to those observed for mixtures with AcN can be mainly attributed to the solvent–solvent interactions (that affect the solute–solvent interactions). It is known that the strong HBA solvents EAc or DMSO can form intersolvent complexes via hydrogen bonding with the polar and highly polarizable polychlorinated HBD cosolvents.[7] The mixtures of AcN with $CHCl_3$ or CH_2Cl_2 show preferential solvation response models that differ from those of EAc or DMSO with both cosolvents. This different behavior could be attributed to the potential HBD ability of AcN: this solvent is able to compete with the cosolvent to donate a hydrogen atom.

At this point, in order to understand better the nature of the molecular–microscopic properties of the explored mixed solvents, it was of interest to analyze the preferential solvation response models of the cited solutes in binary mixtures of the strong HBA solvent EAc with AcN as HBD cosolvent. Equation (1) gives good fits to the solvatochromic data. The results are presented in Table 5. According to the solvation parameter values, all solutes (except **I**) are preferentially solvated by the intersolvent complex, whereas the strongest preferential solvation of **I** is performed by AcN rather than by the complex: this behavior can be explained by taking into account that this solute is a dipolar molecule with a good hydrogen-bond acceptor capability. Also, Table 5 includes the results obtained for EAc–MeOH mixtures. It is well known that the pure components form intersolvent complexes or cross-associated species by hydrogen bonding. According to the solvation parameters values ($f_{12/1}$ and $f_{2/1} > 1$; $f_{12/1} > f_{2/1}$), the order of preferential solvation of the solutes is EAc–MeOH complexes >MeOH >EAc. These results are consistent with those obtained for EAc–$CHCl_3$ mixtures.

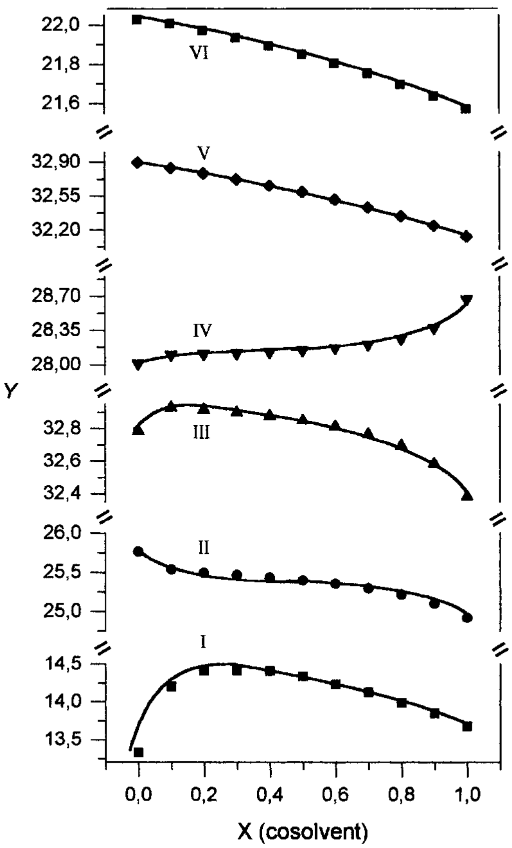

Figure 1. Computed wavenumbers [Eqn. (1)] of the absorption maximum of the solvatochromic solutes **I–VI** in EAc–$CHCl_3$ mixtures versus mole fraction X of the cosolvent $CHCl_3$

Response models of the explored binary mixtures from the chemical properties of the reference solutes

In order to interpret the solvatochromic response of the same solvent mixtures to different chemical probes, the plots of computed $\tilde{\nu}$ values [by means of Eqn. (1)] as a function of the composition of the mixtures are presented in Figs 1–4 for EAc or AcN–$CHCl_3$ and EAc–AcN or MeOH solvent systems selected as representative exam-

