Solute–solvent and solvent–solvent interactions in binary solvent mixtures. Part 5. Preferential solvation of solvatochromic indicators in mixtures of propan-2-ol with hexane, benzene, ethanol and methanol

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The solvatochromic shifts of several indicators {2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate [Reichardt's $E_T(30)$ betaine dye], 4-nitroanisole, 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline} have been measured in binary mixtures of propan-2-ol with hexane, benzene, ethanol and methanol at 25 °C over the whole range of solvent composition. From the UV–VIS spectroscopic data the preferential solvation of the indicators has been studied. The solvatochromic parameters $E_T(30)$, π^*, α and β of the binary solvent mixtures studied have been calculated from the solvatochromic shifts.

The use of solvatochromic indicators is a suitable and easy method for studying solute–solvent interactions, since the transition energy of the indicator depends on the solvation's sphere composition and the solvent properties.[1] In addition, it gives information about some specific solvent properties such as polarity and hydrogen bonding capabilities.[1–5]

In previous work[6] the preferential solvation of some solvatochromic indicators in binary mixtures of 2-methylpropan-2-ol with hexane, benzene, propan-2-ol, ethanol and methanol was studied. In this paper, the preferential solvation of the same indicators in binary mixtures of propan-2-ol with hexane, benzene, ethanol and methanol is studied and the results compared with those obtained in binary 2-methylpropan-2-ol mixtures.

The solvatochromic indicators studied are 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate [Reichardt's $E_T(30)$ betaine dye], 4-nitroanisole, 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline. The $E_T(30)$ betaine dye is the solvatochromic indicator most widely used.[1,7] It was proposed by Reichardt for measuring empirically the polarity of solvents. This indicator is sensitive to the dipolarity/polarizability (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 solvent properties.[2–5] 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 solvent dipolarity and polarizability (π^*).

Preferential solvation models

In previous studies[6,8–10] we compared several models that relate the transition energy of a solvatochromic indicator with the composition of a binary solvent mixture.

The most simple model is based on the solvent exchange equilibrium (Scheme 1) where I(S1) and I(S2) indicate the solvatochromic indicator (I) solvated by solvents 1 and 2, respectively. S1 and S2 are the two single solvents that comprise the binary mixture.

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

Scheme 1

The constant of this equilibrium is defined by the preferential solvation parameter $f_{2/1}$ [eqn. (1)] where x_1^s, x_2^s are the mole

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

fractions of solvents S1 and S2 in the microsphere of solvation of the indicator and x_1^0, x_2^0 are the mole fractions of the two solvents in the bulk mixed solvent. The parameter $f_{2/1}$ measures the tendency of the indicator to be solvated with the solvent S2 in reference to solvent S1.

The Y values of the mixture, where Y is an appropriate solvatochromic property, are calculated from the solvent composition (x_2^0), the preferential solvation parameter, $f_{2/1}$ and the Y values of the pure solvents S1 and S2 (Y_1 and Y_2),[6,8–10] eqn. (2) is obtained where a is defined in eqn. (3).

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

$$a = f_{2/1}(Y_2 - Y_1) \qquad (3)$$

A more general model based in two solvent exchange processes such as Scheme 2 was proposed later.[9–11]

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

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

Scheme 2

In this model, S1 and S2 indicate the two pure solvents yielding the binary solvent mixture, and S12 represents a solvent formed by the intermolecular interaction of solvents 1 and 2. This new solvent can have properties which are quite different from those of solvents 1 and 2.[9] m is the number of solvent molecules solvating the solvatochromic indicator I. It was demonstrated[9,10] that for many binary solvent systems, the m value that gives the best results is close to 2. In this instance, our general model becomes the two-steps model proposed by Skwierczynski and Connors.[12]

The constants of the two processes are defined by the preferential solvation parameters $f_{2/1}$ [eqn. (1)] and $f_{12/1}$,[9,10] given by eqn. (4), where x_{12} stands for the mole fraction of the solvent

S_{12} and $f_{12/1}$ measures the tendency of the indicator to be solvated by solvent S12 in reference to solvent S1.

