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Structural characterization of the ternary solvent mixture methanol–acetonitrile–1-propanol[†]

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ABSTRACT: Refractive indices and E_T values were measured for the ternary mixture methanol–acetonitrile–1-propanol at 25.0 °C for 13 mole fractions, and also for the corresponding binary mixtures, methanol–1-propanol, methanol–acetonitrile and 1-propanol–acetonitrile, at 25.0 and 50.0 °C, at 10 different compositions. Solvent exchange equilibrium models were applied to the transition energy of the Dimroth–Reichardt $E_T(30)$ solvatochromic indicator in the binary systems and the Redlich–Kister polynomial was used to correlate excess E_T^N and n_D values for the binary solvent mixtures data. The results allowed the analysis of synergetic behaviours, polarizability effects and preferential solvation trends both in the binary and in the ternary mixtures. Our results point towards the prevalence of specific solute–solvent–solvent interactions mainly due to hydrogen bonding by the hydroxylic components of the ternary mixture. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: ternary mixtures; methanol; acetonitrile; 1-propanol; solute–solvent interactions; preferential solvation; polarizability; synergism

INTRODUCTION

The study of solute–solvent–solvent interactions in mixed solvents has become increasingly important in the last few years owing to the numerous applications of this type of media in different processes. Although the properties of binary mixtures have been extensively studied,[1–8] very little work has been done on ternary systems. However, these systems have considerable interest in fields such as analytical chemistry, industrial processes and the simulation design of biological environments.[9,10]

This study was aimed at the structural characterization of the ternary solvent mixture methanol–acetonitrile–1-propanol (MeOH–MeCN–1-PrOH). For this purpose, we determined, both for the ternary and for the corresponding binary mixtures, (i) the refractive index, n_D, taken as a measure of non-specific interactions due to solvent polarizability, and (ii) the Dimroth–Reichardt polarity parameter, E_T, defined on the basis of the excitation energy (in kcal mol^{-1}; 1 kcal = 4.184 kJ) of the solvatochromic indicator, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate, known as $E_T(30)$ dye,[1,3] in a given solvent, calculated from the wavenumber of the maximum of its absorption spectrum ($\tilde{\nu}_{max}$ in cm^{-1}). This parameter reflects a blend of non-specific solvent dipolarity interactions and specific solvent hydrogen bond acidity interactions.

The E_T values have been normalized with reference to tetramethylsilane (TMS) ($E_T^N = 0$) and water ($E_T^N = 1$), according to the equation

$$E_T^N = \frac{E_T(30) - E_T(30)_{TMS}}{E_T(30)_{H_2O} - E_T(30)_{TMS}} = \frac{E_T(30) - 30.7}{32.4} = \frac{2.8591 \times 10^{-3}\bar{\nu}_{max} - 30.7}{32.4} \tag{1}$$

In mixed solvents, the solvatochromic indicator usually interacts to a different extent with each of the mixture components. Therefore, and in contrast to what happens in pure solvents, the composition of the cybotatic region of the dye can be distinct from the composition of the bulk solvent, leading to preferential solvation phenomena. This behaviour is expected to be enhanced in ternary solvent systems.

E_T^N data for the various binary solvent mixtures were analysed through the preferential solvation model of Rosés, Bosch and co-workers.[11–13] This model, based on solvent-exchange equilibria, comprises different equa-

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tion forms depending on the number (m) of solvent molecules in the solvation microsphere of the solvatochromic indicator. In its general form, the model can be represented as shown in Scheme 1.

$$\mathrm{I(S1)}_m + m\mathrm{S2} \rightleftharpoons \mathrm{I(S2)}_m + m\mathrm{S1} \qquad \text{(a)}$$

$$\mathrm{I(S1)}_m + \frac{m}{2}\mathrm{S2} \rightleftharpoons \mathrm{I(S12)}_m = \frac{m}{2}\mathrm{S1} \qquad \text{(b)}$$

Scheme 1

Here S1 and S2 are the two pure solvents that compose the binary mixture and S12 represents the 'mixed solvent' formed by the interaction of solvents 1 and 2. $\mathrm{I(S1)}_m$, $\mathrm{I(S2)}_m$ and $\mathrm{I(S12)}_m$ represent the E_T indicator solvated by solvents S1, S2 and S12, respectively. These solvent-exchange processes are defined by two preferential solvation parameters, namely $f_{2/1}$ and $f_{12/1}$, which are a measure of the tendency of the indicator to be preferentially solvated by solvents S2 and S12 rather than by solvent S1:

$$f_{2/1} = \frac{x_2^s/x_1^s}{(x_2^0/x_1^0)^m} \qquad (2)$$

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{\sqrt{(x_2^0/x_1^0)^m}} \qquad (3)$$

where $x_1{}^s$, $x_2{}^s$ and $x_{12}{}^s$ are the mole fractions of solvents S1, S2 and S12, respectively, in the solvation sphere of the indicator and $x_1{}^0$ and $x_2{}^0$ are the mole fractions of the two solvents in the bulk mixed solvent.