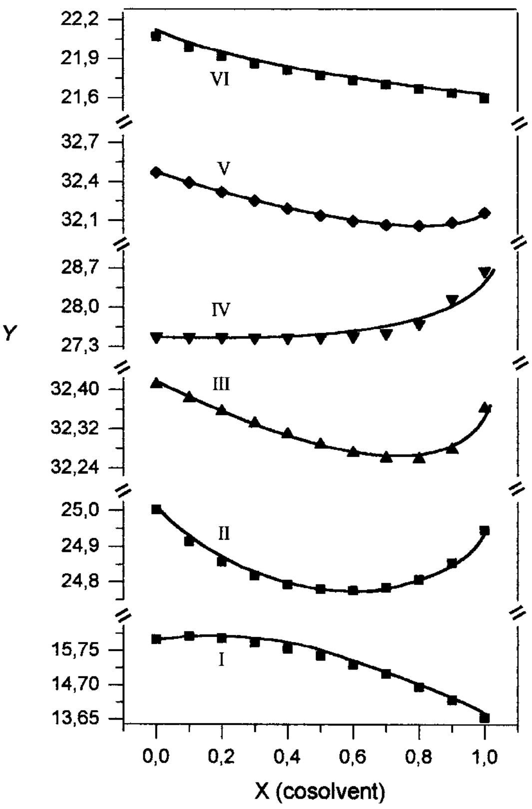

Figure 2. Computed wavenumbers [Eqn. (1)] of the absorption maximum of the solvatochromic solutes **I–VI** in AcN–$CHCl_3$ mixtures versus mole fraction *X* of the cosolvent $CHCl_3$

ples. By comparing the obtained response models (reflected by the shape of the solvation curves), the following patterns of behavior are observed.

(i) The positively solvatochromic indicators **II** and **III**[8a,b] are basically similar chemical probes, mainly sensitive to non-specific interactions with the solvent. The plots show an S-shaped curve for **II** and positive deviations from linearity for **III** indicating the same response models of EAc–$CHCl_3$ or AcN mixtures for each indicator. These results reveal that the solvent–solvent interactions affect the solute–solvent interactions for solute **II** differently to that for solute **III**. On the other hand, the response models observed from both indicators (being highly sensitive to changes in the solvent composition) in AcN–$CHCl_3$ mixtures are of the same type: the addition of the HBD cosolvent to AcN produces a strong decrease of $\tilde{\nu}$ values until a minimum, then increasing to the value in pure $CHCl_3$. This behavior reveals similar non-specific solute–solvent interactions of AcN–$CHCl_3$ mixtures with both solutes. Moreover, the shape of the curves for EAc–MeOH mixtures shows the same general trend observed for EAc–$CHCl_3$ or AcN mixtures, being clearly different from those observed for AcN–$CHCl_3$. From the point of view of these solutes, the results obtained show that the mixtures of the strong

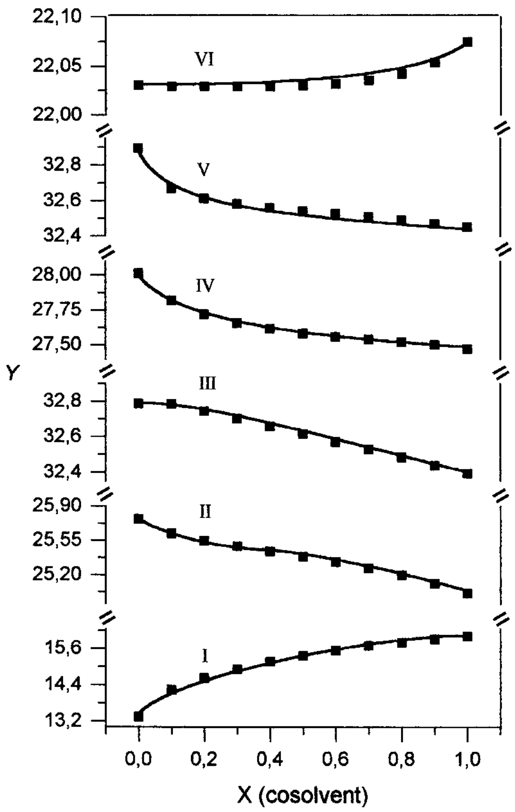

Figure 3. Computed wavenumbers [Eqn. (1)] of the maximum of absorption of the solvatochromic solutes **I–VI** in EAc–AcN mixtures versus mole fraction *X* of the cosolvent AcN

