Solute–solvent and solvent–solvent interactions in binary solvent mixtures. Part 6.† A quantitative measurement of the enhancement of the water structure in 2-methylpropan-2-ol–water and propan-2-ol–water mixtures by solvatochromic indicators

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A preferential solvation model that takes into account the enhancement of the structure of water when small amounts of alcohol are added is proposed and tested for solvatochromic indicators in binary mixtures of 2-methylpropan-2-ol and propan-2-ol with water. The model modifies an equation previously developed for solvatochromic indicators in binary solvent mixtures. The new model includes a correction term for the effect of the enhancement of the water structure on the measured solvatochromic property that allows a quantitative estimation of this effect. It is shown that the enhanced water structure is more polar and has a larger hydrogen-bond donor capability, but a smaller hydrogen-bond acceptor ability, than the common water structure.

The anomalous behaviour of thermodynamic and physical properties of alcohol–water mixtures has long been known.[1] Evidence from these data strongly suggests that at low alcohol concentrations, water molecules tend to organize around the hydrophobic groups of the alcohol forming low entropy structures or 'cages' of fairly regular and longer lived hydrogen bonds.[2–4] The enhancement of the structure of water is not only observed in alcohol–water mixtures, but also in other mixtures, such as those of water with dimethyl sulfoxide,[5] acetonitrile[6] or acetone.[7] In all these cases, the enhancement of the water structure changes its properties to a greater degree than expected.[1–18] In particular, alcohol–water mixtures show a minimum in partial molar volume[8–10] and adiabatic compressibility,[3,4,11,12] a maximum in excess heat capacity[8,10] and ultrasonic speed,[9,13] and a remarkable increase in light scattering[14] in the composition range 0–0.2 mol fraction of alcohol. This maximum or minimum tends to move towards lower alcohol content with increase in the length of the alcohol carbon chain.

Although there are many studies on the effect of the enhancement of the water structure on the macroscopic properties of solvent mixtures, as far as we know, this has not been studied from microscopic measurements such as solvatochromic properties.

In previous parts of this series, we set up models and equations that relate the behaviour of solvatochromic indicators with the composition of binary solvent mixtures. The models take into account the solvent–solvent interactions between the two solvents mixed and the solute–solvent interactions between the solvatochromic indicator and the different solvents that compose the mixture (preferential solvation).

The equations were first tested for all the available literature E_T (30) data, covering 70 binary systems.[19,20] They were also successfully applied to the E_T (30) data of some selected synergetic systems (mixtures of acetonitrile, nitromethane and dimethyl sulfoxide with alcohols and water) studied at several temperatures.[21] Later, the same equations were applied to different solvatochromic indicators in binary mixtures of 2-methylpropan-2-ol[22] and propan-2-ol[23] with hexane, benzene and other alcohols. However, the mixtures of 2-methylpropan-2-ol or propan-2-ol with water were not investigated because of the effect of the enhancement of the water structure, which cannot be described with the models already proposed.

In this paper, we shall modify the proposed models to include this enhancement effect and test the modified model for different solvatochromic indicators in mixtures of 2-methylpropan-2-ol and propan-2-ol with water. The indicators tested were 2-nitroanisole, 4-nitroanisole and 1-ethyl-4-nitrobenzene, which are sensitive to the dipolarity and polarizability of the solvent (π^*), 4-nitroaniline and 4-nitrophenol, sensitive to the hydrogen-bond acceptor capability of the solvent (β) in addition to π^*, and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-phenolate [Reichardt's E_T (30) betaine dye] and its water-soluble carboxylic derivative (sodium {4-[4-(4-carboxylatophenyl)-2,6-diphenyl-1-pyridinio]-2,6-diphenylphenolate}), which are mostly sensitive to π^* and to the hydrogen-bond donor capability of the solvent (α).

Preferential solvation models

In Part 1 of this series,[19] we proposed a general preferential solvation model based on two solvent exchange processes, eqn. (*a*) and (*b*), in order to relate the E_T (30) parameter of

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

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

binary solvent mixtures with the solvent compositions. S1 and S2 indicate the two pure solvents mixed (in this study, alcohol and water, respectively), and S12 represents a solvent formed by the interaction of solvents 1 and 2 (alcohol–water). The solvent S12 can have properties quite different from those of solvents 1 and 2, as was demonstrated for the synergetic mixtures.[19,21] m is the average number of solvent molecules solvating the solvatochromic indicator I. It was demonstrated that for many binary systems, the m value that gives the best results is close to 2, and this value will be used in all further derivations.[19–21] In this instance, the general model becomes the two-step model proposed by Skwierczynski and Connors.[24]

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† For Part 5, see ref. 23.

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The constants of the two processes are defined by the preferential solvation parameters $f_{2/1}$ and $f_{12/1}$ according to eqn. (1) and (2), where x_1^S, x_2^S and x_{12}^S are the mole fractions of

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

$$f_{12/1} = \frac{x_{12}^S/x_1^S}{x_2^0/x_1^0} \qquad (2)$$

solvents S1, S2 and S12 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 parameters $f_{2/1}$ and $f_{12/1}$ measure the tendency of the indicator to be solvated by solvents S2 and S12 in reference to solvent S1.