The $E_T{}^N$ parameter of the binary mixture is derived as an average of the corresponding values for solvents S1, S2 and S12 in the solvation microsphere of the indicator, as given by the equation

$$E_T^N = x_1^s E_{T1}^N + x_2^s E_{T2}^N + x_{12}^s E_{T12}^N \qquad (4)$$

From Eqns. (2)–(4), a general equation can be derived for $E_T{}^N$ of the binary mixture in terms of $E_T{}^N$ of the pure solvents, the preferential solvation parameters and the solvent composition:

$$E_T^N = E_{T1}^N + \frac{a\left(x_2^0\right)^m + c\sqrt{\left[\left(1-x_2^0\right)x_2^0\right]^m}}{\left(1-x_2^0\right)^m + f_{2/1}\left(x_2^0\right)^m + f_{12/1}\sqrt{\left[\left(1-x_2^0\right)x_2^0\right]^m}} \qquad (5)$$

where

$$a = f_{2/1}\left(E_{T2}^N - E_{T1}^N\right) \qquad (6)$$

$$c = f_{12/1}\left(E_{T12}^N - E_{T1}^N\right) \qquad (7)$$

The two-step ($m = 2$) solvent-exchange model equation is a particular case of Eqn. (5). The one-step solvent exchange model, represented by equilibrium (a) in Scheme 1 when $m = 1$, and described by the corresponding equilibrium constant [Eqn. (2)], leads to

$$E_T^N = E_{T1}^N + \frac{a(x_2^0)}{(1-x_2^0) + f_{2/1}(x_2^0)} \qquad (8)$$

Equation (8) is also comprised in the general model equation [Eqn. (5)], when $m = 1$, provided that $f_{12/1} \to 0$. Whenever Eqn. (8) is found to be suitable to describe the $E_T{}^N$ values of a binary mixture, then the preferential solvation parameter $f_{12/1}$ and the E_{T12}^N parameter are given by the following expressions:

$$f_{12/1} = 1 + f_{2/1} \qquad (9)$$

$$E_{T12}^N = \frac{E_{T1}^N + f_{2/1}E_{T2}^N}{1 + f_{2/1}} \qquad (10)$$

For most binary mixtures, m is either 1 or 2, but when a synergetic behaviour is present, the simpler model ($m = 1$) cannot predict all the observed range of $E_T{}^N$ values. When both equations are applicable, the best-fit equation is chosen according to statistical criteria.

The excess properties, Y^E, related to $E_T{}^N$ and n_D were calculated for the studied binary solvent mixtures through the equation

$$Y^E = Y - \sum_{i=1}^{2} x_i Y_i \qquad (11)$$

where Y is the value of the property for the mixture and Y_i and x_i are the values of the property in the pure component i and the correspondent molar fraction.

Since solution physicochemical models are frequently unable to describe accurately the observed behaviour in real solutions, a polynomial approach has been used to describe these excess quantities. The choice of the polynomial function should take into consideration its suitability for computer manipulation, *e.g.* for the application of equilibrium calculation programs. Given its simplicity, the Redlich–Kister[14] representation was chosen as it is the most commonly used approach. For a binary system, the series for the excess property Y^E is given by a common term, (x_1x_2), multiplied by a power series of $(x_1 - x_2)$ argument, multiplied by coefficients that may be temperature and pressure dependent:

$$Y^E = x_1x_2\sum_{i=0}^{n} a_i(x_1 - x_2)^i \qquad (12)$$

The common term ensures that the function is zero for pure solvents, whereas the use of argument $(x_1 - x_2)$