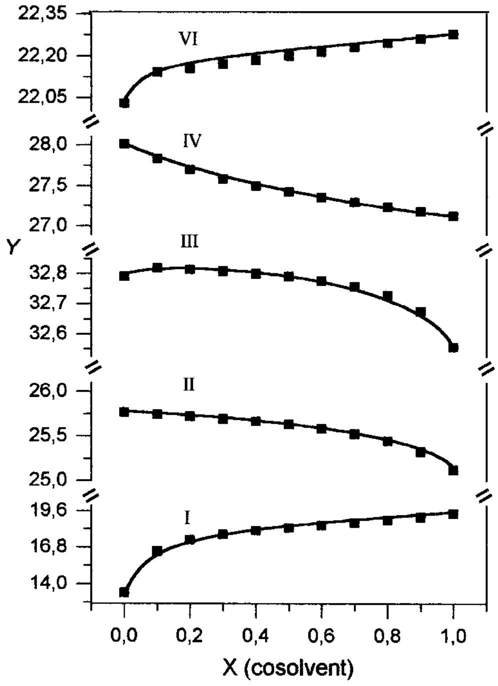

Figure 4. Computed wavenumbers [Eqn. (1)] of the maximum of absorption of the solvatochromic solutes **I–IV** and **VI** in EAc–MeOH mixtures versus mole fraction *X* of the cosolvent MeOH.

Table 6. Second-order rate constants k_A (1 mol^{-1} s^{-1}) for the S_NAr reaction between FDNB (5×10^{-5} M) and Mo in binary mixtures EAc–MeOH, measured at 25 °C (including the data in the pure solvents)

MeOH mole fraction	[Mo]							
	0.002	0.004	0.008	0.010	0.016	0.020	0.040	0.080
0	0.110	0.201	0.331	0.392	0.473	0.630	1.33	2.52
0.1	0.210	0.353	0.576	0.581	0.740	0.751	1.03	1.41
0.2	0.522	0.598	0.699	0.735	0.806	0.821	1.01	1.33
0.3	0.627	0.680	0.766	0.788	0.850	0.864	0.997	1.18
0.4	0.718	0.741	0.814	0.830	0.880	0.915	1.00	1.09
0.5	0.766	0.768	0.834	0.851	0.886	0.919	0.978	1.03
0.6	0.755	0.758	0.806	0.820	0.848	0.878	0.893	0.970
0.7	0.718	0.734	0.766	0.792	0.811	0.845	0.893	0.956
0.8	0.672	0.682	0.705	0.723	0.727	0.809	0.778	0.750
0.9	0.613	0.639	0.670	0.672	0.676	0.686	0.702	0.712
1	0.544	0.554	0.550	0.580	0.591	0.590	0.621	0.623

HBA solvent EAc with MeOH or with the potential HBD solvents $CHCl_3$ or AcN exhibit similar properties that are clearly different from those corresponding to the mixtures between AcN (acting as HBA solvent) and $CHCl_3$. This fact can be mainly attributed to the specific intersolvent interactions by hydrogen bonding.

(ii) The positively solvatochromic indicators **IV** and **V**[8c,d] are basically similar chemical probes that are sensitive to both non-specific and specific interactions with the solvent (the different nature of N—H with respect to O—H should be noted).[9] The response models of the compared mixtures with respect to both solutes are similar (except EAc–$CHCl_3$ and indicator **V**), exhibiting negative deviations from linearity. For mixtures with $CHCl_3$, the deviations are larger for $CHCl_3$-rich mixtures than for AcN-or EAc-rich mixtures. In contrast, the deviations are larger for EAc-rich mixtures in the case of EAc–AcN. The results obtained show that (from the point of view of these solutes) the mixtures are considered to be basically similar, but clearly different from EAc–$CHCl_3$ mixtures with respect to **V** (the tendency to linearity suggests dissimilar effects of solvation).

(iii) The negatively solvatochromic betaine dye **I**[10] is particularly sensitive to the dipolarity and HBD ability of solvents. The mixed solvent response models seem to be basically similar, showing positive deviations from linearity. However, high synergism is observed (maximum in the curve) for EAc–$CHCl_3$ mixtures in which the pure components have similar property values. This is related to the hydrogen-bonded complexes present in the solution and the chemical properties of the solute (a dipolar molecule with a strong HBA capability). The betaine dye can be preferentially solvated by the intersolvent complexes (more polar than the pure solvent components).

