Solute–solvent and solvent–solvent interactions in binary solvent mixtures. Part 4.† Preferential solvation of solvatochromic indicators in mixtures of 2-methylpropan-2-ol with hexane, benzene, propan-2-ol, ethanol and methanol

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The Dimroth–Reichardt $E_T(30)$ betaine dye, 4-nitroanisole, 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline have been used to study preferential solvation in binary mixtures of 2-methylpropan-2-ol with hexane, benzene, propan-2-ol, ethanol and methanol at 30 °C over the whole range of solvent compositions. A theoretical equation which takes into account the solute–solvent and the solvent–solvent interactions has been successfully employed to correlate the experimental values with solvent composition. The indicators have been used to compute the Dimroth–Reichardt $E_T(30)$, and Kamlet–Taft π^*, α and β solvatochromic parameters of the mixtures.

The study of solute–solvent interactions in binary mixtures is more complex than in pure solvents. In a pure solvent the composition of the microsphere of solvation of a solute, the so-called cybotatic region, is the same as in the bulk solvent, but in binary mixtures the composition in this microsphere can be different. The solute 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. The effect of varying the composition of the mixture from the bulk solvent to the solvation sphere is called preferential solvation.

Moreover, the solvent–solvent interactions produced in solvent mixtures can affect solute–solvent interactions, and therefore preferential solvation.

In previous work,[1,2] we studied the preferential solvation of several electrolytes (acids and tetraalkylammonium salts) in mixtures of 2-methylpropan-2-ol and small amounts of other alcohols (up to *ca.* 16% in volume). Later, we correlated the variation on the dissociation p*K* values of the electrolytes in 2-methylpropan-2-ol–alcohol, 2-methylpropan-2-ol–hexane and 2-methylpropan-2-ol–benzene mixtures with the variation of the microscopic properties of the mixture.[3] The microscopic properties were measured by the Kamlet–Taft solvatochromic parameters of polarity/polarizability (π^*), hydrogen bond acidity (α) and hydrogen bond basicity (β).[4–8]

Some macroscopic properties (densities, refractive indices, viscosities and relative permittivities) the 2-methylpropan-2-ol mixtures were also studied over the whole range of solvent compositions.[9] Macroscopic properties of solvent mixtures provide information about the solvent–solvent interactions, but not about the solute–solvent interactions.

The use of solvatochromic indicators is a suitable method for studying solute–solvent interactions, since the transition energy of the indicator depends on the solvation's sphere composition and properties.[4] This method also provides information about some solvent properties such as polarity and hydrogen bonding capabilities.[4–8]

The $E_T(30)$ betaine dye [2,6-diphenyl-4-(2,4,6-triphenylpyridin-1-io)-1-phenolate] is the solvatochromic indicator most widely used.[4,10] It was proposed by Reichardt for measuring empirically the polarity of solvents. The indicator is sensitive to the polarity (π^*) and hydrogen bond donor capability (α) of the solvent.

4-Nitroanisole, 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline belong to a series of indicators proposed by Kamlet, Taft *et al.* for measuring different properties of the solvents.[5–8] 4-Nitroanisole and *N*,*N*-diethyl-4-nitroaniline are mainly sensitive to the dipolarity and polarizability of the solvent (π^*). 4-Nitroaniline is capable of acting as hydrogen bond donor in hydrogen bond acceptor solvents and, therefore, it is sensitive to this solvent property (β), in addition to polarity and polarizability (π^*).

The solvatochromic parameters [$E_T(30)$, π^*, β and α] are calculated from the maximum of absorbance of the indicators, expressed in wavenumber ($\tilde{\nu}$) as kK (1 kK = 1000 cm^{-1}).

The $E_T(30)$ polarity was defined as the excitation energy (kcal mol^{-1}; 1 cal = 4.184 J) of the Reichardt's betaine dye in a particular solvent.[4,10] This energy can be calculated from the maximum of the long-wavelength absorption band of the indicator ($\tilde{\nu}_A$) according to eqn. (1).

$$E_T(30)/(\text{kcal/mol}^{-1}) = hc\tilde{\nu}_A N_A = 2.859\tilde{\nu}_A/(\text{kK}) \quad (1)$$

A normalized parameter E_T^N in reference to tetramethylsilane ($E_T^N = 0$) and water ($E_T^N = 1$) is now recommended instead of $E_T(30)$[4,10] eqn. (2).

$$E_T^N = \frac{E_T(30) - E_T(30)_{\text{TMS}}}{E_T(30)_{\text{H}_2\text{O}} - E_T(30)_{\text{TMS}}} = \frac{E_T(30) - 30.7}{32.4} \quad (2)$$

The π^*, α and β parameters can be calculated from 4-nitroanisole,[7] Reichardt's betaine,[11] 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline[5] wavenumbers ($\tilde{\nu}_B$, $\tilde{\nu}_A$, $\tilde{\nu}_C$ and $\tilde{\nu}_D$), respectively, according to eqns. (3)–(5)[3] where δ is a

$$\pi^* = \frac{34.12 - \tilde{\nu}_B}{2.343} \quad (3)$$

$$\beta = \frac{1.035\tilde{\nu}_D + 2.64 - \tilde{\nu}_C}{2.80} \quad (4)$$

$$\alpha = 0.198\tilde{\nu}_A - 2.091 - 0.899(\pi^* - 0.211\delta) - 0.148\beta \quad (5)$$

polarizability correction term ($\delta = 1$ for aromatic, 0.5 for polychlorinated and 0 for the other organic pure solvents). For solvent mixtures a good estimation of δ can be obtained

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† For Parts 1–3, see refs. 21–23.

averaging the δ values of pure solvents mixed according to their mole fractions.[3]

Marcus and Migron[12] have proposed another approach to calculate β from 4-nitroaniline and the π^* parameter. We shall discuss this approach in the Results and discussion.

Several attempts have been made to obtain measures of preferential solvation in binary solvents from solvatochromic indicators. Dawber *et al.*[13] proposed the deviation of experimental $E_T(30)$ values from linearity as a measure of preferential solvation, and related this deviation with thermodynamic and kinetic properties.[14] Using a similar approach, but with *N*-alkylpyridinium instead of $E_T(30)$ dye and introducing the solvent exchange model of Covington *et al.*,[15] Chatterjee and Bagchi[16,17] described the preferential solvation of that solvatochromic indicator.

In a previous study,[18] we derived an equation that embodied preferential solvation, based on a one-step solvent exchange model, to describe preferential solvation of $E_T(30)$ indicator. This equation did not consider the solvent–solvent interactions and because of this limitation did not apply to 'synergetic' mixtures. The term 'synergetic' was proposed[19] to describe the behaviour showed by some mixtures of dipolar hydrogen bond acceptors (dimethyl sulfoxide, acetonitrile, *etc.*) with good hydrogen bond donors (*e.g.* alcohols). These mixtures have $E_T(30)$ values higher than those of the pure solvents mixed.

Skwiercynski and Connors[20] proposed a model with a solvent exchange equilibrium which takes into account the solvent–solvent interactions, but owing to the restrictions included in the model, this did not apply to synergetic mixtures.[21]

Recently, we have derived a two-step solvent exchange model that can be applied to synergetic mixtures.[21–23] In many instances, this model can be simplified to the Skwierczynski and Connors model, but avoids their restrictions.