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Table 1. n_D and E_T^N values for the studied binary and ternary solvent mixtures

			n_D		E_T^N	
Mixture	x_1	x_2	25.0 °C	50.0 °C	25.0 °C	50.0 °C
MeOH–1-PrOH	1.000	0.000	1.3269	1.3165	0.763	0.743
	0.955	0.045	1.3312	1.3211	0.759	0.730
	0.910	0.090	1.3352	1.3251	0.746	0.717
	0.810	0.190	1.3438	1.3335	0.730	0.705
	0.750	0.250	1.3480	1.3378	0.721	0.699
	0.500	0.500	1.3631	1.3532	0.684	0.657
	0.250	0.750	1.3709	1.3611	0.657	0.637
	0.125	0.875	1.3784	1.3682	0.631	0.603
	0.075	0.925	1.3804	1.3700	0.625	0.595
	0.000	1.000	1.3831	1.3724	0.614	0.579
MeOH–MeCN	1.000	0.000	1.3269	1.3165	0.763	0.743
	0.955	0.045	1.3279	1.3171	0.769	0.746
	0.910	0.090	1.3291	1.3184	0.766	0.740
	0.810	0.190	1.3314	1.3201	0.769	0.746
	0.750	0.250	1.3325	1.3211	0.769	0.743
	0.500	0.500	1.3365	1.3246	0.763	0.730
	0.250	0.750	1.3388	1.3263	0.746	0.711
	0.125	0.875	1.3404	1.3276	0.699	0.651
	0.075	0.925	1.3409	1.3281	0.657	0.617
	0.000	1.000	1.3414	1.3288	0.469	0.451
1-PrOH–MeCN	1.000	0.000	1.3831	1.3724	0.614	0.579
	0.925	0.075	1.3808	1.3702	0.640	0.614
	0.875	0.125	1.3789	1.3684	0.645	0.620
	0.750	0.250	1.3724	1.3613	0.657	0.631
	0.500	0.500	1.3656	1.3542	0.663	0.631
	0.250	0.750	1.3544	1.3423	0.648	0.614
	0.190	0.810	1.3514	1.3393	0.642	0.598
	0.090	0.910	1.3462	1.3339	0.614	0.566
	0.045	0.955	1.3439	1.3314	0.574	0.536
	0.000	1.000	1.3414	1.3288	0.469	0.451
MeOH–MeCN–1-PrOH	0.950	0.025	1.3298		0.763	
	0.900	0.050	1.3329		0.763	
	0.750	0.125	1.3410		0.749	
	0.500	0.250	1.3513		0.730	
	0.333	0.333	1.3570		0.708	
	0.250	0.250	1.3650		0.699	
	0.250	0.500	1.3524		0.714	
	0.125	0.125	1.3750		0.660	
	0.125	0.750	1.3475		0.699	
	0.050	0.050	1.3801		0.637	
	0.050	0.900	1.3439		0.648	
	0.025	0.025	1.3816		0.626	
	0.025	0.950	1.3428		0.612	

simplifies the expression of Y^E as a function of either of the two composition variables and ensures that the maxima for the different terms do not occur at the same composition, therefore minimizing the correlation among coefficients.

With the information collected, we have drawn several conclusions on the structure of the ternary solvent system.

RESULTS AND DISCUSSION

We have determined the Dimroth–Reichardt parameter, E_T^N, and the refractive index, n_D, for 13 different compositions of the ternary solvent system at 25.0 °C and for 10 different compositions of each of the three binary solvent mixtures at 25.0 and 50.0 °C (Table 1).

E_T^N and n_D analysis for the binary solvent mixtures

The application of the preferential solvation model of Rosés, Bosch and co-workers[11–13] (Table 2 and Fig. 1) shows that this model successfully describes the E_T^N parameter behaviour for all three binary solvent mixtures at both temperatures. The application of the model equations was evaluated according to the standard

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Table 2. Regression parameters for the Rosés, Bosch and co-workers equation model applied to the binary solvent mixtures