(iv) The plots obtained for indicator **VI**[11] (a non-polar solute particularly sensitive to non-specific interactions) exhibit nearly linear curves predicting nearly ideal behavior, except for EAc–MeOH mixtures. These results can be related to the solvent dipole–solute induced dipole interactions and the dispersion forces, which do not modify the composition of the solvation shell with respect to the one of the bulk solvent. In the case of the protic cosolvent, the plot shows a region with pronounced changes in $\tilde{\nu}$ values ($X_{MeOH} \leq 0.10$), continued by a zone that exhibits a linear variation with the increase in MeOH concentration. In this case the protic cosolvent manifests its properties already in dilute solutions, modifying the microscopic environment of the solute.

S_NAr reactions in binary solvent mixtures. Preferential solvation effects on kinetic results

In order to compare the influence of the preferential solvation on two different solvent-dependent processes so as to understand better the solvation effects, it is of interest to relate the kinetic data of the S_NAr reaction between 1-fluoro-2,4-dinitrobenzene (FDNB) and morpholine (Mo) in EAc–MeOH mixtures with the solvent composition, by extending the application of the PSM when the solutes are the reagents and/or intermediates of the explored reaction. This reaction was selected for the analysis taking into account that we have recently reported kinetic synergetic effects (k_A values higher than those in the pure individual solvents in some binary mixtures and for certain amine concentrations) for the cited reaction carried out in EAc–$CHCl_3$ or CH_2Cl_2 mixtures.[1d] The results were related to a special combination of base catalysis and specific solvent effects (particularly hydrogen-bond interactions).

As is known, the two-step mechanism of S_NAr reactions involving halonitrobenzenes with primary and secondary amines is well established:[12,13] either the first step (formation of the intermediate ZH) or the second step (decomposition of ZH) can be rate-determining, with the possibility of base catalysis. Depending on the identities of the amine and the nucleofuge, and the properties of the solvent in which the reaction is carried out, the breakdown of ZH can occur spontaneously or by

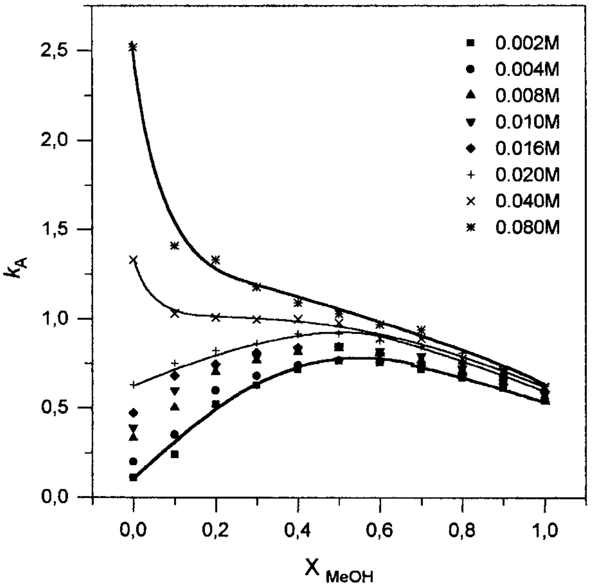

Figure 5. Plots of k_A vs X_{MeOH} for the FDNB–Mo reaction, measured in EAc–MeOH mixtures at different amine concentrations

a base-catalyzed mechanism. In general, base catalysis is more often observed with secondary than with primary amines, with poor leaving groups and in less polar aprotic solvents. As it has been reported, in the particular case of the reaction systems FDNB–Mo in EAc–$CHCl_2$ or CH_2Cl_2, each solvent part of the mixtures affects the possibility of base catalysis in a different way. The reaction is base catalyzed in EAc, it is less influenced by catalysis in CH_2Cl_2 and it is uncatalyzed in $CHCl_3$.