$$f_{12/1} = \frac{x_{12}^{s}/x_1^{s}}{x_2^{0}/x_1^{0}} \tag{4}$$

The Y values of the binary mixture can be calculated by eqn. (5). Eqn. (6) defines c.

$$Y = Y_1 + \frac{a(x_2^0)^2 + c(1 - x_2^0)x_2^0}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_0^2} \tag{5}$$

$$c = f_{12/1}(Y_{12} - Y_1) \tag{6}$$

Note that if the preferential solvation and solvatochromic parameters of the mixed solvent S12 fulfil eqns. (7) and (8),[9] eqn. (5) becomes eqn. (2).

$$f_{12/1} = 1 + f_{2/1} \tag{7}$$

$$Y_{12} = \frac{Y_1 + f_{2/1}Y_2}{1 + f_{2/1}} \tag{8}$$

A further simplification for some binary solvent systems is that if eqns. (7) and (8) are fulfilled and $f_{2/1} = 1$, the system shows an ideal behaviour,[6,10] eqn. (9).

$$Y = x_1^0 Y_1 + x_2^0 Y_2 \tag{9}$$

Experimental

Apparatus

A Beckman DU-7 spectrophotometer, with 10 mm cells, connected to a microcomputer *via* its serial port was used for acquisition and numerical treatment of the absorbance data.

Solvents

The solvents used were propan-2-ol (Carlo-Erba RPE-ACS > 99.5%), ethanol (Merck GR > 99.8%), methanol (Merck GR > 99.5%), benzene (Merck GR > 99.7%), hexane (Merck GR > 99.0%) and triply distilled water.

Solvatochromic indicators

The dyes studied were the same used in a previous work.[6]

Procedure

For the UV–VIS spectrophotometric measurements, indicator dye solutions of *ca.* 10^{-4} M (for Reichardt's betaine and 4-nitroanisole) or 5×10^{-5} M (for 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline) in propan-2-ol-cosolvent mixtures were prepared. The solvent mixtures studied cover all the solvent composition range (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 vol%).

The UV–VIS spectrum of the indicator dye was recorded at 0.1 nm intervals in the following ranges: λ 430–730 nm for Dimroth–Reichardt's betaine dye; 260–350 nm for 4-nitroanisole; 340–410 nm for 4-nitroaniline and 370–460 nm for *N*,*N*-diethyl-4-nitroaniline. All the measurements were taken at 25 ± 0.1 °C with a spectrophotometric cell outwardly thermostatted with a water flow.

The acquisition of the spectrophotometric data was made by means of the Dumod program.[13]

Computation

The spectra of the solvatochromic dyes in each solvent mixture was processed by a numerical smooth of the absorbance data,[6] and the wavelength of the maximum of the UV–VIS spectra was obtained.

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

$E_T(30)$ was calculated from the wavenumber of betaine through eqn. (10) and from $E_T(30)$, the normalized parameter E_T^N in reference to SiMe$_4$ ($E_T^N = 0$) and water ($E_T^N = 1$)[1,7] was calculated using eqn. (11).

$$E_T(30)/(\text{kcal mol}^{-1}) = hc\tilde{\nu}_A N_A = 2.859\tilde{\nu}_A/(\text{kK}) \tag{10}$$

$$E_T^N = \frac{E_T(30) - E_T(30)_{TMS}}{E_T(30)_{H_2O} - E_T(30)_{TMS}} = \frac{E_T(30) - 30.7}{32.4} \tag{11}$$

The π^* parameter is calculated from 4-nitroanisole according to eqn. (12).

$$\pi^* = \frac{34.12 - \tilde{\nu}_B}{2.343} \tag{12}$$

Two equations can be used to calculate the β parameter. The first one is based on the method of measuring pairs of indicators proposed by Kamlet and Taft.[2] In this work, the indicators used are 4-nitroaniline ($\tilde{\nu}_C$) and *N*,*N*-diethyl-4-nitroaniline ($\tilde{\nu}_D$) for which eqn. (13) is used to calculate β.