Binary mixture	T (°C)	$E^{N}_{T,1} \pm \sigma\ (E^{N}_{T,1})$	$E^{N}_{T,2} \pm \sigma\ (E^{N}_{T,2})$	$E^{N}_{T,12} \pm \sigma\ (E^{N}_{T,12})$	$f_{2/1} \pm \sigma\ (f_{2/1})$	$f_{12/1} \pm \sigma\ (f_{12/1})$	r^2	σ_{fit}	F
MeOH–1-PrOH	25.0	$0.762_6 \pm 0.002$	$0.616_2 \pm 0.003$	$0.6_8 \pm 0.1$	$1.1_2 \pm 0.1$	$2.1_2 \pm 0.1$	0.9970	0.0036	1185
($m = 1$)	50.0	$0.735_7 \pm 0.004$	$0.583_8 \pm 0.005$	$0.6_6 \pm 0.2$	$0.9_3 \pm 0.2$	$1.9_3 \pm 0.2$	0.9903	0.0067	359
MeOH–MeCN	25.0	$0.771_2 \pm 0.003$	$0.468_3 \pm 0.006$	$0.758_1 \pm 0.008$	$0.045_0 \pm 0.004$	$1.045_0 \pm 0.004$	0.9966	0.0063	1013
($m = 1$)	50.0	$0.747_2 \pm 0.002$	$0.450_5 \pm 0.006$	$0.729_8 \pm 0.008$	$0.062_4 \pm 0.004$	$1.062_4 \pm 0.004$	0.9973	0.0056	1297
1-PrOH–MeCN	25.0	$0.614_5 \pm 0.002$	$0.468_8 \pm 0.002$	$0.676_0 \pm 0.002$	$0.35_4 \pm 0.04$	$7_{.9} \pm 1$	0.9994	0.0019	2082
($m = 2$)	50.0	$0.579_2 \pm 0.003$	$0.451_6 \pm 0.003$	$0.644_8 \pm 0.003$	$0.9_1 \pm 0.2$	$13_{.9} \pm 3$	0.9984	0.0030	796

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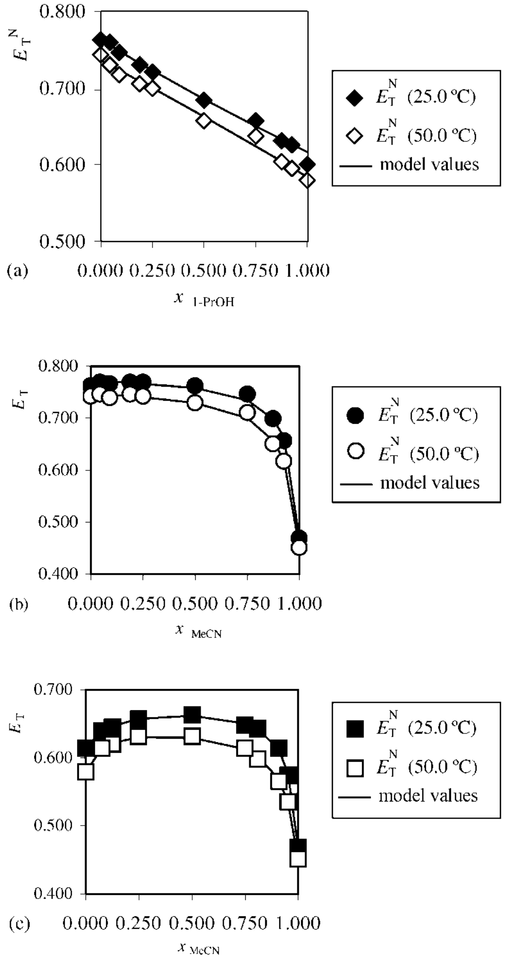

Figure 1. Application of the Rosés, Bosch and co-workers model to three binary solvent mixtures at 25.0 and 50.0 °C: (a) MeOH–1-PrOH; (b) MeOH–MeCN; (c) 1-PrOH–MeCN

deviation of the fit (σ_{fit}), the multiple determination coefficient (r^2), the F-value and the t-values associated with regression coefficients at a 99% significance level. When both model equations were statistically meaningful, the best-fit equation was chosen based on an F-test of the additional term. A detailed examination of Table 2 and Fig. 1, leads us to the following conclusions. First, the mixture MeOH–1-PrOH [Fig. 1(a)] is described by the simple model equation [Eqn. (8)] and shows a behaviour close to ideality at both temperatures. This is confirmed by the values of $f_{2/1} \rightarrow 1$ and $f_{12/1} \rightarrow 2$ and corresponding standard deviations (Table 2). Thus, we expect that the betaine dye tends to be equally solvated by the two components of the binary solvent mixture.