Table 6 presents the second-order rate constants determined for the FDNB–Mo reaction in EAc–MeOH mixtures at 25 °C. Figure 5 presents the plots of k_A vs X_{CoS} (at each amine concentration studied) for the binary mixtures and the pure solvents. The reported results clearly reflect two different kinetic response models depending on the nucleophile concentrations and as a function of the mixed solvent composition. At low amine concentrations ([Mo] $\leq$ 0.020 M) the k_A values increase from pure EAc (in which the reaction is base catalyzed) with increasing molar fractions of the protic solvent (in which no significant rate acceleration occurs on increasing the amount of amine) until a maximum, and then decrease to the corresponding value in the cosolvent. On the other hand, at high amine concentrations ([Mo] $\leq$0.04 M) the k_A values decrease continuously with increase in the amount of MeOH. Therefore, kinetic synergistic behavior is detected verifying the same effect observed previously when the reaction is carried out in mixtures of EAc with $CHCl_3$ or CH_2Cl_2. The observed results could be related to the HBD character of the cosolvent and the mixture composition. As is known, a solvent with HBD abilities as part of a binary mixture produces inhibition of the base catalysis owing to its capability to assist fluoride detachment: the decomposition of the intermediate ZH is not rate limiting and its formation is the slow step. It can be remarked that the kinetic behavior shows that the sensitivity of the reaction rate to small amounts of the HBD solvent is different at low nucleophile concentrations with respect to higher concentrations. This fact is related to the influence of base catalysis in the explored reaction.

Table 7. Preferential solvation parameters for the FDNB–Mo reaction in EAc–MeOH solvent mixtures, calculated from the data in Table 6 and Eqn. (1)

[Mo]	$f_{2/1}$	$f_{12/1}$	ssr
0.002	2.91	0.25	0.008
0.004	2.50	1.57	0.004
0.008	2.09	4.48	0.001
0.010	2.09	3.14	0.0001
0.016	3.13	6.96	0.002
0.020	3.13	6.96	0.002
0.040	1.50	4.87	0.004
0.080	50.7	67.5	0.011

The solvation parameters obtained by the application of the PSM to the experimental kinetic data as a function of the solvent composition (at each amine concentration) are presented in Table 7. The fits obtained are good (SD $\leq$ 0.038) and Eqn. (1) can be successfully applied. At low amine concentrations ([Mo] $\leq$ 0.004 M), $f_{2/1}$ values are higher than unity and higher than $f_{12/1}$, indicating that the preferential solvation of the critical state of the reaction is by MeOH, in preference to the intersolvent complexes and EAc. These results are in agreement with the preferential solvation order previously reported for the same reaction in EAc–$CHCl_3$ mixtures at low nucleophile concentration.[1d] In contrast, at [Mo] $\geq$ 0.008 M, $f_{12/1}$ and $f_{2/1}$ are higher than unity and $f_{12/1} > f_{2/1}$, indicating in all cases that preferential solvation is by the intersolvent species.

The comparison between the parameters of solvation obtained for both solvent-dependent processes (the solvatochromic and the kinetic processes) in EAc–MeOH mixtures reveals agreement in the order of preferential solvation only at high amine concentrations: the order of preferential solvation is intersolvent complexes >MeOH > EAc. On the other hand, the preferential solvation of the critical state of the explored reaction at lower amine concentrations is by MeOH.

The results obtained suggest that the explored S_NAr reaction is highly sensitive to the influence of the nucleophile concentration at low cosolvent concentrations.

Validity of solvatochromic indicators for the characterization of mixed solvents. Analysis of the convergence for solvent property values obtained from a set of comparable solutes

The empirical descriptors of the properties of binary

Table 8. Differences between the fitted and the calculated π^*(**II**) values for eight binary mixtures of solvents

PAHBA solvent	Cosolvent	$\lvert\Delta\pi^*(\mathbf{II})\rvert^a$	$\lvert\Delta\pi^*(\mathbf{II})\rvert^b$
EAc	$CHCl_3$	$0.078 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.097$	$0.063 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.075$
AcN	$CHCl_3$	$0.028 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.062$	$0.078 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.111$
DMSO	$CHCl_3$	$0.060 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.139$	$0.027 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.123$
EAc	CH_2Cl_2	$0.004 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.028$	$0.0005 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.008$
AcN	CH_2Cl_2	$4\times10^{-4} \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.027$	$0.009 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.028$
DMSO	CH_2Cl_2	$0.011 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.046$	$0.017 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.043$
EAc	AcN	$9\times10^{-5} \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.050$	$0.003 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.021$
EAc	MeOH		$0.074 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.125$

[a] Values calculated from π^*(**III**) and Eqn. (3).
[b] Values calculated from π^*(**III**) and Eqn. (4).

solvent mixtures determined from specific solutes may not be generally valid for general solutes when the preferential solvation phenomenon is operative. The expressions used to convert the raw measured data to the quantities describing the chemical characteristics for neat solvents are customarily employed directly also for mixed solvents.[14] Here, in order to test the validity of the particular parameters obtained from comparable solutes, the degree of convergence of the property values obtained from **II**/**III** and **IV**/**V**, each one considered as an individual solute, in the explored mixtures, is analyzed.