In this work, we shall generalize the model derived for $E_T(30)$ to any solvatochromic indicator. The model will be applied to study the preferential solvation of Reichardt's $E_T(30)$ betaine dye, 4-nitroanisole, 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline in binary mixtures of 2-methylpropan-2-ol with hexane, benzene, propan-2-ol, ethanol and methanol over the whole range of solvent compositions.

Preferential solvation models

The general model proposed[21–23] is based on two solvent exchange processes in Scheme 1.

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

$$\frac{m}{2}\,\mathrm{S2} \rightleftharpoons \mathrm{I(S12)}_m + \frac{m}{2}\,\mathrm{S1}$$

Scheme 1

S1 and S2 indicate the two pure solvents to be mixed, and S12 represents a solvent formed by the interaction of solvents 1 and 2. This new solvent can have properties quite different from those of solvents 1 and 2, as we demonstrated for synergetic mixtures.[21] The term m is the number of solvent molecules solvating the solvatochromic indicator **I**. It has been demonstrated[21,22] that for many binary systems, the m value that gives the best results is close to 2. In this instance, the general model becomes the two-step model proposed by Skwierczynski and Connors,[20] Scheme 2.

$$\mathrm{I(S1)}_2 + 2\mathrm{S2} \rightleftharpoons \mathrm{I(S2)}_2 + 2\mathrm{S1}$$

$$\mathrm{I(S1)}_2 + \mathrm{S2} \rightleftharpoons \mathrm{I(S12)}_2 + 2\mathrm{S1}$$

Scheme 2

The constants of these processes are defined by the preferential solvation parameters,[21–23] eqns. (6) and (7), that

$$f_{2/1} = \frac{x_2^s/x_1^s}{(x_2^0/x_1^0)^2} \qquad (6)$$

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{x_2^0/x_1^0} \qquad (7)$$

relate the ratio of mole fractions of solvents **S1**, **S2** and **S12** solvating the indicator (x_1^s, x_2^s and x_{12}^s, respectively) with the ratio of mole fractions of the two solvents in the bulk mixed solvent (x_1^0 and x_2^0, respectively).

The constants $f_{2/1}$ and $f_{12/1}$ measure the tendency of the indicator to be solvated with solvents **S2** and **S12**, respectively, with reference to solvent **S1**.

The Y values of the mixture, where Y is an appropriate solvatochromic property, can be calculated as an average of the Y values in pure solvents **S1**, **S2** and **S12** (Y_1, Y_2 and Y_{12}, respectively) according to the mole fractions of these solvents in the indicator's microsphere of solvation, eqn. (8).

$$Y = x_1^sY_1 + x_2^sY_2 + x_{12}^sY_{12} \qquad (8)$$

Substituting eqns. (6) and (7) into eqn. (8) and considering eqn. (9), eqn. (10) can be derived, where a and c are given

$$x_1^0 + x_2^0 = x_1^s + x_2^s + x_{12}^s = 1 \qquad (9)$$

$$Y = Y_1 + \frac{a(x_2^0)^2 + c(1 - x_2^0)x_2^0}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_2^0} \qquad (10)$$

by eqns. (11) and (12).

$$a = f_{2/1}(Y_2 - Y_1) \qquad (11)$$

$$c = f_{12/1}(Y_{12} - Y_1) \qquad (12)$$

Eqn. (9) is the main equation that was used to relate the $E_T(30)$ parameter with the solvent composition.[20–23] Additionally, the same equation can be applied not only to the transition energies of a solvatochromic indicator (E_T), but also to any other solvatochromic parameter linearly related to the transition energy, without change of the preferential solvation parameters $f_{2/1}$ and $f_{12/1}$. Therefore, the Y parameters of the equation may represent a transition energy (E_T), wavenumber of maximum absorption ($\tilde{\nu}$), or even a solvatochromic parameter dependent on only a single indicator [$E_T(30)$, E_T^N or π^*]. Since β and α parameters depend on the wavenumber of two or three solvatochromic indicators [eqns. (4) and (5)], they must be described by the combination of several equations similar to eqn. (10).

Although eqn. (10) is a general all-purpose equation, sometimes it can be simplified.

If the solvatochromic and preferential parameters of the mixed solvent **S12** fulfil eqns. (13) and (14),[21] then eqn. (10)

$$f_{12/1} = 1 + f_{2/1} \qquad (13)$$

$$Y_{12} = \frac{Y_1 + f_{2/1}Y_2}{1 + f_{2/1}} \qquad (14)$$

becomes eqn. (15) which was the equation used in an earlier

$$Y = Y_1 + \frac{ax_2^0}{(1 - x_2^0) + f_{2/1}x_2^0} \qquad (15)$$

study to relate the $E_T(30)$ values of many binary solvent mixtures with solvent composition.[18] It is also the equation derived from the one-step solvent exchange equilibrium proposed by Skwierczynski and Connors;[20] Scheme 3.

$$\mathbf{I(S1)} + \mathbf{S2} \rightleftharpoons \mathbf{I(S2)} + \mathbf{S1}$$

Scheme 3

A further simplification for some systems is that if $f_{2/1} = 1$, eqn. (15) becomes[23] eqn. (16).

$$Y = x_1^0 Y_1 + x_2^0 Y_2 \qquad (16)$$

Eqn. (16) applies to the so-called ideal binary systems, which show a linear relationship between the solvatochromic property Y and the solvent composition. For these systems there is no preferential solvation [$f_{2/1} = 1$, and $f_{12/1} = 2$, according to eqn. (13)] and the solvatochromic parameter of the mixed solvent **S12**, Y_{12}, is the simple average of the solvatochromic parameters of the pure solvents **S1** and **S2**, Y_1 and Y_2, according to eqn. (14).

Experimental

Apparatus

A Beckman DU-7 spectrophotometer, with a 10 mm cell, connected to a microcomputer was used for acquisition and numerical treatment of the absorbance data.

Solvatochromic indicators

The following dyes were used for determination of solvatochromic parameters: 2,6-diphenyl-4-(2,4,6-triphenylpyridin-1-io)-1-phenolate (Reichardt's betaine), >95% Aldrich; 4-nitroanisole Merck (handled with activated coal and crystallized from acetone–water); 4-nitroaniline RPE, >99% Carlo Erba; and *N*,*N*-diethyl-4-nitroaniline (kindly provided by Professor R. W. Taft, University of California, Irvine).