Considering that the addition of all different mole fractions must be equal to unity, eqn. (3), the mole fractions in the sphere

$$x_1^S + x_2^S + x_{12}^S = 1 \qquad (3)$$

of solvation of the indicator can be easily calculated from the preferential solvation parameters and the solvent composition (x_2^0) through eqn. (4)–(6).

$$x_1^S = \frac{(1 - x_2^0)^2}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_2^0} \qquad (4)$$

$$x_2^S = \frac{f_{2/1}(x_2^0)^2}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_2^0} \qquad (5)$$

$$x_{12}^S = \frac{f_{12/1}(1 - x_2^0)x_2^0}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_2^0} \qquad (6)$$

The solvatochromic property (Y) of the mixture is calculated as an average of the properties 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. (7) and by substituting eqn. (4)–(6) into eqn. (7), the general eqn. (8) can be derived.

$$Y = x_1^S Y_1 + x_2^S Y_2 + x_{12}^S Y_{12} \qquad (7)$$

$$Y = \frac{Y_1(1 - x_2^0)^2 + Y_2 f_{2/1}(x_2^0)^2 + Y_{12} f_{12/1}(1 - x_2^0)x_2^0}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)\, x_2^0} \qquad (8)$$

Eqn. (8) gave satisfactory results for all the mixtures and solvatochromic indicators tested.[19–23] In some instances, it can be simplified,[19,20,22] but since these simplifications cannot be applied to the 2-methylpropan-2-ol–water and propan-2-ol–water mixtures studied, they will not be considered here. Conversely, eqn. (8) does not take into account the reinforcement of the structure of water in mixtures containing small amounts of a cosolvent, and it must be modified to consider this effect for the studied mixtures. The enhanced water structure is more ordered than the clusters of alcohol (x_1^S), usual structured water (x_2^S), and alcohol–water (x_{12}^S) present in the microsphere of solvation of the indicator and, therefore, it can modify the solvatochromic properties of the indicator (Y). Since the enhancement of the water structure depends on the presence of alcohol molecules and already structured water clusters, a very simple continuous model is to assume that the modification (ΔY) is proportional to the product of the corresponding mole fractions. The mole fraction of structured water in the microsphere of solvation of the indicator is x_2^S, but the alcohol molecules exist in alcohol (x_1^S) and alcohol–water (x_{12}^S) clusters. The alcohol–water clusters contain equal parts of water and alcohol, and the number of alcohol molecules in one cluster is half the number of alcohol molecules in one alcohol cluster of the same molecular size. Therefore, the model for the modification of the solvatochromic property should be eqn. (9), where k is a proportionality constant.

$$\Delta Y = k x_2^S(x_1^S + x_{12}^S/2) \qquad (9)$$

Substituting eqn. (4)–(6) into eqn. (9), we obtain eqn. (10).

$$\Delta Y = \frac{k f_{2/1}(x_2^0)^2[(1 - x_2^0)^2 + f_{12/1}(1 - x_2^0)x_2^0/2]}{[(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_2^0]^2} \qquad (10)$$

Eventually combination of eqn. (8) and (10) gives the general eqn. (11), that we shall test for the mixtures studied in this paper.

$$Y = \frac{Y_1(1 - x_2^0)^2 + Y_2 f_{2/1}(x_2^0)^2 + Y_{12} f_{12/1}(1 - x_2^0)x_2^0}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_2^0} + \Delta Y \qquad (11)$$

Experimental

Apparatus

A Perkin-Elmer Lambda-19 spectrophotometer, with 10 mm cells, electronically thermostatted at 25 °C, connected to a microcomputer, was used for acquisition of the UV–VIS absorbance data.

Solvents and solvatochromic indicators

2-Methylpropan-2-ol GR, >99.5% Merck, propan-2-ol GR, >99.7% Merck and deionized water treated by the Milli-Q system (Millipore) were used to prepare the solvent mixtures studied. The water contents determined by the Karl–Fischer method for the two pure alcohols were for 2-methylpropan-2-ol 0.073% and propan-2-ol 0.035%.

The dyes studied were: 1-ethyl-4-nitrobenzene and 2-nitroanisole, >99% Aldrich; 4-nitroanisole, Merck (handled with activated charcoal and crystallized from acetone–water); 4-nitroaniline, >98% Merck; 4-nitrophenol, >99% Fluka; 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's betaine dye), >95% Aldrich; and sodium {4-[4-(4-carboxylatophenyl)-2,6-diphenyl-1-pyridinio]-2,6-diphenylphenolate} (Reichardt's water-soluble betaine dye) provided by Professor Reichardt from Philipps University, Marburg, Germany.