$$\beta = \frac{1.035\tilde{\nu}_D + 2.64 - \tilde{\nu}_C}{2.80} \tag{13}$$

The second one is the equation proposed by Marcus and Migron[14] that correlates the solvatochromic shift of a single β indicator with the solvatochromic parameters β and π^*. For 4-nitroaniline ($\tilde{\nu}_C$) the equation proposed is eqn. (14).

$$\beta = \frac{31.10 - 3.14\pi^* - \tilde{\nu}_C}{2.79} \tag{14}$$

In previous work[6] we observed that β values for the pure solvents calculated with eqn. (13) agree better with the literature values than the β values calculated by eqn. (14). Therefore, the preferred β values (Tables 1–5) seem to be those calculated from eqn. (13).

The α parameter is calculated from the $\tilde{\nu}_4$ value of Reichardt's betaine dye[15] according to eqn. (15) where δ is a polarizability correction term ($\delta = 1$ for aromatic, 0.5 for polychlorinated and 0 for the other organic pure solvents). For solvent mixtures a good estimate of δ can be obtained by averaging the δ values of the pure solvents mixed according to their mole fractions.[16]

$$\alpha = 0.198\tilde{\nu}_A - 2.091 - 0.899(\pi^* - 0.211\delta) - 0.148\beta \tag{15}$$

Results and discussion

The measured wavenumbers, expressed in kK of maximum absorption ($\tilde{\nu}$) for each solvatochromic indicator, and the solvatochromic parameters E_T^N, α, β and π^* for the binary mixtures studied are presented in Tables 1–5. The values given for the propan-2-ol–2-methylpropan-2-ol mixtures are the same presented in the previous work[6] for 30 °C. The maximum of absorption of the Reichardt's $E_T(30)$ indicator in propan-2-ol–hexane mixtures (Table 1) has not been measured for mole fractions of hexane higher than 0.7 because of the very low solubility of the indicator in non-polar solvents.[1] Consequently,

Table 1 Experimental wavenumbers (kK ≡ 1000 cm^{-1}) and solvatochromic parameters for binary solvent mixtures of propan-2-ol–hexane at 298.2 K[a]

		Indicators							
v_2	x_2	A	B	C	D	E_T^N	α	β	π*
0.000	0.0000	16.91	32.97	26.57	25.56	0.544	0.67	0.90	0.49
0.100	0.0615	16.81	33.00	26.67	25.60	0.536	0.66	0.88	0.48
0.200	0.1284	16.70	33.06	26.73	25.68	0.526	0.66	0.89	0.45
0.300	0.2016	16.56	33.11	26.78	25.81	0.514	0.65	0.92	0.43
0.400	0.2821	16.36	33.21	26.94	25.94	0.496	0.65	0.91	0.39
0.500	0.3708	16.23	33.30	27.15	26.12	0.485	0.66	0.90	0.35
0.600	0.4692	16.03	33.42	27.33	26.31	0.467	0.66	0.91	0.30
0.700	0.5790	15.95	33.59	27.62	26.63	0.460	0.71	0.92	0.23
0.800	0.7021	15.71	33.77	28.18	26.93	0.439	0.75	0.83	0.15
0.900	0.8414		33.98	28.94	27.23			0.68	0.06
1.000	1.0000	10.84[b]	34.27	31.27	27.75	0.009	0.10	0.03	−0.06

[a] v_2 = Volume fraction of hexane. x_2 = Mole fraction of hexane. A = 2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate. B = 4-Nitroanisole. C = 4-Nitroaniline. D = *N*,*N*-Diethyl-4-nitroaniline. [b] Data from ref. 1.