Solvents

The solvents were the same used in a previous work.[9]

Procedure

For the spectrophotometric measurements, indicator dye solutions of about 10^{-4} M (Dimroth-Reichardt's betaine dye and 4-nitroanisole) or 5×10^{-5} M (for 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline) were prepared. The solvent mixtures studied were the same used previously for 2-methylpropan-2-ol rich mixtures,[2,3] plus seven others to cover the whole range of solvent compositions (at 30, 40, 50, 65, 85, 95 and 100% vol. of solvent 2). All the mixtures were prepared and measured for this work, and therefore some solvatochromic data may be slightly different from that reported previously for 2-methylpropan-2-ol rich mixtures.[3]

The spectrum of the indicator dye was recorded in the ranges: 450–800 nm (Reichardt's dye), 260–350 nm (4-nitroanisole), 330–410 nm (4-nitroaniline) and 350–460 nm (*N*,*N*-diethyl-4-nitroaniline). All the measurements were taken in a closed vessel outwardly thermostatted at 30 ± 0.1 °C with a water flow. The absorbance data were acquired by means of the DUMOD program.[24]

Computation

The spectra of the solvatochromic dyes in each solvent mixture were processed by numerical smoothing of the absorbance data, and the wavelength of the maxima of the spectra were obtained. The 'moving window averaging' technique was used to smooth the absorbance data. In this method, each data point is replaced by the arithmetic average of the point and *n* previous and *n* posterior points (*n* = 5–10 in this work). The smoothing was repeated until a constant maximum was obtained.

Results and discussion

The applicability of the equations proposed has been tested for the four indicators studied [Reichardt's $E_T(30)$, 4-nitroanisol, 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline] in mixtures of 2-methylpropan-2-ol with hexane, benzene, propan-2-ol, ethanol and methanol. Table 1 presents the literature solvatochromic properties[4,6,8,11] of these solvents at 25 °C together with the ones obtained here for the pure solvents at 30 °C. There is good agreement between the values obtained in this work by application of eqns. (3)–(5) and the literature ones. However, we have also examined the possibility of using the Marcus and Migron approach[12] to calculate β. These authors set up general LSER equations which related the wavenumber of maximum absorption of several indicators with the solvatochromic

Table 1 Experimental (303.2 K) and literature (298.2 K)[4,6,8,11] solvatochromic parameters for the pure solvents used in the preparation of binary mixtures, and calculated solvatochromic parameters (303.2 K) for the mixed **S12** solvents formed

Solvents		E_T^N	π^*	β	α	δ
Hexane	Lit.	0.009	−0.08	0.00	0.00	0
	Exp.	—	−0.06	0.03 (0.01)[c]	—	
Benzene	Lit.	0.111	0.59	0.10	0.00	1
	Exp.	0.118	0.60	0.09 (0.08)	−0.06	
2-Methylpropan-2-ol	Lit.	0.389	0.41	1.01	0.42	0
	Exp.	0.392	0.50	0.94 (1.07)	0.32	
Propan-2-ol	Lit.	0.546	0.48	0.95	0.76	0
	Exp.	0.536	0.50	0.87 (1.04)	0.66	
Ethanol	Lit.	0.654	0.54	0.77	0.83	0
	Exp.	0.649	0.56	0.74 (0.88)	0.88	
Methanol	Lit.	0.762	0.60	0.62	0.93	0
	Exp.	0.749	0.60	0.62 (0.79)	1.09	
Hexane–2-methylpropan-2-ol	Avg.[a]	0.20	0.22	0.47	0.16	0
	Calc.[b]	0.29	0.22	−0.07 (0.00)	0.49	
Benzene–2-methylpropan-2-ol	Avg.	0.26	0.55	0.52	0.13	0.5
	Calc.	0.21	0.56	0.58 (0.64)	−0.08	
Propan-2-ol–2-methylpropan-2-ol	Avg.	0.46	0.50	0.90	0.49	0
	Calc.	0.49	0.51	0.92 (1.08)	0.54	
Ethanol–2-methylpropan-2-ol	Avg.	0.52	0.53	0.84	0.60	0
	Calc.	0.51	0.52	0.87 (1.02)	0.59	
Methanol–2-methylpropan-2-ol	Avg.	0.57	0.55	0.78	0.70	0
	Calc.	0.49	0.52	0.82 (0.96)	0.54	

[a] Avg. = average of the experimental values of pure 2-methylpropan-2-ol and cosolvent. [b] Calc. = calculated from the Y_{12} values of Tables 7 or 8. [c] β values in brackets have been calculated by eqn. (17).

parameters. For 4-nitroaniline ($\tilde{\nu}_C$) they propose eqn. (17).

$$\beta = \frac{31.10 - 3.14\pi^* - \tilde{\nu}_C}{2.79} \qquad (17)$$

In Table 1, the β values calculated by this equation are given in brackets. These β values are in general higher than the literature and than the ones calculated by eqn. (4). These two last sets of values agree better and therefore we have used eqn. (4) to calculate the β values of the mixtures. Anyway, there is a good linear relationship between the β values calculated by eqn. (4) (β_4) and eqn. (17) (β_{17}) for all the studied mixtures, eqn. (18).

$$\beta_{17} = 1.156\beta_4 \quad r = 0.9943 \quad \text{sd} = 0.024 \quad n = 90 \qquad (18)$$

Hexane is an apolar solvent without hydrogen bonding properties. Benzene similarly has no hydrogen bonding properties, but its polarity is similar to that of 2-methylpropan-2-ol, and it is the most polarizable solvent studied ($\delta = 1$). Propan-2-ol has polarity and hydrogen bond acceptor capabilities similar to those of 2-methylpropan-2-ol, but it is a stronger hydrogen bond donor. Ethanol and methanol are stronger hydrogen bond donors and weaker hydrogen bond acceptors than 2-methylpropan-2-ol, but their polarities are slightly higher.

The measured wavenumbers of maximum absorption ($\tilde{\nu}$) for the four solvatochromic indicators in the mixtures studied are presented in Tables 2–6, expressed as wavenumber in kK. Tables 2–6 also present the solvatochromic parameters E_T^N, α, β and π^* calculated from the wavenumbers by means of eqns. (1)–(5). The maximum of absorption of the Reichardt's $E_T(30)$ indicator in 2-methylpropan-2-ol–hexane mixtures has not been measured for mole fractions of hexane higher than 0.6 because of the very low solubility of the indicator in non-polar solvents (Table 1).[4] Consequently, the corresponding E_T^N and α parameters for these mixtures cannot be calculated. The value given for pure hexane has been taken from the literature,[4] and the E_T^N and α values given in Table 2 for pure hexane have been calculated using this literature value.

Table 7 and Figs. 1–4, present the results obtained in the application of eqn. (10) to the studied mixtures. The fits obtained are very good (sd < 0.05) and eqn. (10) can be successfully applied to all the indicators and mixtures studied. The Y_{12} value is intermediate between Y_1 and Y_2 except for 4-nitroanisole in propan-2-ol mixtures, 4-nitroaniline in propan-2-ol and ethanol mixtures, and *N*,*N*-diethyl-4-nitroaniline in propan-2-ol mixtures, where it is lower than Y_1 and Y_2. Therefore, these last mixtures can be considered synergetic,[21,22] although the variation of the wavenumbers is so small that the synergism is almost imperceptible in Figs. 2–4 and it is doubtful whether the synergetic behaviour really exists or it is a consequence of the instrumental uncertainty in the measurements (that we presume to be about ±0.5 nm which corresponds to *ca.* ±0.04 kK).