Procedure

Indicator dye solutions of *ca.* 5×10^{-5} to 10^{-4} mol dm^{-3} were prepared in 25 binary solvent mixtures prepared by mass for each binary system, at intervals of *ca.* 0.05 mol fraction. Since the reinforcement of the structure of water is mainly observed at mol fractions of water between 0.80 and 1.00, the solvent mixtures were spaced at 0.025 mol fraction intervals in this solvent area. When the data for Reichardt's water-soluble betaine dye were fitted to the proposed eqn. (11), an apparent maximum appeared between the two solvent mixtures most concentrated in water ($x_2^0 = 0.975$ and $x_2^0 = 1.000$). In order to investigate this possible maximum, another solvent mixture at $x_2^0 = 0.99$ was prepared and measured for this indicator dye only.

The spectrum of the indicator dyes in the solvent mixtures was recorded in the ranges: $\lambda = 250$–310 nm (1-ethyl-4-nitrobenzene), 260–350 nm (4-nitroanisole), 220–360 nm (2-nitroanisole), 350–410 nm (4-nitroaniline), 280–350 nm (4-nitrophenol) and 420–700 nm (Reichardt's dyes). All measurements were taken in triplicate and averaged.

Computation

The spectra of the solvatochromic dyes were processed by a numerical smoothing of the absorbance data using the 'moving window averaging' method with a window size of 21 points, and the wavelength of the maximum of the spectra was obtained.[22]

Results and discussion

Solvatochromic indicators

The wavenumbers of maximum absorption of the indicator dyes in the binary mixtures studied are presented in Tables 1 and 2. The wavenumbers are given in kK (1 kK = 1000 cm^{-1}). These data have been fitted to the proposed eqn. (11) and the parameters obtained are given in Table 3.

All the indicators studied are sensitive to solvent dipolarity/polarizability. 2-Nitrophenol and 4-nitroaniline can give hydrogen bonds and thus they are sensitive to the hydrogen-bond acceptor capability of the solvent. Reichardt's betaine dye and Reichardt's water-soluble betaine are almost equally sensitive to solvent dipolarity/polarizability and hydrogen-bond donor ability.[25–27]

The behaviour of the indicators which are not sensitive to solvent hydrogen-bond donor ability is very similar (Fig. 1–3). The symbols in Fig. 1–4 represent the experimental points of Tables 1 and 2. The continuous line is the fitting line obtained by application of eqn. (11). The dashed line is the line that would be obtained omitting the ΔY term in eqn. (11), that is to say, it represents the wavenumber variation that would be obtained if the reinforcement of the structure of water were not present. If this effect were not present, S-shaped curved lines for wavenumber variation would be observed in general. These lines are similar to those observed for E_T (30) variation in mixtures of water with dipolar hydrogen-bond acceptor solvents.[19,21] They are caused by the Y_{12} values intermediate between those of Y_1 and Y_2 and the preferential solvation of the indicator by the water–alcohol S12 solvent.

The reinforcement of the structure of water by addition of the alcohol produces a decrease in the wavenumber of the solvatochromic indicator in the water-rich region, which can be measured by the *k* constant of Table 3. The effect is smaller for the propan-2-ol–water system than for 2-methylpropan-2-ol–

Table 1 Experimental wavenumbers (in kK = 10^3 cm^{-1}) for binary solvent mixtures of 2-methylpropan-2-ol–water

	Indicator						
$x_2^{0\,a}$	*A*	*B*	*C*	*D*	*E*	*F*	*G*
0.000	36.70	32.97	31.24	31.81	26.43	15.33	15.33
0.050	36.64	32.88	31.18	31.79	26.44	15.70	15.76
0.100	36.62	32.83	31.13	31.77	26.47	15.95	16.05
0.150	36.58	32.80	31.07	31.74	26.49	16.19	16.34
0.201	36.55	32.76	31.03	31.74	26.49	16.39	16.58
0.250	36.51	32.73	30.97	31.72	26.49	16.57	16.77
0.300	36.48	32.69	30.93	31.71	26.49	16.74	16.98
0.360	36.45	32.64	30.89	31.69	26.48	16.89	17.10
0.400	36.42	32.61	30.84	31.69	26.48	17.06	17.24
0.451	36.38	32.58	30.81	31.68	26.47	17.21	17.35
0.500	36.35	32.55	30.76	31.67	26.44	17.35	17.49
0.550	36.31	32.51	30.73	31.67	26.42	17.50	17.61
0.600	36.28	32.48	30.67	31.66	26.42	17.62	17.68
0.650	36.25	32.45	30.62	31.65	26.40	17.76	17.78
0.700	36.21	32.40	30.58	31.64	26.38	17.91	17.94
0.750	36.16	32.36	30.52	31.64	26.34	18.05	18.06
0.800	36.12	32.30	30.45	31.62	26.31	18.22	18.23
0.825	36.08	32.27	30.41	31.62	26.30	18.31	18.24
0.850	36.04	32.23	30.36	31.60	26.24	18.40	18.35
0.875	35.96	32.18	30.29	31.59	26.22	18.57	18.50
0.900	35.86	32.08	30.18	31.56	26.21	18.79	18.71
0.925	35.65	31.95	30.02	31.50	26.08	19.14	19.02
0.950	35.19	31.66	29.76	31.40	25.99	20.06[b]	19.77
0.975	34.97	31.58	29.67	31.47	26.19	21.29[b]	20.84
0.990						21.64[b]	21.14
1.000	35.04	31.58	29.71	31.53	26.36	22.08[c]	21.58