Table 2 Experimental wavenumbers (kK) and solvatochromic parameters for binary solvent mixtures of propan-2-ol–benzene at 298.2 K[a]

		Indicators							
v_2	x_2	A	B	C	D	E_T^N	α	β	π*
0.000	0.0000	16.89	32.95	26.57	25.56	0.543	0.65	0.90	0.50
0.100	0.0879	16.72	32.88	26.61	25.53	0.528	0.62	0.88	0.53
0.200	0.1781	16.51	32.79	26.69	25.48	0.509	0.56	0.83	0.57
0.300	0.2709	16.33	32.67	26.87	25.44	0.493	0.51	0.75	0.62
0.400	0.3662	16.16	32.65	26.98	25.42	0.478	0.49	0.70	0.63
0.500	0.4643	15.93	32.63	27.17	25.46	0.458	0.47	0.65	0.64
0.600	0.5653	15.62	32.62	27.33	25.49	0.431	0.42	0.61	0.64
0.700	0.6692	15.38	32.62	27.56	25.52	0.410	0.41	0.54	0.64
0.800	0.7761	15.07	32.63	27.90	25.56	0.382	0.39	0.43	0.64
0.900	0.8864	14.57	32.66	28.39	25.63	0.338	0.35	0.28	0.62
1.000	1.0000	12.22	32.72	29.00	25.71	0.131	−0.04	0.09	0.60

[a] v_2 = Volume fraction of benzene. x_2 = Mole fraction of benzene. A, B, C and D as in Table 1.

Table 3 Experimental wavenumbers (kK) and solvatochromic parameters for binary solvent mixtures of propan-2-ol–2-methylpropan-2-ol at 303.2 K[a]

		Indicators							
v_2	x_2	A	B	C	D	E_T^N	α	β	π*
0.000	0.000	16.81	32.96	26.65	25.56	0.536	0.66	0.87	0.50
0.050	0.040	16.76	32.97	26.62	25.57	0.531	0.65	0.89	0.49
0.150	0.123	16.68	32.93	26.56	25.53	0.524	0.62	0.89	0.51
0.350	0.299	16.50	32.93	26.53	25.52	0.508	0.59	0.90	0.51
0.500	0.442	16.32	32.92	26.48	25.52	0.493	0.54	0.92	0.51
0.600	0.545	16.20	32.91	26.45	25.52	0.482	0.51	0.93	
0.700	0.651	16.05	32.92	26.46	25.54	0.469	0.49	0.93	0.51
0.833	0.800	15.77	32.93	26.46	25.60	0.444	0.43	0.96	0.51
0.862	0.833	15.70	32.92	26.47	25.60	0.438	0.42	0.95	0.51
0.877	0.851	15.65	32.93	26.48	25.61	0.433	0.41	0.95	0.51
0.909	0.889	15.56	32.93	26.49	25.61	0.426	0.39	0.95	0.51
0.943	0.930	15.44	32.94	26.51	25.61	0.415	0.37	0.94	0.50
0.962	0.952	15.37	32.95	26.52	25.61	0.409	0.36	0.94	0.50
0.980	0.975	15.28	32.95	26.52	25.61	0.401	0.35	0.94	0.50
0.992	0.990	15.23	32.95	26.52	25.61	0.396	0.34	0.94	0.50
0.996	0.995	15.21	32.95	26.52	25.62	0.395	0.33	0.94	0.50
0.998	0.997	15.20	32.95	26.52	25.62	0.394	0.33	0.94	0.50
1.000	1.000	15.20	32.94	26.52	25.62	0.394	0.33	0.94	0.50

[a] v_2 = Volume fraction of 2-methylpropan-2-ol. x_2 = Mole fraction of 2-methylpropan-2-ol. A, B, C and D as in Table 1.

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.[1]

The solvatochromic properties of the pure solvents at 25 °C are shown in Table 6. This table includes two experimental values of β, one (β_{13}) calculated using eqn. (13) and the other (β_{14}) calculated by eqn. (14). As in the previous study,[6] it can be observed that these values are somewhat different, especially for the alcohols. The β values calculated by the method proposed by Marcus [eqn. (14)] are, in general, higher than the ones calculated by the method proposed by Kamlet and Taft [eqn. (13)] and also higher than the literature values. Table 6 shows that these two last sets of values agree very well, although in fact, the literature values have been mostly calculated by the pairs of indicators methods. Nevertheless, the two sets of β values are proportional, eqn. (16).

$$\beta_{13} = 1.160\beta_{14} \quad r = 0.986 \quad \text{sd} = 0.041 \quad n = 43 \qquad (16)$$

Table 4 Experimental wavenumbers (kK) and solvatochromic parameters for binary solvent mixtures of propan-2-ol–ethanol at 298.2 K[a]