Figs. 1–4 show clearly that the susceptibility of the four solvatochromic indicators is very different. The variation of Reichardt's $E_T(30)$ indicator in going from the most polar and hydrogen bond donor solvent methanol to the less polar and hydrogen bond donor hexane is almost 9 kK (Fig. 1). The variation between the hexane and the other solvents for the π^*

Table 2 Experimental wavenumbers (in kK = 10^3 cm^{-1}) and solvatochromic parameters for binary solvent mixtures of 2-methylpropan-2-ol–hexane at 303.2 K

	Indicators[b]							
x_2[a]	A	B	C	D	E_T^N	α	β	π^*
0.0000	15.19	32.93	26.55	25.62	0.393	0.32	0.93	0.51
0.0015	15.16	32.95	26.60	25.62	0.390	0.33	0.91	0.50
0.0029	15.16	32.95	26.62	25.63	0.390	0.33	0.91	0.50
0.0058	15.15	32.95	26.58	25.65	0.389	0.32	0.93	0.50
0.0144	15.14	32.95	26.62	25.63	0.388	0.32	0.91	0.50
0.0284	15.09	32.98	26.65	25.65	0.384	0.33	0.91	0.49
0.0420	15.07	33.00	26.70	25.67	0.382	0.33	0.90	0.48
0.0681	15.03	33.05	26.75	25.70	0.379	0.34	0.89	0.46
0.0928	14.98	33.07	26.81	25.75	0.374	0.34	0.89	0.45
0.1047	14.97	33.09	26.83	25.78	0.373	0.35	0.89	0.44
0.1276	14.91	33.11	26.88	25.81	0.368	0.34	0.88	0.43
0.2403	14.62	33.27	27.21	26.05	0.343	0.35	0.85	0.36
0.3298	14.38	33.40	27.48	26.27	0.321	0.36	0.84	0.31
0.4246	14.29	33.56	27.88	26.55	0.313	0.41	0.80	0.24
0.5782	13.71	33.74	28.51	26.87	0.262	0.38	0.69	0.16
0.8070	—	34.00	29.41	27.24	—	—	0.51	0.05
0.9334	—	34.20	30.29	27.61	—	—	0.33	−0.03
1.0000	10.80[c]	34.27	31.27	27.75	0.006	0.10	0.03	−0.06

[a] x_2 = Mole fraction of hexane. [b] A = 2,6-diphenyl-4-(2,4,6-triphenylpyridin-1-io)-1-phenolate. B = 4-Nitroanisole. C = 4-Nitroaniline. D = *N*,*N*-diethyl-4-nitroaniline. [c] Data from ref. 4.

Table 3 Experimental wavenumbers (in kK) and solvatochromic parameters for binary solvent mixtures of 2-methylpropan-2-ol–benzene at 303.2 K

	Indicators[b]							
x_2[a]	A	B	C	D	E_T^N	δ	β	π^*
0.0000	15.15	32.94	26.54	25.61	0.389	0.32	0.93	0.50
0.0021	15.14	32.94	26.56	25.62	0.388	0.32	0.93	0.50
0.0043	15.13	32.95	26.58	25.61	0.388	0.32	0.92	0.50
0.0085	15.13	32.94	26.62	25.62	0.388	0.32	0.91	0.50
0.0210	15.08	32.94	26.64	25.61	0.383	0.31	0.90	0.50
0.0411	15.05	32.94	26.67	25.61	0.381	0.31	0.88	0.50
0.0605	15.00	32.93	26.70	25.61	0.376	0.31	0.87	0.51
0.0969	14.97	32.92	26.84	25.61	0.373	0.31	0.82	0.51
0.1305	14.94	32.92	26.92	25.63	0.371	0.31	0.80	0.51
0.1465	14.90	32.91	26.93	25.63	0.367	0.30	0.80	0.52
0.1766	14.84	32.91	27.01	25.63	0.362	0.30	0.77	0.52
0.3170	14.46	32.84	27.22	25.63	0.328	0.24	0.70	0.55
0.4192	14.22	32.81	27.37	25.64	0.307	0.21	0.65	0.56
0.5199	14.11	32.79	27.54	25.64	0.298	0.21	0.59	0.57
0.6679	13.78	32.75	27.92	25.65	0.268	0.17	0.45	0.59
0.8599	13.45	32.72	28.47	25.67	0.239	0.16	0.26	0.60
0.9536	13.22	32.72	28.85	25.69	0.219	0.15	0.14	0.60
1.0000	12.07	32.72	29.00	25.71	0.118	−0.06	0.09	0.60

[a] x_2 = Mole fraction of benzene. [b] A, B, C and D as in Table 2.

Table 4 Experimental wavenumbers (in kK) and solvatochromic parameters for binary solvent mixtures of 2-methylpropan-2-ol–propan-2-ol at 303.2 K

	Indicators[b]							
x_2[a]	A	B	C	D	E_T^N	α	β	π^*
0.0000	15.20	32.94	26.52	25.62	0.394	0.33	0.94	0.50
0.0025	15.20	32.95	26.52	25.62	0.394	0.33	0.94	0.50
0.0050	15.21	32.95	26.52	25.62	0.395	0.33	0.94	0.50
0.0099	15.23	32.95	26.52	25.61	0.396	0.34	0.94	0.50
0.0243	15.28	32.95	26.52	25.61	0.401	0.35	0.94	0.50
0.0475	15.37	32.95	26.52	25.61	0.409	0.36	0.94	0.50
0.0696	15.44	32.94	26.51	25.61	0.415	0.37	0.94	0.50
0.1108	15.56	32.93	26.49	25.61	0.426	0.39	0.95	0.51
0.1485	15.65	32.93	26.48	25.61	0.433	0.41	0.95	0.51
0.1662	15.70	32.92	26.47	25.60	0.438	0.42	0.95	0.51
0.1995	15.77	32.93	26.46	25.60	0.444	0.43	0.96	0.51
0.3490	16.05	32.92	26.46	25.54	0.469	0.49	0.93	0.51
0.4545	16.20	32.91	26.45	25.52	0.482	0.51	0.93	0.52
0.5572	16.32	32.92	26.48	25.52	0.493	0.54	0.92	0.51
0.7003	16.50	32.93	26.53	25.52	0.508	0.59	0.90	0.51
0.8770	16.68	32.93	26.56	25.53	0.524	0.62	0.89	0.51
0.9598	16.76	32.97	26.62	25.57	0.531	0.65	0.89	0.49
1.0000	16.81	32.96	26.65	25.56	0.536	0.66	0.87	0.50

[a] x_2 = Mole fraction of propan-2-ol. [b] A, B, C and D as in Table 2.