Second, the mixture MeOH–MeCN [Fig. 1(b)], showing no synergetic behaviour, is also described by the simple model equation [Eqn. (8)] and, based on the $f_{2/1}$ and $f_{12/1}$ values (Table 2), we conclude that the solute–solvent interactions occur, at both temperatures, in the order MeOH > intermediate S_1–S_2 complex > MeCN. This behaviour is not in agreement with that observed by Rosés, Bosch and co-workers[12,15] for the same binary solvent mixture. These authors calculated the preferential solvation parameters based on the two-step solvent-exchange model equation [Eqn. (5) with $m = 2$]. Since our experimental E_T values are well fitted to Eqn. (8), the three parameters E_{T1}, E_{T2} and $f_{2/1}$ are sufficient to describe this system. Therefore, the use of the five-parameter model equation [Eqn. (5) with $m = 2$] results in an overparameterization and the mathematical fit can lead, as those authors well emphasized,[12] to different parameter combinations with similar standard deviations ($\sigma_{\text{fit}} = 0.0063$ in Table 1 *vs* 0.0065 in Ref. 12, for 25.0 °C). This can rationalize the different order of polarity observed in both studies.

Furthermore, our experimental E_T values are coincident with those calculated from the parameters presented on Refs. 12 and 15. Given the fact that both components of the mixture have similar ε_r (relative permittivity) and π^* (Kamlet–Taft dipolarity/polarizability parameter)[16] values, the non-specific solute–solvent interactions should be comparable, with a slight prevalence in the case of MeCN. On the other hand, the magnitude of α (Kamlet–Taft hydrogen-bond donor acidity parameter)[16] is much greater for MeOH, conferring to this solvent a better ability for specific interactions via hydrogen bonding. Hence it is expected that the betaine, owing to its molecular structure, *i.e.* through the phenolate oxygen, should be preferentially solvated by MeOH, as our results indicate.

Third, the mixture 1-PrOH–MeCN [Fig. 1(c)] is described by the two-step solvent-exchange equilibrium model equation [Eqn. (5) with $m = 2$] and based on the $f_{2/1}$ and $f_{12/1}$ values (Table 2), we conclude that solute–solvent interactions occur, at both temperatures, in the order intermediate S_1–S_2 complex > 1-PrOH > MeCN. In this particular binary solvent system, we observe a strong synergetic effect over a large range of mole fractions. Apparently, the mixed S_1–S_2 complex gives the solvent mixture characteristics of a polarity much greater than for any of the two pure components, which would not be expected on a mere additivity basis.

The behaviour of the binary solvent mixture MeOH–MeCN [Fig. 1(b)] and that of various binary MeOH–aprotic solvent systems, suggests the existence of structural microheterogeneities:[17,18] (i) In regions rich in the protic component, the mixture retains the typical protic structure and the addition of the aprotic solvent seems to produce no effect in the solute–protic solvent interactions. The molecules of the aprotic component tend ‘simply’ to occupy the free spaces in the protic solvent structure. (ii) In regions rich in the aprotic component, a severe bathochromic shift is observed with the increase in MeCN concentration. In these regions, individual molecules of the protic solvent interact with individual molecules of acetonitrile, producing a disruption in the structure of the aprotic solvent, *i.e.* a disruption of its dipole–dipole interaction pattern. In these aceto-

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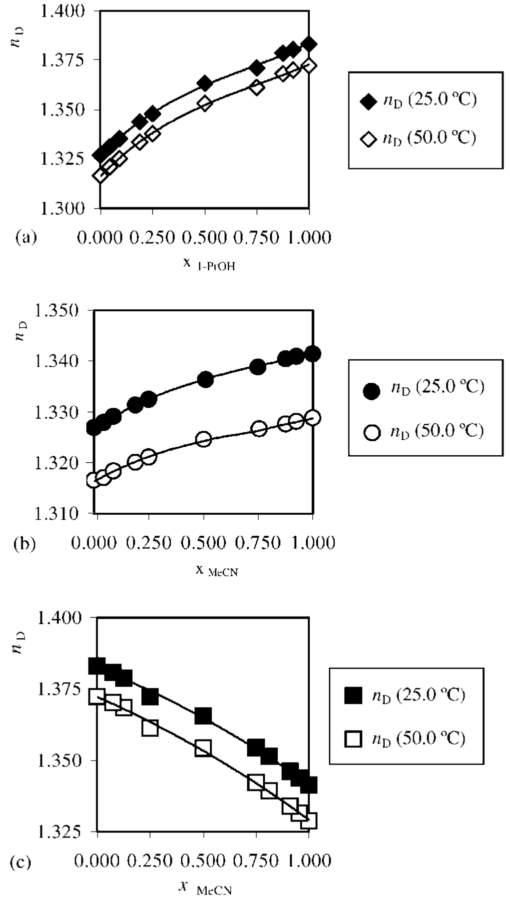