		Indicators							
v_2	x_2	A	B	C	D	E_T^N	α	β	π*
0.000	0.0000	16.88	32.96	26.57	25.56	0.542	0.66	0.90	0.50
0.100	0.1279	17.06	32.96	26.62	25.54	0.558	0.70	0.88	0.50
0.200	0.2481	17.20	32.94	26.67	25.55	0.570	0.72	0.86	0.50
0.300	0.3612	17.39	32.89	26.75	25.54	0.587	0.74	0.83	0.52
0.400	0.4680	17.53	32.91	26.77	25.53	0.599	0.78	0.82	0.52
0.500	0.5689	17.61	32.87	26.81	25.52	0.606	0.78	0.80	0.53
0.600	0.6643	17.76	32.87	26.85	25.51	0.620	0.81	0.79	0.53
0.700	0.7548	17.84	32.85	26.85	25.50	0.627	0.82	0.78	0.54
0.800	0.8407	18.00	32.84	26.87	25.48	0.641	0.85	0.76	0.55
0.900	0.9223	18.14	32.83	26.90	25.47	0.653	0.88	0.75	0.55
1.000	1.0000	18.13	32.82	26.90	25.46	0.652	0.87	0.75	0.56

[a] v_2 = Volume fraction of ethanol. x_2 = Mole fraction of ethanol. A, B, C and D as in Table 1.

Table 5 Experimental wavenumbers (kK) and solvatochromic parameters for binary solvent mixtures of propan-2-ol–methanol at 298.2 K[a]

		Indicators							
v_2	x_2	A	B	C	D	E_T^N	α	β	π*
0.000	0.0000	16.89	32.96	26.53	25.56	0.543	0.66	0.92	0.50
0.100	0.1741	17.37	32.91	26.62	25.53	0.585	0.74	0.87	0.52
0.200	0.3217	17.77	32.88	26.74	25.50	0.621	0.82	0.82	0.53
0.300	0.4485	18.08	32.86	26.85	25.48	0.648	0.88	0.77	0.54
0.400	0.5585	18.29	32.84	26.90	25.44	0.667	0.91	0.74	0.55
0.500	0.6549	18.51	32.80	26.94	25.41	0.686	0.94	0.71	0.56
0.600	0.7400	18.59	32.77	26.97	25.36	0.693	0.95	0.69	0.58
0.700	0.8157	18.90	32.75	26.96	25.32	0.721	1.01	0.67	0.58
0.800	0.8836	19.18	32.73	26.98	25.28	0.745	1.06	0.66	0.59
0.900	0.9447	19.17	32.71	27.01	25.25	0.744	1.05	0.63	0.60
1.000	1.0000	19.39	32.70	27.01	25.21	0.764	1.09	0.61	0.61

[a] v_2 = Volume fraction of methanol. x_2 = Mole fraction of methanol. A, B, C and D as in Table 1.

Table 6 Experimental and literature[1,14] solvatochromic parameters for the pure solvents used in the preparation of binary mixtures, and calculated solvatochromic parameters for the mixed S12 solvents formed

Solvents		E_T^N	π*	β_{13}	β_{14}	α	δ
Hexane	Lit.	0.009	−0.08	0.00		0.00	0
	Exp.	—	−0.06	0.03	0.01	—	
Benzene	Lit.	0.111	0.59	0.10		0.00	1
	Exp.	0.931	0.60	0.09	0.08	−0.03	
2-Methylpropan-2-ol	Lit.	0.389	0.41	1.01		0.42	0
	Exp.[6]	0.392	0.50	0.94	1.07	0.30	
Propan-2-ol	Lit.	0.546	0.48	0.95		0.76	0
	Exp.	0.543	0.50	0.91	1.07	0.63	
Ethanol	Lit.	0.654	0.54	0.77		0.83	0
	Exp.	0.652	0.56	0.75	0.88	0.85	
Methanol	Lit.	0.762	0.60	0.62		0.93	0
	Exp.	0.764	0.61	0.61	0.78	1.07	
Propan-2-ol–hexane	Avg.[a]	0.28	0.21	0.47		0.38	0
	Calc.[b]	0.41	0.28	0.92	1.01	0.54	
Propan-2-ol–benzene	Avg.	0.34	0.55	0.50		0.30	0.5
	Calc.	0.35	0.79	0.54	0.51	0.13	
Propan-2-ol–2-methylpropan-2-ol	Avg.	0.46	0.50	0.91		0.47	0
	Calc.	0.49	0.50	0.92	1.08	0.52	
Propan-2-ol–ethanol	Avg.	0.60	0.53	0.83		0.74	0
	Calc.	0.60	0.52	0.82	0.96	0.77	
Propan-2-ol–methanol	Avg.	0.65	0.56	0.77		0.85	0
	Calc.	0.65	0.55	0.76	0.90	0.88	