Table 5 Experimental wavenumbers (in kK) and solvatochromic parameters for binary solvent mixtures of 2-methylpropan-2-ol–ethanol at 303.2 K

	Indicators[b]							
x_2[a]	A	B	C	D	E_T^N	δ	β	π^*
0.0000	15.19	32.95	26.53	25.62	0.393	0.33	0.94	0.50
0.0033	15.22	32.95	26.53	25.61	0.396	0.34	0.93	0.50
0.0065	15.27	32.95	26.52	25.61	0.400	0.35	0.94	0.50
0.0129	15.31	32.95	26.52	25.61	0.403	0.35	0.94	0.50
0.0316	15.46	32.95	26.51	25.61	0.417	0.38	0.94	0.50
0.0613	15.65	32.94	26.49	25.60	0.433	0.42	0.95	0.50
0.0893	15.79	32.93	26.48	25.60	0.446	0.44	0.95	0.51
0.1404	16.01	32.93	26.48	25.60	0.465	0.48	0.95	0.51
0.1861	16.22	32.93	26.48	25.58	0.484	0.53	0.94	0.51
0.2072	16.30	32.93	26.48	25.56	0.491	0.54	0.93	0.51
0.2463	16.43	32.93	26.49	25.57	0.502	0.57	0.93	0.51
0.4127	16.78	32.91	26.56	25.52	0.533	0.64	0.89	0.52
0.5220	17.04	32.89	26.63	25.53	0.556	0.68	0.87	0.53
0.6225	17.27	32.89	26.70	25.50	0.576	0.73	0.83	0.53
0.7539	17.59	32.88	26.78	25.52	0.605	0.80	0.81	0.53
0.9033	17.85	32.85	26.86	25.49	0.628	0.84	0.77	0.54
0.9691	18.00	32.83	26.89	25.47	0.641	0.87	0.75	0.55
1.0000	18.09	32.82	26.91	25.46	0.649	0.88	0.74	0.56

[a] x_2 = Mole fraction of ethanol. [b] A, B, C and D as in Table 2.

Table 6 Experimental wavenumbers (in kK) and solvatochromic parameters for binary solvent mixtures of 2-methylpropan-2-ol–methanol at 303.2 K

	Indicators[b]							
x_2[a]	A	B	C	D	E_T^N	δ	β	π^*
0.0000	15.16	32.95	26.54	25.63	0.390	0.32	0.94	0.50
0.0047	15.34	32.95	26.56	25.62	0.406	0.36	0.93	0.50
0.0093	15.40	32.95	26.57	25.61	0.411	0.37	0.92	0.50
0.0185	15.49	32.95	26.57	25.61	0.419	0.39	0.92	0.50
0.0450	15.77	32.94	26.57	25.61	0.444	0.44	0.92	0.50
0.0861	16.08	32.94	26.57	25.60	0.471	0.50	0.92	0.50
0.1238	16.29	32.93	26.59	25.59	0.490	0.54	0.91	0.51
0.1906	16.65	32.92	26.61	25.58	0.522	0.61	0.90	0.51
0.2480	16.88	32.92	26.64	25.56	0.542	0.66	0.88	0.51
0.2737	16.98	32.93	26.65	25.56	0.551	0.69	0.87	0.51
0.3202	17.11	32.93	26.70	25.54	0.562	0.72	0.85	0.51
0.5047	17.76	32.91	26.82	25.50	0.620	0.84	0.79	0.52
0.6132	18.12	32.88	26.87	25.47	0.651	0.91	0.76	0.53
0.7039	18.40	32.85	26.93	25.45	0.676	0.96	0.73	0.54
0.8153	18.73	32.81	26.97	25.38	0.705	1.01	0.69	0.56
0.9309	19.11	32.75	27.01	25.27	0.739	1.07	0.64	0.59
0.9783	19.22	32.73	27.01	25.24	0.749	1.09	0.63	0.59
1.0000	19.23	32.72	27.01	25.21	0.749	1.09	0.62	0.60

[a] x_2 = Mole fraction of methanol. [b] A, B, C and D as in Table 2.

Table 7 Parameters from eqn. (10) for the mixtures of 2-methylpropan-2-ol (**S1**) with hexane, benzene, propan-2-ol, ethanol and methanol for the different indicators used

Cosolvent (**S2**)	Y_1	Y_2	Y_{12}	$f_{2/1}$	$f_{12/1}$	N[a]	sd[b]
2,6-Diphenyl-4-(2,4,6-triphenylpyridin-1-io)-1-phenolate							
Hexane	15.17	10.80	14.14	0.46	2.1	16	0.04
Benzene	15.15	12.07	13.17	0.0072	1.1	18	0.04
Propan-2-ol	15.19	16.81	16.26	1.9	3.7	18	0.01
Ethanol	15.19	18.08	16.55	4.6	6.8	18	0.02
Methanol	15.21	19.27	16.29	19	18	18	0.03
4-Nitroanisole							
Hexane	32.94	34.27	34.07	0.18	1.3	18	0.01
Benzene	32.94	32.72	32.88	3.9	1.3	18	0.01
Propan-2-ol	32.95	32.96	32.91	0.65	5.1	18	0.01
Ethanol	32.95	32.82	32.90	0.69	3.0	18	0.01
Methanol	32.95	32.72	32.73	0.022	0.25	18	0.01
4-Nitroaniline							
Hexane	26.57	31.27	30.42	0.0059	0.67	18	0.04
Benzene	26.56	29.02	27.02	3.8	8.9	18	0.03
Propan-2-ol	26.53	26.64	26.37	1.2	2.6	18	0.01
Ethanol	26.53	26.91	26.20	3.1	2.0	18	0.01
Methanol	26.56	27.02	26.68	1.8	0.87	18	0.01
N,*N*-Diethyl-4-nitroaniline							
Hexane	25.63	27.68	25.61	17	16	18	0.04
Benzene	25.61	25.71	25.64	0.54	3.6	18	0.01
Propan-2-ol	25.62	25.56	23.21	0.85	0.055	18	0.01
Ethanol	25.62	25.46	25.50	0.26	2.2	18	0.01
Methanol	25.62	25.20	25.56	1.2	4.9	18	0.01

[a] N = number of data points. [b] sd = standard deviation.

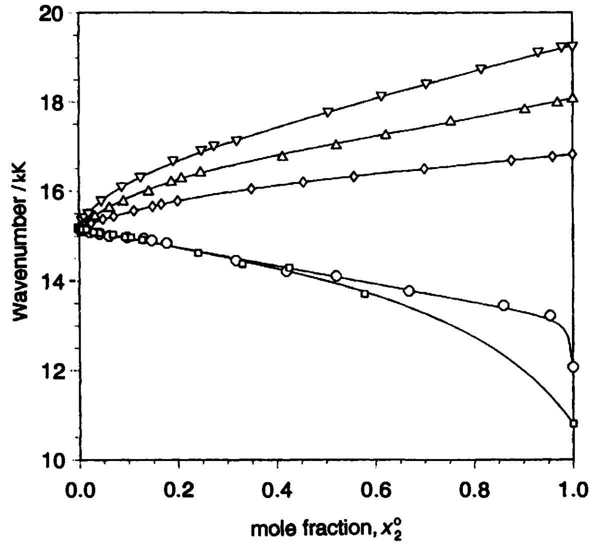

Fig. 1 Wavenumbers of maximum of absorption of 2,6-diphenyl-4-(2,4,6-triphenylpyridin-1-io)-1-phenolate (Reichardt's dye) for binary solvent mixtures of 2-methylpropan-2-ol with: hexane (□), benzene (○), propan-2-ol (◇), ethanol (△) and methanol (▽). Lines computed using eqn. (10) from the parameters of Table 7.

indicators 4-nitroanisol and *N*,*N*-diethyl-4-nitroaniline is about 1.5 and 2.5 kK only (Figs. 2 and 4). And, in going from the alcohols to hexane, the β indicator 4-nitroaniline varies about 5 kK (Fig. 3). The variation on β and π^* values for the alcohols is very small and this means that the variation in the wavenumbers of 4-nitroaniline, 4-nitroanisol and *N*,*N*-diethyl-4-nitroaniline for the mixtures of 2-methylpropan-2-ol with other alcohols is very small too (Figs. 2–4). Therefore, the uncertainty of the measurements may have a strong influence on the calculated $f_{2/1}$ and $f_{12/1}$ parameters for these indicators and mixtures. In this instance, the synergetic behaviour of some of these mixtures cannot be assured.