[a] x_2^0 = Mole fraction of water. *A* = 1-ethyl-4-nitrobenzene. *B* = 4-nitroanisole. *C* = 2-nitroanisole. *D* = 4-nitrophenol. *E* = 4-nitroaniline. *F* = Reichardt's dye. *G* = Reichardt's water-soluble dye. [b] Calculated by eqn. (14). [c] Literature value.[25,26]

Table 2 Experimental wavenumbers (in kK = 10^3 cm^{-1}) for binary solvent mixtures of propan-2-ol–water

	Indicator						
$x_2^{0\,a}$	*A*	*B*	*C*	*D*	*E*	*F*	*G*
0.000	36.68	32.94	31.25	31.98	26.54	16.90	16.97
0.050	36.60	32.86	31.19	31.93	26.52	17.04	17.10
0.107	36.57	32.79	31.09	31.87	26.52	17.13	17.13
0.150	36.47	32.74	31.02	31.83	26.50	17.23	17.31
0.200	36.47	32.69	30.97	31.80	26.48	17.35	17.42
0.252	36.40	32.63	30.91	31.77	26.45	17.48	17.55
0.300	36.36	32.58	30.85	31.75	26.44	17.58	17.62
0.350	36.35	32.55	30.80	31.72	26.42	17.71	17.73
0.400	36.29	32.51	30.77	31.72	26.38	17.78	17.78
0.451	36.27	32.48	30.71	31.69	26.36	17.88	17.84
0.501	36.22	32.42	30.67	31.66	26.34	18.01	18.00
0.550	36.19	32.39	30.62	31.67	26.32	18.08	17.95
0.600	36.14	32.35	30.56	31.66	26.28	18.19	18.09
0.650	36.09	32.31	30.52	31.64	26.27	18.28	18.05
0.700	36.06	32.26	30.45	31.61	26.24	18.40	18.29
0.750	35.98	32.19	30.40	31.59	26.21	18.51	18.37
0.800	35.89	32.09	30.28	31.58	26.17	18.69	18.54
0.825	35.80	32.05	30.21	31.56	26.14	18.80	18.67
0.850	35.71	31.99	30.13	31.52	26.10	18.99	18.78
0.874	35.59	31.90	30.01	31.49	26.05	19.15	18.87
0.900	35.40	31.77	29.91	31.43	25.99	19.47	19.19
0.925	35.14	31.61	29.76	31.35	25.95	19.97	19.72
0.950	35.05	31.58	29.68	31.42	26.03	20.75[b]	20.37
0.975	35.00	31.58	29.70	31.51	26.18	21.51[b]	21.03
0.990						21.73[b]	21.22
1.000	35.05	31.59	29.72	31.51	26.34	22.08[c]	21.56

[a] x_2^0 = Mole fraction of water. *A*–*G* as in Table 1. [b] Calculated by eqn. (14). [c] Literature value.[25,26]

Table 3. Parameters from eqn. (11) for the mixtures of 2-methylpropan-2-ol (S1) and propan-2-ol (S1) with water (S2)

Indicator	Y_1	Y_2	Y_{12}	$f_{2/1}$	$f_{12/1}$	*k*	sd	*N*
2-Methylpropan-2-ol–water								
1-Ethyl-4-nitrobenzene	36.71	35.04	36.38	0.061	4.0	−8.2	0.05	25
4-Nitroanisole	32.96	31.58	32.53	0.088	3.5	−4.2	0.03	25
2-Nitroanisole	31.25	29.71	30.71	0.080	2.7	−4.4	0.03	25
4-Nitrophenol	31.82	31.53	31.69	0.20	6.9	−1.4	0.02	25
4-Nitroaniline	26.43	26.37	26.56	0.30	5.3	−2.9	0.03	25
Reichardt's dye	15.31	22.00	17.68	0.063	3.4	11.7	0.13	26
Reichardt's water-soluble dye	15.29	21.55	17.73	0.084	4.4	9.7	0.11	26
Propan-2-ol–water								
1-Ethyl-4-nitrobenzene	36.69	35.06	36.39	0.39	8.2	−5.3	0.05	25
4-Nitroanisole	32.95	31.60	32.52	0.33	5.1	−3.4	0.03	25
2-Nitroanisole	31.27	29.73	30.77	0.32	4.7	−3.9	0.03	25
4-Nitrophenol	31.99	31.53	31.72	0.55	7.1	−1.5	0.03	25
4-Nitroaniline	26.54	26.36	26.45	0.36	4.1	−3.0	0.03	25
Reichardt's dye	16.85	22.03	17.93	0.10	3.5	10.0	0.10	26
Reichardt's water-soluble dye	16.92	21.51	17.82	0.14	4.7	8.9	0.10	26