[a] Avg. = Average of the experimental values of pure propan-2-ol and cosolvent. [b] Calc. = Calculated from the Y_{12} values of Table 7.

This relationship is almost the same as that obtained for mixtures with 2-methylpropan-2-ol,[6] eqn. (17).

$$\beta_{13} = 1.156\beta_{14} \quad r = 0.994 \quad \mathrm{sd} = 0.024 \quad n = 90 \qquad (17)$$

The proportionality between the two sets of β values means that either eqn. (13) or (14) gives almost the same β value for poor hydrogen bond donor solvents (*e.g.* hexane and benzene), but that the two β values separate when the hydrogen bond donor ability of the solute increases (alcohols, see Table 6).

Eqns. (2), (5) and (9) have been tested for the four indicators studied in the binary mixtures of propan-2-ol. All the indicators can be fitted to eqn. (2) with the exception of Reichardt's dye in mixtures of propan-2-ol with hexane and benzene, as well as 4-nitroanisole and *N*,*N*-4-nitroaniline in mixtures of

Table 7 Parameters from eqns. (2), (5) or (9) for the mixtures of propan-2-ol (S1) with hexane, benzene, 2-methylpropan-2-ol, ethanol and methanol for the different indicators used

Cosolvent	Eqn.	Y_1	Y_2	Y_{12}	$f_{2/1}$	$f_{12/1}$	N[a]	sd[b]
	2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate							
Hexane	5	16.93	10.84	15.33	5.le-5	1.30	10	0.04
Benzene	5	16.89	12.22	14.71	0.022	0.88	11	0.03
2-Methylpropan-2-ol	2	16.78	15.21	16.28	0.46	1.46	18	0.02
Ethanol	9	16.90	18.19	17.54	1.0	2.0	11	0.03
Methanol	9	16.94	19.36	18.15	1.0	2.0	11	0.07
	4-Nitroanisole							
Hexane	2	32.94	34.28	33.47	0.64	1.64	11	0.02
Benzene	5	32.96	32.71	32.27	2.13	1.61	11	0.02
2-Methylpropan-2-ol	2	32.96	32.94	32.94	22.8	23.8	18	0.01
Ethanol	9	32.97	32.82	32.89	1.0	2.0	11	0.01
Methanol	2	32.96	32.69	32.84	0.77	1.77	11	0.01
	4-Nitroaniline							
Hexane	2	26.60	31.26	27.39	0.20	1.20	11	0.05
Benzene	2	26.55	29.01	27.20	0.36	1.36	11	0.03
2-Methylpropan-2-ol	2	26.66	26.49	26.51	13.11	14.11	18	0.03
Ethanol	2	26.45	26.91	26.78	1.77	2.77	11	0.01
Methanol	2	26.41	27.03	26.85	1.98	2.98	11	0.03
	N,*N*-diethyl-4-nitroaniline							
Hexane	2	25.51	27.76	26.40	0.67	1.67	11	0.04
Benzene	5	25.57	25.70	25.18	1.46	1.71	11	0.01
2-Methylpropan-2-ol	2	25.53	25.62	25.55	0.27	1.27	18	0.02
Ethanol	2	25.56	25.46	25.53	0.46	1.46	11	0.01
Methanol	2	25.56	25.20	25.45	0.42	1.42	11	0.01