Since the variation on the wavenumbers of many solvent mixtures is small and none of the other mixtures shows an evident minimum, maximum or inflection point such as those observed in previous work,[21–23] the simplified eqn. (15) should fit most mixtures well. The results obtained in the application of this equation are presented in Table 8. The standard deviations obtained are about 0.1 or less, except for Reichardt's $E_T(30)$ indicator in the mixtures with benzene. The Y_{12} value for this system (Tables 7 and 8) do not fulfil eqn. (14), and therefore this system is much better described by the general eqn. (10). The Y_{12} values obtained for $E_T(30)$ indicator and hexane and propan-2-ol mixtures (Table 7) are very close to the Y_{12} value calculated by eqn. (14) (given in Table 8) and the $f_{12/1}$ values are about one unit higher than $f_{2/1}$ [eqn. (13)]. Therefore, these mixtures can be well described by the simplified eqn. (15) with almost no variation in the standard deviations. For the same indicator but for ethanol and methanol mixtures, the $f_{12/1}$ and Y_{12} values of Table 7 and those calculated by eqns. (13) and (14) are very different, and the standard deviations obtained by eqn. (15) (Table 8) are about three times higher than those obtained from the general eqn. (10) (Table 7). Therefore, these two systems are

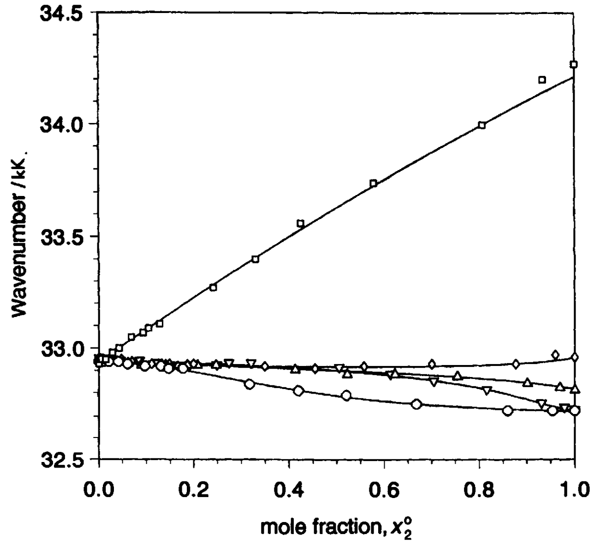

Fig. 2 Wavenumbers of maximum of absorption of 4-nitroanisole for binary solvent mixtures of 2-methylpropan-2-ol. Symbols and lines as in Fig. 1.

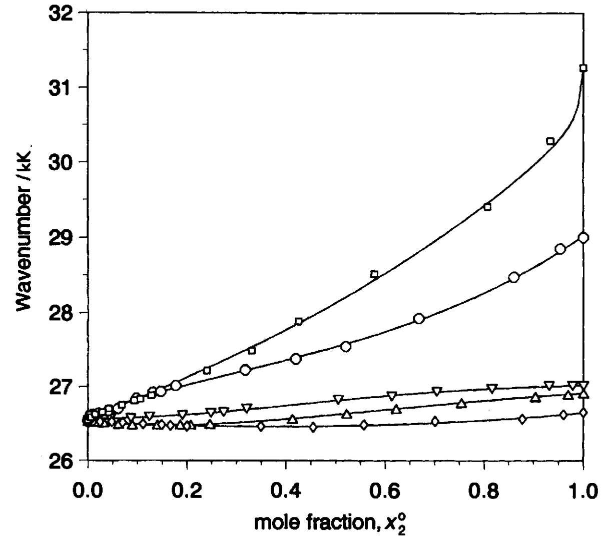

Fig. 3 Wavenumbers of maximum of absorption of 4-nitroaniline for binary solvent mixtures of 2-methylpropan-2-ol. Symbols and lines as in Fig. 1.

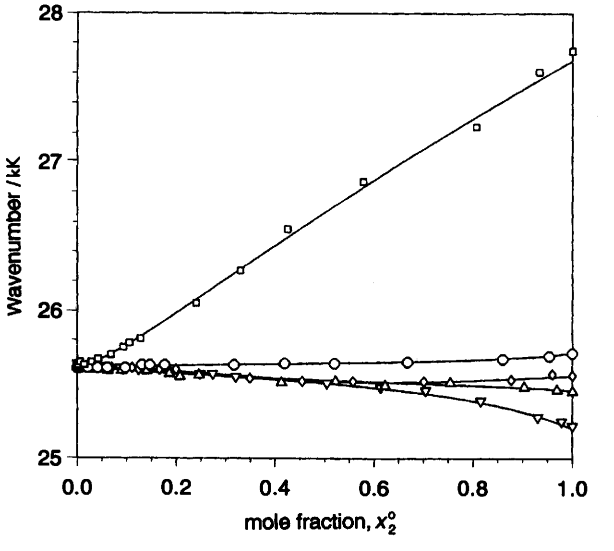

Fig. 4 Wavenumbers of maximum of absorption of *N*,*N*-diethyl-4-nitroaniline for binary solvent mixtures of 2-methylpropan-2-ol. Symbols and lines as in Fig. 1.

Table 8 Parameters from eqns. (15) and (16) for the mixtures of 2-methylpropan-2-ol with hexane, benzene, propan-2-ol, ethanol and methanol for the different indicators used

Cosolvent	Y_1	Y_2	$f_{2/1}$	sd	Y_{12}[a]
2,6-Diphenyl-4-(2,4,6-triphenylpyridin-1-io)-1-phenolate					
Hexane	15.15	10.80	0.37	0.04	13.98
Benzene	15.10	12.51	0.51	0.18	14.23
Propan-2-ol	15.20	16.78	2.2	0.02	16.28
Ethanol	15.26	17.98	2.1	0.07	17.10
Methanol	15.36	19.18	1.9	0.10	17.86
4-Nitroanisole					
Hexane	32.94	34.26	1.1	0.01	33.63
	32.95	34.28	1	0.02	33.61
Benzene	32.95	32.71	1.6	0.01	32.80
Propan-2-ol	32.95	32.93	17	0.01	32.93
Ethanol	32.95	32.82	0.57	0.01	32.90
Methanol	32.95	32.71	0.28	0.01	32.90
4-Nitroaniline					
Hexane	26.61	31.08	0.47	0.11	28.03
Benzene	26.62	28.98	0.66	0.06	27.55
Propan-2-ol	26.49	26.65	0.077	0.03	26.50
Ethanol	26.49	26.94	0.43	0.04	26.63
Methanol	26.54	27.04	1.0	0.02	26.80
	26.54	27.04	1	0.02	26.79
N,*N*-Diethyl-4-nitroaniline					
Hexane	25.59	27.71	0.97	0.04	26.63
	25.59	27.70	1	0.04	26.65
Benzene	25.62	25.71	0.35	0.01	25.64
Propan-2-ol	25.62	25.53	3.3	0.02	25.55
Ethanol	25.62	25.47	1.4	0.01	25.53
	25.61	25.46	1	0.01	25.53
Methanol	25.61	25.20	0.33	0.01	25.51

[a] Y_{12} calculated from eqn. (14).

better described by the general model than by the simplified one.