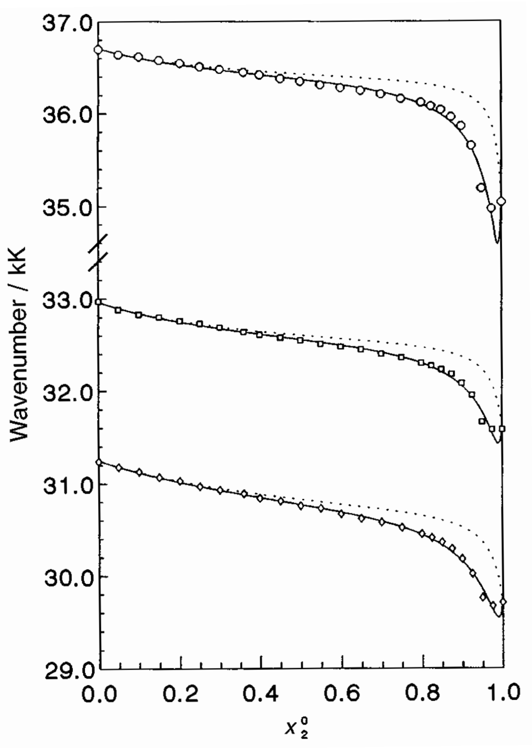

Fig. 1 Wavenumbers of the maximum of absorption of dipolarity/polarizability sensitive indicators in 2-methylpropan-2-ol–water mixtures: 1-ethyl-4-nitrobenzene (○), 4-nitroanisole (□) and 2-nitroanisole (◇). Continuous lines calculated using eqn. (11) from the parameters of Table 3, dashed lines calculated using eqn. (11) from the parameters of Table 3 but neglecting the ΔY term.

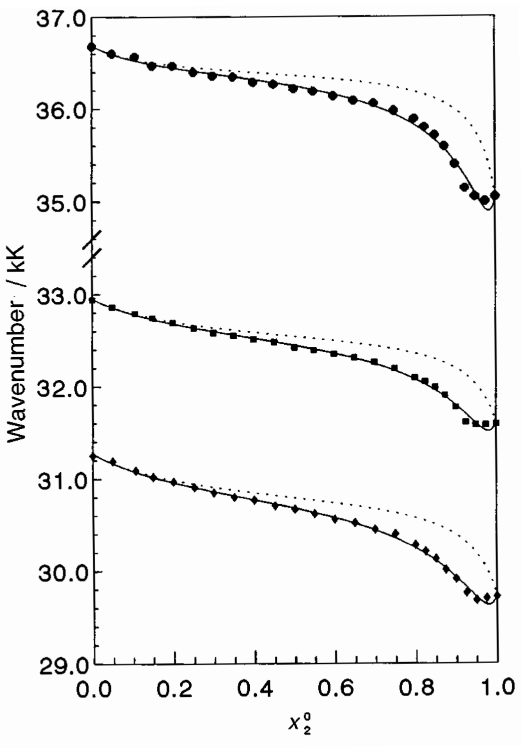

Fig. 2 Wavenumbers of the maximum of absorption of dipolarity/polarizability sensitive indicators in propan-2-ol–water mixtures: 1-ethyl-4-nitrobenzene (●), 4-nitroanisole (■) and 2-nitroanisole (◆). Lines as in Fig. 1.

water, and also smaller for the indicators sensitive to solvent hydrogen-bond acceptor ability (Fig. 3). This seems to indicate that the variation in the hydrogen-bond donor capability partially compensates the variation in dipolarity/polarizability when the enhanced structure of water is formed.

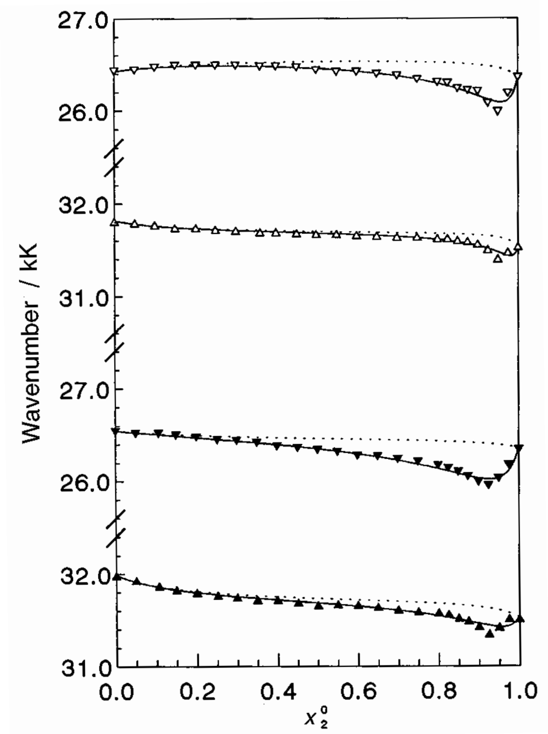

Fig. 3 Wavenumbers of the maximum of absorption of hydrogen-bond donor sensitive indicators: 4-nitroaniline (▽) and 4-nitrophenol (△) in 2-methylpropan-2-ol–water and 4-nitroaniline (▼) and 4-nitrophenol (▲) in propan-2-ol–water. Lines as in Fig. 1.