Figure 2. Variation of n_D with the molar fraction for three binary solvent mixtures at 25.0 and 50.0 °C: (a) MeOH–1-PrOH; (b) MeOH–MeCN; (c) 1-PrOH–MeCN

nitrile-rich regions, although the indicator is preferentially solvated by MeOH, there is already a considerable amount of MeCN molecules in the betaine solvation microsphere, which cause a reduction in the local polarity and, therefore, a strong decrease in the E_T values. A similar behaviour, even if less marked, can be observed for the binary mixture 1-PrOH–MeCN [Fig. 1(c)], for similar composition ranges in MeCN.

Given the observed behaviour for the three solvent mixtures, and considering the above remarks, an interaction pattern can be recognized: the betaine–solvent interaction is dominated by specific interactions, via hydrogen bonding, from the protic solvent to the phenolate oxygen of the solvatochromic pyridinium-*N*-phenolate betaine dye.

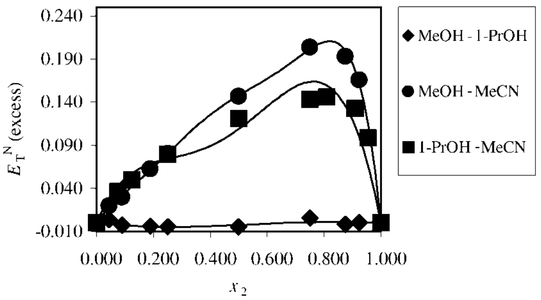

Figure 3. Excess E_T^N values and application of the Redlich–Kister equation (—) to the experimental data for the binary solvent mixtures, at 25.0 °C

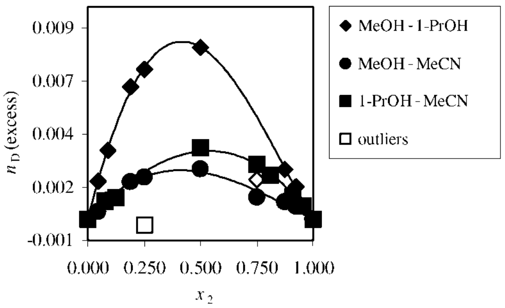

Figure 4. Excess n_D values and application of the Redlich–Kister equation (—) to the experimental data for the binary solvent mixtures, at 25.0 °C

As expected, E_T^N values increase with decreasing temperature, owing to the enhancement of solvent–betaine ground-state interactions at lower temperatures.[15,19]

From Fig. 1(c), it can be seen that there is a slight increase in synergism at 25.0 °C, which can be explained by the temperature influence on the formation equilibrium of the S_1–S_2 solvent–solvent complex.

Figure 2 shows a monotonous type of variation of n_D with the mole fraction for all three solvent mixtures. As expected, we verify a decrease in n_D with increasing temperature, due to a decrease of polarizability in the same direction.

Excess E_T^N and n_D analysis for the binary solvent mixtures

The excess properties related to E_T^N and n_D are shown in Figs. 3 and 4 as a function of the molar fraction of the

Table 3. Regression parameters for the Redlich–Kister equation applied to the excess E_T^N values at 25.0 °C

Binary mixture	$a_0 \pm \sigma (a_0)$	$a_1 \pm \sigma (a_1)$	$a_2 \pm \sigma (a_2)$	$a_3 \pm \sigma (a_3)$	$a_4 \pm \sigma (a_4)$	r^2	σ_{fit}	F
MeOH–1-PrOH	$-0.010_0 \pm 0.007$	$0.02_9 \pm 0.01$	—	—	—	—	0.0028	—
MeOH–MeCN	$0.590_6 \pm 0.002$	$0.39_4 \pm 0.05$	$0.4_2 \pm 0.1$	$1.0_1 \pm 0.1$	$0.8_8 \pm 0.2$	0.9984	0.0043	615
1-PrOH–MeCN	$0.43_4 \pm 0.07$	$0.47_7 \pm 0.09$	$0.8_0 \pm 0.2$	—	—	0.9166	0.0185	26

Table 4. Regression parameters for the Redlich–Kister equation applied to the excess n_D values at 25.0 °C