For 4-nitroanisole the standard variations obtained from eqn. (10) (given in Table 7) and from the simplified eqn. (15) (Table 8) are practically the same. Moreover, the variation of the wavenumbers for the mixtures of 2-methylpropan-2-ol with the other alcohols and also benzene is very small. Therefore, all these systems can be well fitted to the simplified eqn. (15) without a significant increase of the standard deviation. The variation for 2-methylpropan-2-ol–hexane mixtures is higher, but the $f_{12/1}$ value of this system is about one unit higher than $f_{2/1}$ and the Y_{12} value of Table 7 is close to the one predicted by eqn. (14) (see Table 8), therefore this system can be also well fitted to the simplified eqn. (15). Moreover, the $f_{2/1}$ value of Table 8 for this system is close to unity and the system can be considered ideal and described by the most simplified eqn. (16), the results for which are also given in Table 8. The behaviour of 4-nitroanisol for mixtures of 2-methylpropan-2-ol and propan-2-ol can also be considered ideal since the wavenumber remains virtually unchanged for the full range of solvent compositions (Tables 4 and 8).

For 4-nitroaniline, the variation of the wavenumbers of the mixtures with alcohols is small and they can be fitted to the simplified eqn. (15). The $f_{2/1}$ value for methanol mixtures is 1.0 and these mixtures fit well the linear eqn. (16). The variation is higher for the 2-methylpropan-2-ol-benzene mixtures, but the Y_{12} value is close to the one calculated using eqn. (15) and even the $f_{12/1}$ value is much higher than the $f_{2/1}$ value, the system can be fitted well to eqn. (15) too. However, the Y_{12} value for hexane mixtures (30.42) is quite far away from that calculated from eqn. (14) (28.03), and this system must be fitted to the general eqn. (10).

As for the other π^* indicator 4-nitroanisole the variation in wavenumber of *N*,*N*-diethyl-4-nitroaniline is very small for the mixtures of 2-methylpropan-2-ol with the other alcohols and benzene, which can be described by the simplified eqn. (15). The

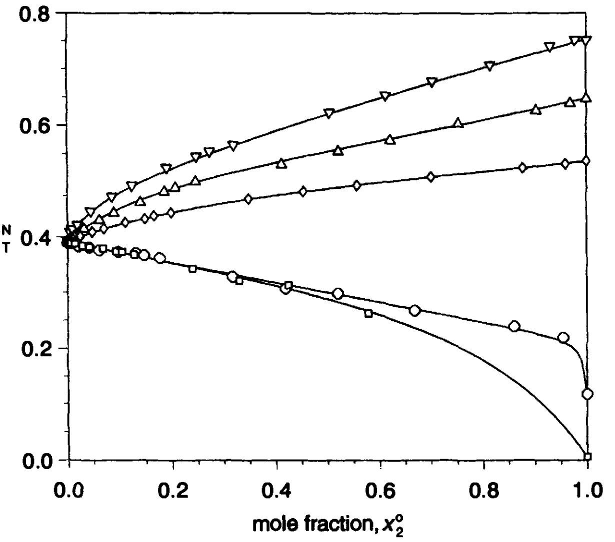

Fig. 5 E_T^N values of binary mixtures of 2-methylpropan-2-ol. Symbols as in Fig. 1.

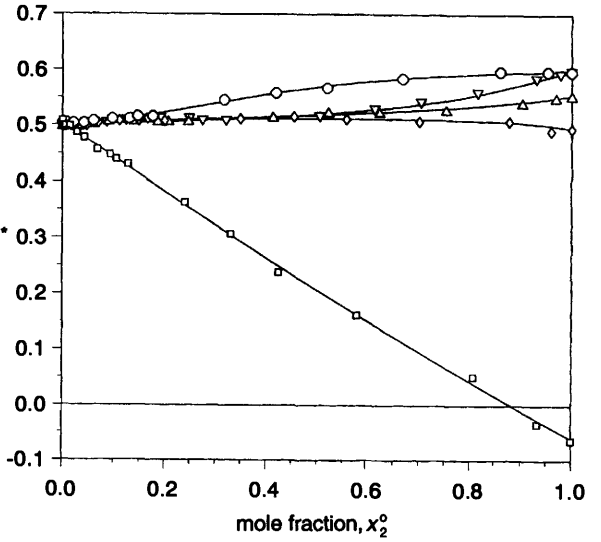

Fig. 6 π^* values of binary mixtures of 2-methylpropan-2-ol. Symbols as in Fig. 1.

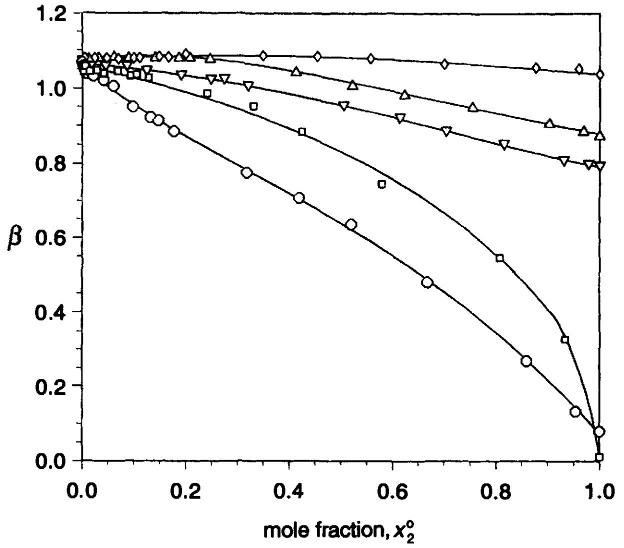

Fig. 7 β values of binary mixtures of 2-methylpropan-2-ol. Symbols as in Fig. 1.

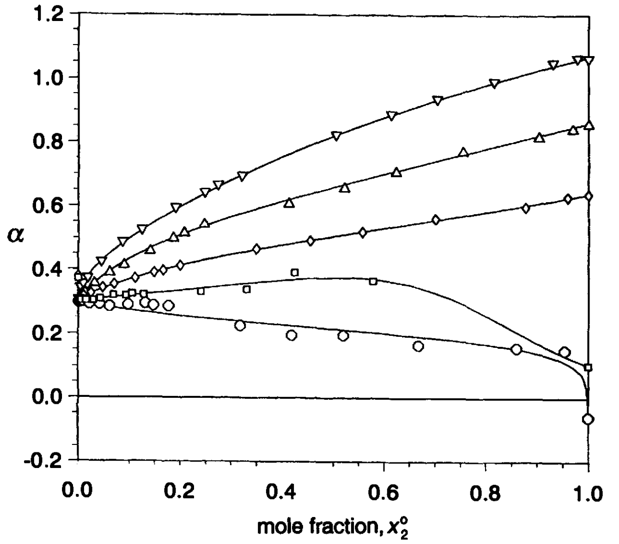

Fig. 8 α values of binary mixtures of 2-methylpropan-2-ol. Symbols as in Fig. 1.

variation for hexane mixtures is higher and even though Y_{12} is somewhat different from the value calculated by eqn. (14), the wavenumber of this system fits eqn. (15) well. The $f_{2/1}$ values of hexane and ethanol in Table 8 are close to unity and the two systems fulfil eqn. (16).