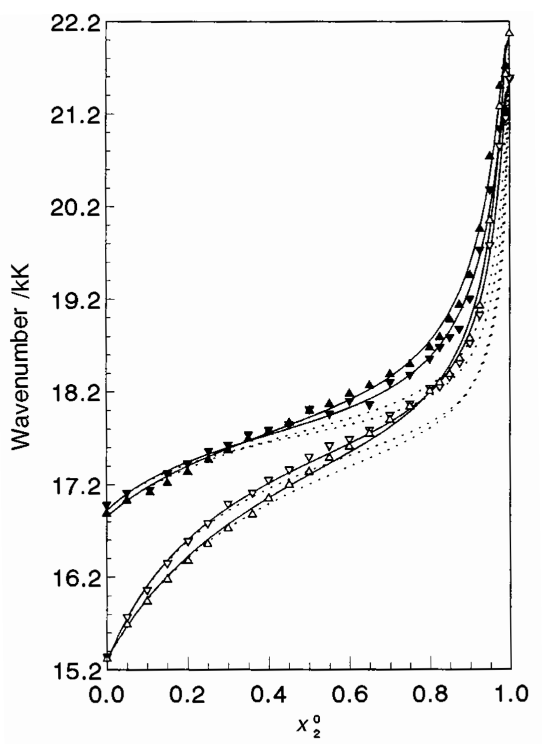

Fig. 4 Wavenumbers of the maximum of absorption of hydrogen-bond donor sensitive indicators: Reichardt's betaine dye (△) and Reichardt's water-soluble betaine dye (▽) in 2-methylpropan-2-ol–water and Reichardt's betaine dye (▲) and Reichardt's water-soluble betaine dye (▼) in propan-2-ol–water. Lines as in Fig. 1.

In contrast to the other studied indicators, Reichardt's betaine dyes show a large negative solvatochromism. This can be observed in Fig. 4 in comparison with Fig. 1–3. In 2-methylpropan-2-ol–water mixtures, the wavenumber of the Reichardt's dyes increases by almost 7 kK and in propan-2-ol–water mixtures by more than 5 kK, whereas the dipolarity/

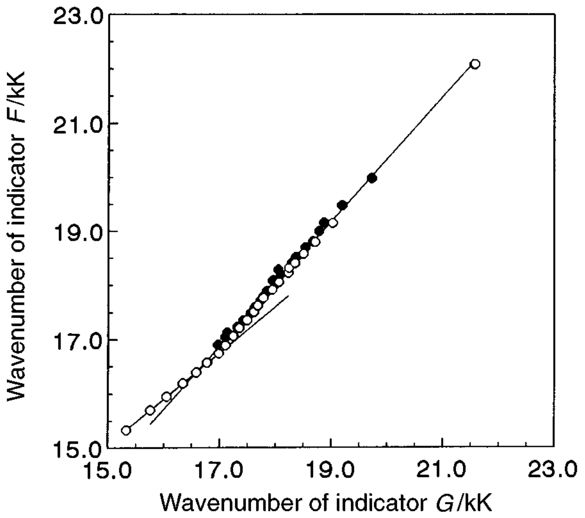

Fig. 5 Correlations between the wavenumbers of the maximum of absorption of Reichardt's betaine dye (*F*) and Reichardt's water-soluble betaine dye (*G*) indicators in 2-methylpropan-2-ol–water (○) and propan-2-ol–water (●) mixtures. Lines calculated using eqn. (14) and (15).

polarizability indicators decrease by less than 2 kK and the hydrogen-bond acceptor indicators by less than 1 kK.

Reichardt's betaine is the most studied solvatochromic indicator and its wavenumber is directly used to calculate the E_T (30) polarity parameter.[25] However, it is not soluble in water-rich regions ($x_2^0 > 0.95$ for the sytems studied here) and since the effect of the reinforcement of the structure of water is at maximum in this region, we decided to measure its carboxylic acid derivative (Reichardt's water-soluble betaine dye) which has been much less studied, but is soluble in the whole range of solvent compositions studied.