Binary mixture	$a_0 \pm \sigma\ (a_0)$	$a_1 \pm \sigma\ (a_1)$	$a_2 \pm \sigma\ (a_2)$	$a_3 \pm \sigma\ (a_3)$	$a_4 \pm \sigma\ (a_4)$	r^2	σ_{fit}	F
MeOH–1-PrOH	$0.0324_1 \pm 0.0004$	$-0.0123_6 \pm 0.0006$	$-0.002_2 \pm 0.001$	—	—	0.9990	0.0001	2034
MeOH–MeCN	$0.0088_3 \pm 0.0004$	$-0.0035_0 \pm 0.0008$	—	—	—	0.9668	0.0002	116
1-PrOH–MeCN	$0.0133_4 \pm 0.0003$	$0.0020_3 \pm 0.0005$	$-0.0026_2 \pm 0.0009$	—	—	0.9959	0.0001	486

second mixture component, at 25.0 °C, together with the best fits provided by the Redlich–Kister equation. The statistical parameters are given in Tables 3 and 4.

From these figures, it is possible to conclude that the Redlich–Kister equation is a good model equation to describe our data points, within experimental uncertainty.

As expected, from a careful examination of Table 3, the MeOH–1-PrOH mixtures show excess E_T^N fluctuations around zero (Fig. 3). In contrast, the other two binary solvent systems show a systematic positive deviation, consistent with preferential solvation of the betaine solute by the component with higher polarity.

Regarding excess n_D, Fig. 4 shows a similar positive deviation for the whole range of composition for all three solvent mixtures. However, the MeOH–1-PrOH system has a larger deviation than the other two, which can be attributed to the nature and magnitude of the established specific solvent–solvent interactions, stronger than the specific —O—H···N≡C— interactions in the mixtures involving MeCN.

Ternary solvent system analysis

The data for the ternary solvent mixture are plotted in Fig. 5.

With respect to the behaviour of E_T^N, different types of responses can be observed in three composition ranges:

(a) For $0.25 < x_{1-\text{PrOH}} < 1$ (for whichever composition of the other two components), the behaviour of the E_T^N parameter in the ternary solvent mixture is similar to that of the binary mixture MeOH–1-PrOH, leading to the conclusion that the presence of MeCN is negligible with respect to the solute–solvent interactions, in this range of compositions. This means that alcohol–alcohol hydrogen bonding interactions prevail over dipolar electrostatic interactions in MeOH–MeCN and 1-PrOH–MeCN and therefore that the hydroxylic mixture components preferentially solvate the betaine dye.

(b) For $0 < x_{1-\text{PrOH}} < 0.25$ and $0.75 < x_{\text{MeOH}} < 0.95$ (MeOH-rich regions), the behaviour resembles also that of the binary mixture MeOH–1-PrOH. In this composition range, the E_T^N parameter reaches its maximum values, confirming the previous inference on the prevalence of the specific interactions in the solvation process of the probe. Considering the structural pattern resulting from solvent–solvent interactions, which is characteristic from MeOH, it is foreseen that 1-PrOH will be more available to interact with the betaine.

(c) For $0 < x_{1-\text{PrOH}} < 0.25$ and $0.75 < x_{\text{MeCN}} < 0.95$ (MeCN-rich regions), the E_T^N values are very close to those for the binary system MeOH–MeCN and are greater than those for 1-PrOH–MeCN. Hence it seems that the presence of MeOH by comparison with 1-PrOH, enhances, on the one hand, the specific solute–solvent interactions, and, on the other hand, MeOH appears to be interacting with 1-PrOH, preventing it from interacting with the betaine. We recognize a different behaviour of 1-PrOH in regions (b) and (c) that could be rationalized in terms of a distinct