The proposed equations can be also used to estimate the solvatochromic parameters of the studied mixtures (Figs. 5–8). According to eqns. (3)–(5), E_T^N and π^* are linearly related to the wavenumber of maximum absorption of Reichardt's $E_T(30)$ and 4-nitroanisole indicators. Therefore, they must follow an equation similar to eqn. (10) with $Y = E_T^N$ or $Y = \pi^*$. It can be observed that the shape of the plot of E_T^N against x_2^0 (Fig. 5) is identical to the plot of Fig. 1. The shape of the plot of π^* against x_2^0 (Fig. 6) is reversed compared to that of Fig. 2 because of the negative coefficient for $\tilde{\nu}_B$ in eqn. (3). The shape of the plot for β and α variation is more complex. The β parameter is calculated from a linear combination of the wavenumbers of 4-nitroaniline and 4-nitroanisol [eqn. (4)], and therefore its plots in Fig. 7 are a linear combination of two different eqns. (10). The α parameter is a linear combination of Reichardt's $E_T(30)$, 4-nitroanisol and 4-nitroaniline wavenumbers, although the contribution of 4-nitroaniline is very small [eqn. (5)]. Therefore, the exact shape of the plots in Fig. 8 must be described by a linear combination of three different eqns (10).

The results of Tables 7 and 8 provide information about the solvatochromic properties of the two pure solvents mixed **S1** and **S2** and also of the solvent **S12** formed by interaction of solvents **S1** and **S2**. The properties of the **S12** solvents have been calculated using eqns. (1)–(5). The polarizability (δ) of the 2-methylpropan-2-ol–benzene solvent ($\delta = 0.5$) has been assumed to be the average of the polarizabilities of 2-methylpropan-2-ol ($\delta = 0$) and benzene ($\delta = 1$). The parameters obtained are presented in Table 1 and compared with the values calculated from the simple average of the parameters of the two pure solvents **S1** and **S2**.

The properties of the mixed **S12** solvents formed by interaction of 2-methylpropan-2-ol with other alcohols are very close to the average properties of the two alcohols, especially for propan-2-ol and ethanol which are the alcohols closest to 2-methylpropan-2-ol. The properties of benzene–2-methylpropan-2-ol are also very close to the average of the properties of the two solvents, except for the hydrogen bond acidity α, which seems to be equal to that of pure benzene (*i.e. ca.* zero). The properties that differ most from the average are observed for the hexane–2-methylpropan-2-ol solvent. The polarity of this solvent is equal to the average, but the E_T^N and hydrogen bond acidity are much higher and the hydrogen bond basicity much lower than expected from the average. The hydrogen bond basicity is equal to zero, as it is for pure hexane, but the hydrogen bond acidity is even higher than that of pure

2-methylpropan-2-ol. This leads to a synergetic behaviour for this parameter and mixtures, which can be observed in Fig. 8. The α values for 2-methylpropan-2-ol–hexane mixtures show a maximum at mole fractions close to 0.5. We do not at present have a complete justification for this behaviour, although it must be related to the preferential solvation of Reichardt's and 4-nitroanisole indicators, from which wavenumber α is mainly calculated. 4-Nitroanisole presents an ideal behaviour in 2-methylpropan-2-ol–hexane mixtures (Table 8) and this gives a π^*_{12} value equal to the average of π^*_1 and π^*_2. But, since Reichardt's indicator shows a strong preferential solvation which leads to an $E^{\mathrm{N}}_{\mathrm{T}12}$ value much higher than the average (about 50% higher) the calculated α_{12} value must be also much higher than expected from the average [eqn. (5)].

Conclusions

The results obtained demonstrate that the general two-step preferential solvation model described by eqn. (10) and previously applied to the Reichardt's $E_{\mathrm{T}}(30)$ indicator[21–23] can be successfully applied to other solvatochromic indicators. When the variation in the wavenumber of maximum absorption of the particular indicator is small or the Y_{12} value is close to the one calculated from eqn. (14), the one-step preferential solvation model described by the simplified eqn. (15) can be also applied. If the one-step model can be applied and the value of the preferential solvation parameter $f_{2/1}$ is close to 1, the behaviour of the indicator can be considered ideal in the particular solvent system and its wavenumber calculated from eqn. (16). By means of the proposed equations and the computed parameters of Tables 7 or 8, the solvatochromic parameters at any solvent composition of the binary solvent–indicator systems can be easily calculated.

Acknowledgements

The financial support of the DGICYT (project PB94-0833) of the Spanish Government is gratefully acknowledged. This work has been partially supported by the CIRIT (1995SGR-00458) of the Catalan Government.

References

1 E. Bosch and M. Rosés, *Anal. Chem.*, 1988, **62**, 2008.
2 M. Rosés, F. Rived and E. Bosch, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 1723.
3 E. Bosch, F. Rived and M. Rosés, *J. Phys. Org. Chem.*, 1994, **7**, 696.
4 C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd edn., VCH, Weinheim, 1988.
5 M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377.
6 M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 2886.
7 M. J. Kamlet, J-L. M. Abboud and R. W. Taft, *J. Am. Chem. Soc.*, 1977, **99**, 6027.
8 M. J. Kamlet, J-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.
9 F. Rived, M. Rosés and E. Bosch, *J. Chem. Eng. Data*, 1995, **40**, 1111.
10 C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319.
11 Y. Marcus, *J. Solution Chem.*, 1991, **20**, 929.
12 Y. Marcus and Y. Migron, *J. Phys. Chem.*, 1991, **95**, 400.
13 J. G. Dawber, J. Ward and R. A. Williams, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 713.
14 J. G. Dawber, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 287.
15 A. K. Covington and K. E. Newman, *Pure Appl. Chem.*, 1979, **51**, 2041.
16 P. Chatterjee and S. Bagchi, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1785.
17 P. Chatterjee and S. Bagchi, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 587.
18 E. Bosch and M. Rosés, *J. Chem. Soc. Faraday Trans.*, 1992, **88**, 3541.
19 I. A. Koppel and J. B. Koppel, *Org. React.* (*Tartu*), 1983, **20**, 523.
20 R. D. Skwierczynski and K. A. Connors, *J. Chem. Soc., Perkin Trans. 2*, 1994, 467.
21 M. Rosés, C. Ràfols, J. Ortega and E. Bosch, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1607.
22 E. Bosch, M. Rosés, K. Herodes, I. Koppel, I. Leito, I. Koppel and V. Taal, *J. Phys. Org. Chem.*, 1996, **9**, 403.
23 J. Ortega, C. Ràfols, E. Bosch and M. Rosés, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1497.
24 J. L. Beltrán, G. Centeno, A. Izquierdo and M. D. Prat, *Talanta*, 1992, **39**, 981.

Paper 6/01920J
Received 19*th March* 1996
Accepted 4*th June* 1996