We have found an excellent linear correlation [eqn. (12)]

$$\nu_\mathrm{F} = -2.12 + 1.12\nu_\mathrm{G} \quad \mathrm{sd} = 0.09 \quad r^2 = 0.996 \quad N = 46 \tag{12}$$

between the wavenumbers of both indicators, which include all experimental points for 2-methylpropan-2-ol–water and propan-2-ol–water mixtures and the literature value for Reichardt's betaine in pure water.[25,26]

In eqn. (12), ν_F and ν_G are the wavenumbers of Reichardt's dye and Reichardt's water-soluble dye, respectively. This correlation is close to the one obtained for pure solvents, eqn. (13).[27]

$$\nu_\mathrm{F} = -1.25 + 1.07\nu_\mathrm{G} \quad \mathrm{sd} = 0.39 \quad r^2 = 0.996 \quad N = 22 \tag{13}$$

However, a close inspection of the wavenumber data reveals that the four or five points more concentrated in 2-methylpropan-2-ol deviate slightly from the correlation line and that the fit is better if two different correlations are considered [eqn. (14) and (15)].

$$\nu_\mathrm{F} = -2.70 + 1.15\nu_\mathrm{G} \quad \mathrm{sd} = 0.07 \quad r^2 = 0.997 \quad N = 42 \tag{14}$$

$$\nu_\mathrm{F} = 2.33 + 0.848\nu_\mathrm{G} \quad \mathrm{sd} = 0.005 \quad r^2 = 0.99991 \quad N = 5 \tag{15}$$

The plots obtained with these two last correlations are in Fig. 5.

Eqn. (14) has been used to calculate the wavenumber values of Reichardt's betaine dye in the water-rich region which are presented in Tables 1 and 2. These points are needed to calculate accurate fitting parameters for Reichardt's indicators. If the points in the water-rich region are not included, the fit tends to give a high *k* value (>100) with a maximum of several hundreds of kK for a x_2^0 value very close to 1. The point of $x_2^0 = 0.99$ for Reichardt's water-soluble dye was measured for a similar reason, although the maximum in this case was less spectacular. Including all points in the fit, the results demonstrate there is no maximum in the water-rich region caused by the reinforcement of the structure of water.

The results show that the behaviour of both indicators in both systems is very similar. A reversed S-shape plot is obtained (Fig. 4) caused by Y_{12} values intermediate between Y_1 and Y_2 and preferential solvations of the indicators by the mixed alcohol–water S12 solvent ($f_{12/1}$ *ca.* 4, slightly higher for the water-soluble dye than for the usual Reichardt's dye). The preferential solvation is also larger for the alcohol than for water.

In contrast to the positively solvatochromic indicators, *k* is positive for the negative solvatochromic indicators and larger in its absolute value. The absolute *k* value is 2–3 times larger than for the nitroanisoles, but since the wavenumber variation is also 2–3 times larger, we can conclude that the relative effect of the reinforcement of the structure of water is quite similar. This effect seems to be slightly larger for Reichardt's dye than for Reichardt's water-soluble dye.

Solvatochromic parameters

Kamlet and Taft[28–31] proposed three different scales of solvent dipolarity/polarizability (π^*), hydrogen-bond acceptor basicity (β) and hydrogen-bond donor acidity (α), which can be measured by means of the UV–VIS spectroscopic shifts of appropriate solvatochromic indicators. From the wavenumbers of the solvatochromic indicators studied here (Tables 1 and 2), the π^*, β and α parameters of 2-methylpropan-2-ol–water and propan-2-ol–water mixtures can be easily calculated by means of eqn. (16)–(22),[30,32] where the subscripts *A*–*G* denote 1-ethyl-4-nitrobenzene, 4-nitroanisole, 2-nitroanisole, 4-nitrophenol, 4-nitroaniline, Reichardt's betaine dye and Reichardt's water-soluble betaine dye, respectively.

$$\pi_A^* = 0.443\,(37.67 - \nu_A) \tag{16}$$

$$\pi_B^* = 0.427\,(34.12 - \nu_B) \tag{17}$$

$$\pi_C^* = 0.412\,(32.56 - \nu_C) \tag{18}$$

$$\beta_D = 0.346\,(35.045 - \nu_D) - 0.57\,\pi^* \tag{19}$$

$$\beta_E = 0.358\,(31.10 - \nu_E) - 1.125\,\pi^* \tag{20}$$

$$\alpha_F = -0.186\,(10.91 - \nu_F) - 0.72\,\pi^* \tag{21}$$

$$\alpha_G = -0.208\,(11.63 - \nu_G) - 0.72\,\pi^* \tag{22}$$

Eqn. (22) for Reichardt's water-soluble betaine dye was not previously established, but we have calculated it from the correlation eqn. for Reichardt's betaine dye [eqn. (21)] and the direct correlation between both dyes [eqn. (12)].

Each one of the solvatochromic parameters for the studied mixtures can be calculated from more than one indicator. This procedure gives different sets of values for the same parameter that agree only partially. Tables 4 and 5 present all these sets and the averaged values. It can be observed that for π^*, the averaged value is very similar to that obtained from 4-nitroanisole, except for the most water-rich region where the averaged values are slightly lower than the ones obtained from 4-nitroanisole. The π^* values calculated from 1-ethyl-4-nitrobenzene and 2-nitroanisole are *ca.* 0.08 units lower and higher, respectively, than the averaged π^* value. The averaged π^* value has been used for the further calculation of β and α [eqn. (19)–(22)].