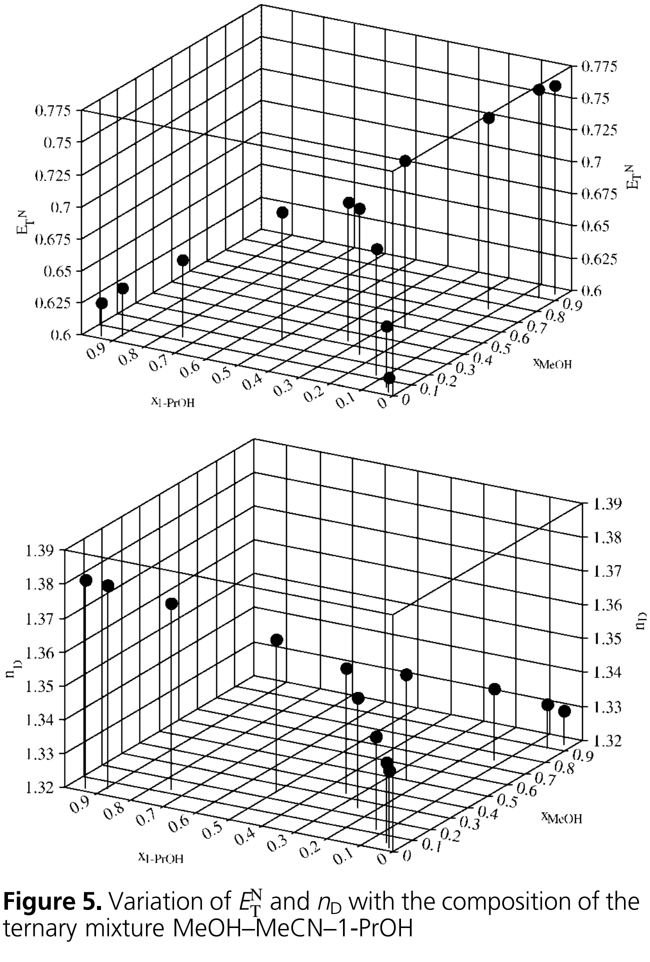

Figure 5. Variation of E_T^N and n_D with the composition of the ternary mixture MeOH–MeCN–1-PrOH

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molecular structuring of the ternary mixture for these composition ranges.

With respect to the behaviour of n_D, different types of responses can also be observed in three composition ranges:

(a) For $x_{MeCN} > 0.333$ (for whichever composition of the other two components), the ternary solvent mixture has n_D values smaller than those for the systems MeOH–1-PrOH and 1-PrOH–MeCN, but greater than those for the system MeOH–MeCN. It seems that the addition of a third component to the binary solvent mixtures MeOH–1-PrOH and 1-PrOH–MeCN, gives rise to a decrease in the polarizability of the mixture, due to the disruption of S_1–S_2 interactions which form the intermediate solvent–solvent complex. On the other hand, the addition of 1-PrOH to the MeOH–MeCN mixture leads to the formation of the strongest 1-PrOH–MeOH complex which is responsible for the increment in the polarizability of the medium.

(b) For $0 < x_{MeCN} < 0.333$ and $0.5 < x_{1-PrOH} < 0.95$ (1-PrOH-rich regions), n_D for the ternary solvent system is smaller than that for the mixture 1-PrOH–MeCN, but greater than those for the mixtures MeOH–MeCN and MeOH–1-PrOH. It seems that the addition of a third component to these latter mixtures gives rise to an exchange of one of the solvent components in the intermediate complex. On the other hand, the addition of MeOH to the 1-PrOH–MeCN seems also to result in an exchange of one of the solvent components in the intermediate complex, but this time giving rise to a decrease in the polarizability of the medium.

(c) For $0 < x_{MeCN} < 0.333$ and $0.5 < x_{MeOH} < 0.95$ (MeOH-rich regions), n_D for the ternary solvent system has a similar behaviour to that of the mixture MeOH–1-PrOH. Therefore, the presence of MeCN in this range of compositions has no effect on the polarizability of the ternary solvent system.

Further studies, in a wider range of compositions, are being carried out in order to investigate the nature and composition of the intermediate solvent–solvent complexes formed, and to clarify outlier occurrence in the excess n_D plots.

EXPERIMENTAL

The chemicals employed were supplied by Sigma-Aldrich. The solvents were of HPLC grade and their purity was verified by ascertaining that the values obtained for the measured physical properties of the pure solvents were in accordance with the literature.[1,20] Precautions were taken to avoid evaporation and contamination by humidity. Mixtures were prepared by mass with an uncertainty of $\pm 2 \times 10^{-4}$ g, and no attempt was made to eliminate dissolved air. No correction was included for the water content of the alcohol in the calculation of the mole fraction. The pyridinium-N-phenolate betaine used was the commercially available Reichardt's dye.

Measurements were carried out at 25.0 and $50.0 \pm 0.1\,°C$. λ_{max} values were measured on a Shimadzu UV-Vis 1603 spectrometer, using quartz analytical cells of 10 mm pathlength, and 3–6 measurements were performed to obtain a mean value. Refractive indices were measured with an Atago Abbé refractometer, 'improved' model, with an uncertainty of $\pm 2 \times 10^{-4}$. At least five values were obtained for each mole fraction.

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