For the pure components that take part in the PAHBA solvent–$CHCl_3$ or CH_2Cl_2 or AcN mixtures [and in addition for dimethylformamide (DMF)],[1b] the correlation between the dipolarity/polarizability parameter values calculated from the wavenumber of the UV–visible absorption maximum of **II** and **III** is represented by

$$\pi^*(\mathbf{II}) = 0.03477 + 0.9843\pi^*(\mathbf{III}) \tag{3}$$

$$r = 0.970;\ \mathrm{SD}[\pi^*(\mathbf{II})] = 0.041;\ n = 6$$

The good linear correlation exhibited by the values obtained from the two solutes can be interpreted as measuring the same dipolarity/polarizability for these pure solvents. This result is closely related to the nature and extent of solute–solvent interactions developed in the immediate vicinity of the indicators in the pure solvents.

In connection with this and in order to analyze the influence of the preferential solvation phenomenon on the microscopic environment of **II** and **III**, the fitted π^*(**II**) values and those calculated from the fitted π^*(**III**) values and Eqn. (3) are compared. The resulting differences $\Delta\pi^*$(**II**) are presented in Table 8 for all solvent systems explored. In order to establish whether the different solutes produce convergent values for the property, the degree of convergence is set as 5% of the total range of values encountered for the property in a large set of diverse solvents: this value would be ±0.025 units, since the total range of the property is 1.00 unit. This value is comparable to the SD[π^*(**II**)] of Eqn. (3). Comparing the reported $\Delta\pi^*$(**II**), failed agreement in the property values obtained from **II** and **III** is observed for PAHBA–$CHCl_3$ mixtures. On the other hand, convergent values [$\Delta\pi^*(\mathbf{II}) \leq 0.046$ units] are obtained from both solutes when the solvent systems are PAHBA–CH_2Cl_2 and EAc–AcN. It should be noted that the convergence is particularly good for mixtures with AcN.

The following conclusions can be drawn from the examination of these results:

(i) The convergence observed for mixtures in which $CHCl_3$ does not take part indicates that the interactions of **II** and **III** with the components of the mixed solvent are less strong than the intersolvent interactions. Both solutes have similar environments in the mixtures and provide convergent values for the property with the expressions employed for the neat solvents. Even though **II** and **III** do not measure exactly the same amount of dipolarity/polarizability of the mixed solvent, they may provide a practically useful approximate measure of this property.

(ii) The behavior observed for mixtures with $CHCl_3$ reflects the different sensitivities of **II** and **III** to solute–solvent interactions which are not only solute dependent but also solvent dependent. In these cases, the interactions of the solutes with one component of the mixed solvent interfere with the intersolvent interactions. This is reflected in the composition of the microscopic environments of the solutes and on the dipolarity/polarizability of the mixed solvent.

At this point, in order to establish the influence of the acidity of the cosolvent on the convergence or divergence of the values obtained by **II** and **III**, the data for MeOH are included in the correlation:

$$\pi^*(\mathbf{II}) = 0.08794 + 0.9270\pi^*(\mathbf{III}) \tag{4}$$

$$r = 0.954;\ \mathrm{SD}[\pi^*(\mathbf{II})] = 0.045;\ n = 7$$

The differences between the fitted and the calculated π^*(**II**) values are obtained by the same treatment, and are also reported in Table 8. The results show that (i) the general trends in the degree of convergence observed in the case of the mixtures without MeOH are verified, and

Table 9. Differences between the fitted and the calculated β(**IV**) values for seven binary mixtures of solvents

PAHBA solvent	Cosolvent	$\lvert\Delta\beta(\mathbf{IV})\rvert$
EAc	$CHCl_3$	$0.101 \leq \lvert\Delta\beta(\mathbf{IV})\rvert \leq 0.454$
AcN	$CHCl_3$	$0.124 \leq \lvert\Delta\beta(\mathbf{IV})\rvert \leq 0.437$
DMSO	$CHCl_3$	$0.076 \leq \lvert\Delta\beta(\mathbf{IV})\rvert \leq 0.482$
EAc	CH_2Cl_2	$0.062 \leq \lvert\Delta\beta(\mathbf{IV})\rvert \leq 0.235$
AcN	CH_2Cl_2	$0.102 \leq \lvert\Delta\beta(\mathbf{IV})\rvert \leq 0.231$
DMSO	CH_2Cl_2	$0.010 \leq \lvert\Delta\beta(\mathbf{IV})\rvert \leq 0.324$
EAc	AcN	$0.008 \leq \lvert\Delta\beta(\mathbf{IV})\rvert \leq 0.065$