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

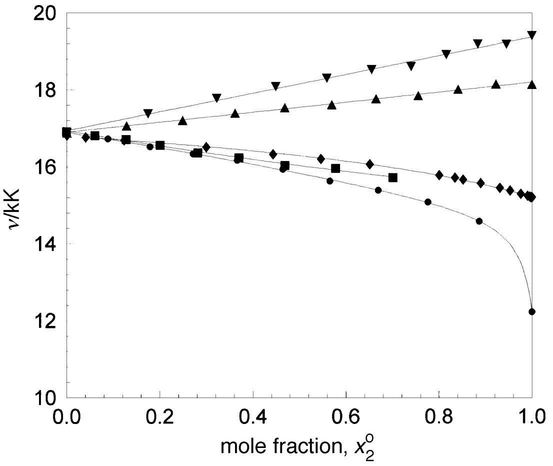

Fig. 1 Wavenumbers of the absorption maximum of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate (Reichardt's dye) for binary solvent mixtures of propan-2-ol with: *n*-hexane (■), benzene (●), 2-methylpropan-2-ol (◆), ethanol (▲) and methanol (▼). Lines computed by using eqn. (10) from the parameters of Table 7.

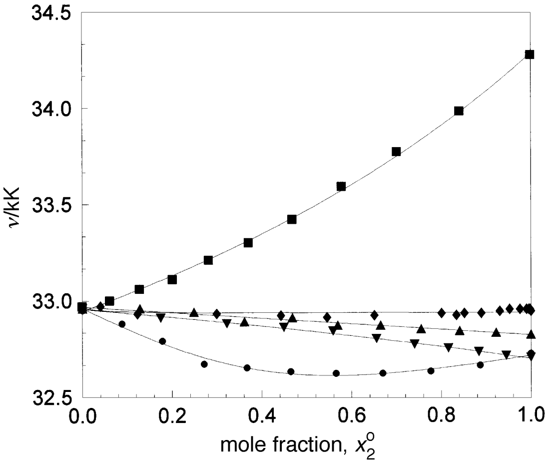

Fig. 2 Wavenumbers of the absorption maximum of 4-nitroanisole for binary solvent mixtures of 2-methylpropan-2-ol. Symbols and lines as in Fig. 1.

propan-2-ol with benzene and 2-methylpropan-2-ol that must be fitted to eqn. (5). The results obtained are presented in Table 7 and Figs. 1–4.

For Reichardt's $E_T(30)$ indicator, the $f_{2/1}$ value for the bindary mixtures of propan-2-ol with ethanol and methanol is *ca.* 1. Therefore, these solvent systems can be considered as ideal and described by the most simplified eqn. (9). Propan-2-ol–ethanol shows also ideal behaviour for 4-nitroanisole.

The mixtures of propan-2-ol with benzene present synergistic effects for the π^* indicators (4-nitroanisole and *N*,*N*-diethyl-4-nitroaniline). The wavenumbers of the propan-2-ol–benzene solvents (S_{12}) are lower than the wavenumbers of the pure solvents propan-2-ol and benzene, with a minimum at *ca.* 0.4–0.5 mole fraction of benzene. Therefore, it can be deduced that the solvent S12 is more polar than the pure components propan-2-ol or benzene. We think that this high polarity is due to the polarization of the π electrons of benzene by propan-2-ol. The effect should be at a maximum when both solvents are in similar concentrations ($x_1 \approx x_2 \approx 0.5$), which agrees with the observed minima. This behaviour was not observed in the mixtures of benzene with 2-methylpropan-2-ol.[6] For the α and β indicators (Reichardt's betaine and 4-nitroaniline), the synergistic effect is overwhelmed by the formation of hydrogen bonds between the indicator and the solvent S12, and the minimum is not observed.