(ii) a pronounced divergence ($0.074 \leq \lvert\Delta\pi^*(\mathbf{II})\rvert \leq 0.125$ is detected for the mixtures with cosolvent MeOH. These results support the conjecture that the HBD ability of the cosolvent affects the degree of convergence because it modifies the preferential solvation of the solutes.

A similar treatment is applied to the HBA basicity parameters (except for mixtures with cosolvent MeOH because $\beta(\mathbf{V})$ is not available). The linear correlation between $\beta(\mathbf{IV})$ and $\beta(\mathbf{V})$ (values calculated from the wavenumber of the UV–visible absorption maxima) for the explored mixtures is poor. This correlation is improved if the data for $CHCl_3$ are removed. The result is given by

$$\beta(\mathbf{IV}) = -0.17166 + 1.38189\beta(\mathbf{V}) \qquad (5)$$

$$r = 0.971;\ \mathrm{SD}[\beta(\mathbf{IV})] = 0.086;\ n = 5$$

The $\Delta\beta(\mathbf{II/IV})$ values calculated as the difference between the fitted $\beta(\mathbf{II/IV})$ values and those calculated from the fitted $\beta(\mathbf{III/V})$ and Eqn. (5) are presented in Table 9. The results clearly indicate that there is good convergence in the HBA basicity values for the explored solutes only for EAc–AcN mixtures. On the other hand, the solute–solvent interactions of the compared solutes with one component of the polychlorinated mixtures interfere with the self- or auto-solvent–solvent interactions.

CONCLUSIONS

The results obtained allow us to conclude that, in general, EAc or DMSO–$CHCl_3$ or CH_2Cl_2 and EAc–AcN or MeOH mixtures manifest similar response models to the solvatochromic processes explored, but clearly different from those exhibited by AcN–$CHCl_3$ mixtures.

The differences in the solvatochromic response models detected could be attributed to (i) the behavior of the first cited mixtures is governed by the complex formation through hydrogen bonding between the PAHBA oxygenated solvents and the HBD cosolvents, and (ii) when AcN is taken as the PAHBA solvent, it also exhibits HBD ability which could affect the hydrogen bond association between the two components determining the properties of the mixtures.

On the other hand, the differences observed among the mixtures with the PAHBA oxygenated solvents could be related to the extent and the strength of the hydrogen-bonded complex formation that is expected to be different in the mixtures with MeOH from those with $CHCl_3$ or CH_2Cl_2 taking into account that the hydrogen atom in MeOH is more acidic than in the other cosolvents and also the self-association of the hydroxylic solvent.

The S_NAr reaction analyzed reflects two different kinetic response models depending on the nucleophile concentration and as a function of the solvent composition. It can be pointed out that high kinetic synergetic effects are observed at those amine concentrations at which preferential solvation by MeOH is detected.

The analysis of the agreement of solvent property values obtained with comparable solutes reveals that the degree of convergence decreases with increase in the HBD capability of the cosolvents. These results could be related to the specific solute–solvent interactions which interfere with the solvent–solvent interactions.

EXPERIMENTAL

The solvatochromic indicators, the reagents and the solvents were prepared and/or purified as reported previously.[1b,c,e] The wavenumbers of maximum absorption were obtained as described in previous studies.[1b,c] For the spectrophotometric measurements, indicator dye solutions of about 2×10^{-4} M (solute **I**), 10^{-4} M (solute **III**), 5×10^{-5} M (solutes **II** and **IV**) and 5×10^{-6} M (solute **VI**) were prepared. The kinetics of the reaction were studied by the procedure already described.[1d]

Computation methods. The parameters of solvation which minimize the squared residuals of the solvatochromic data (wavenumber in *kK*) for the binary solvent systems were computed by non-linear regression using the MATLAB 4.2 program (The Mathworks Inc.).

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