The variation of the solvatochromic parameters in the mixtures of propan-2-ol with hexane, benzene, 2-methylpropan-2-ol, ethanol and methanol has also been studied. E_T^N and π^* are linearly related to the wavenumbers of maximum absorption of Reichardt's $E_T(30)$ dye and 4-nitroanisole indicators, respect-

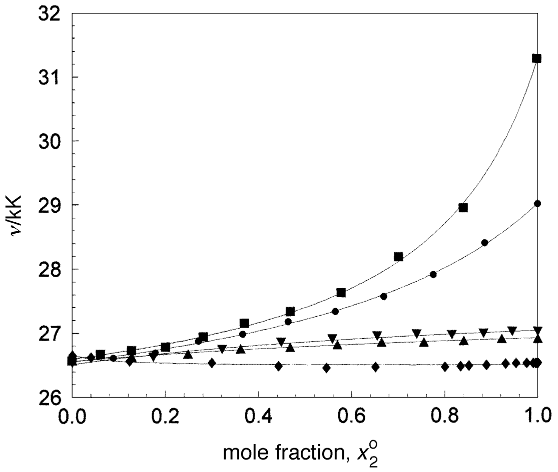

Fig. 3 Wavenumbers of the absorption maximum of 4-nitroaniline for binary solvent mixtures of 2-methylpropan-2-ol. Symbols and lines as in Fig. 1.

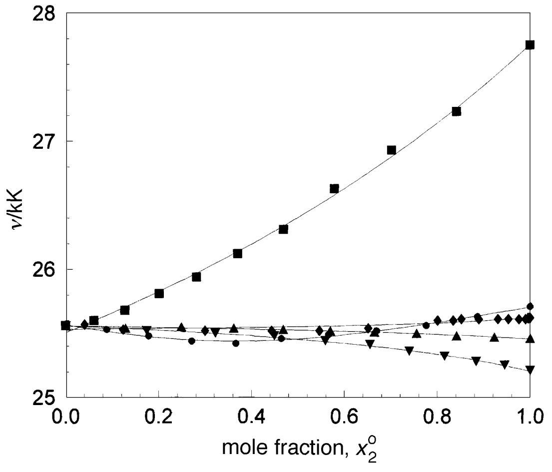

Fig. 4 Wavenumbers of the absorption maximum of *N*,*N*-diethyl-4-nitroaniline for binary solvent mixtures of 2-methylpropan-2-ol. Symbols and lines as in Fig. 1.

ively [eqns. (10)–(12)]. Therefore, their variation must follow an equation similar to the ones used to fit these indicators. β and α parameters can be calculated from a linear combination of the wavenumbers of several indicators: 4-nitroaniline and 4-nitroanisole for β [eqn. (13)] and betaine, 4-nitroanisole and 4-nitroaniline for the α parameter [eqn. (14)]. Therefore their variation is a linear combination of two or three different equations.

The proposed method also allows an estimate of the properties of the solvent S12 formed by interaction of solvents S1 and S2, which have been included in Table 6. The polarizability (δ) of the propan-2-ol–benzene ($\delta = 0.5$) has been assumed to be the average of the polarizabilities of propan-2-ol ($\delta = 0$) and benzene ($\delta = 1$).[6] For comparison, Table 6 includes the values calculated from the simple average of the parameters of the two pure solvents S1 and S2.

For 2-methylpropan-2-ol mixtures,[6] we observed that the properties of the mixed S12 solvents formed by interaction of two similar solvents were very close to the average of the properties of the two solvents. The same is observed in Table 6 for the mixtures of propan-2-ol with the other alcohols.

As for 2-methylpropan-2-ol–hexane,[6] the propan-2-ol–hexane solvent presents a calculated π^* value equal to the average of the π^* values of the two pure solvents, but the E_T^N and α values are much higher than the ones expected from the average. In contrast to 2-methylpropan-2-ol–hexane,[6] the β value of propan-2-ol–hexane is close to that of propan-2-ol and much higher than the average of the β values of propan-2-ol and hexane.

For the propan-2-ol–benzene solvent the E_T^N and β parameters are close to the average of the E_T^N and β parameters of propan-2-ol and benzene, but the α parameter is lower than the average. This was also observed for the 2-methylpropan-2-ol–benzene solvent.[6] However, the calculated π^* value is much higher than the average of the π^* values of propan-2-ol and benzene, and even higher than these values. The reason is the synergistic behaviour of the π^* indicators as already explained.

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