β Values calculated from 4-nitrophenol are *ca.* 0.3 units lower than the ones calculated from 4-nitroaniline in the alcohol-rich region, although in the water-rich region they are *ca.* 0.15 units higher.

α Values calculated from both Reichardt's dyes are, not sur-

Table 4 Solvatochromic parameters for binary solvent mixtures of 2-methylpropan-2-ol–water calculated from the wavenumbers of Table 1

x_2^0 [a]	π^*_A	π^*_B	π^*_C	π^*_{avg}	β_D	β_E	β_{avg}	α_F	α_G	α_{avg}
0.000	0.43	0.49	0.54	0.49	0.84	1.12	0.98	0.47	0.42	0.44
				0.41[b,c]			1.01[b] 0.93[c]			0.68[b] 0.42[c]
0.050	0.46	0.53	0.57	0.52	0.83	1.09	0.96	0.52	0.49	0.50
0.100	0.47	0.55	0.59	0.54	0.83	1.06	0.94	0.55	0.53	0.54
0.150	0.48	0.56	0.61	0.55	0.83	1.03	0.93	0.58	0.58	0.58
0.201	0.50	0.58	0.63	0.57	0.82	1.01	0.92	0.61	0.62	0.61
0.250	0.51	0.59	0.66	0.59	0.82	0.99	0.90	0.63	0.65	0.64
0.300	0.53	0.61	0.67	0.60	0.81	0.97	0.89	0.65	0.68	0.66
0.350	0.54	0.63	0.69	0.62	0.81	0.96	0.88	0.67	0.69	0.68
0.400	0.55	0.64	0.71	0.64	0.80	0.94	0.87	0.69	0.71	0.70
0.451	0.57	0.66	0.72	0.65	0.79	0.93	0.86	0.70	0.72	0.71
0.500	0.58	0.67	0.74	0.67	0.79	0.92	0.86	0.72	0.74	0.73
0.550	0.60	0.69	0.75	0.68	0.78	0.91	0.85	0.74	0.75	0.74
0.600	0.62	0.70	0.78	0.70	0.77	0.89	0.83	0.75	0.76	0.75
0.650	0.63	0.71	0.80	0.71	0.77	0.88	0.82	0.76	0.77	0.76
0.700	0.65	0.73	0.82	0.73	0.76	0.87	0.81	0.77	0.79	0.78
0.750	0.67	0.75	0.84	0.75	0.75	0.86	0.80	0.79	0.79	0.79
0.800	0.69	0.78	0.87	0.78	0.74	0.84	0.79	0.80	0.81	0.81
0.825	0.70	0.79	0.89	0.79	0.73	0.83	0.78	0.81	0.80	0.80
0.850	0.72	0.81	0.91	0.81	0.73	0.83	0.78	0.81	0.81	0.81
0.875	0.76	0.83	0.94	0.84	0.72	0.80	0.76	0.82	0.82	0.82
0.900	0.80	0.87	0.98	0.88	0.70	0.76	0.73	0.83	0.84	0.83
0.925	0.89	0.93	1.05	0.96	0.68	0.72	0.70	0.84	0.85	0.85
0.950	1.10	1.05	1.15	1.10	0.63	0.59	0.61	—	0.90	0.90
0.975	1.20	1.08	1.19	1.16	0.58	0.46	0.52	—	1.08	1.08
1.000	1.17	1.08	1.17	1.14	0.57	0.41	0.49	1.26	1.25	1.25
				1.09[b,c]			0.18[b] 0.47[c]			1.17[b,c]

[a] x_2^0 = Mole fraction of water. *A–G* as in Table 1. [b] Literature values from ref. 31. [c] Literature values from ref. 32.

Table 5 Solvatochromic parameters for binary solvent mixtures of propan-2-ol–water calculated from the wavenumbers of Table 2

x_2^0 [a]	π^*_A	π^*_B	π^*_C	π^*_{avg}	β_D	β_E	β_{avg}	α_F	α_G	α_{avg}
0.000	0.44	0.50	0.54	0.49	0.78	1.08	0.93	0.76	0.76	0.76
				0.48[b,c]			0.95[b] 0.84[c]			0.76[b,c]
0.050	0.47	0.54	0.56	0.53	0.78	1.05	0.91	0.76	0.76	0.76
0.107	0.49	0.57	0.61	0.55	0.78	1.02	0.90	0.76	0.75	0.75
0.150	0.53	0.59	0.63	0.59	0.78	0.99	0.88	0.75	0.76	0.76
0.200	0.53	0.61	0.66	0.60	0.78	0.98	0.88	0.77	0.77	0.77
0.252	0.56	0.64	0.68	0.63	0.78	0.96	0.87	0.77	0.78	0.78
0.300	0.58	0.66	0.70	0.65	0.77	0.94	0.86	0.77	0.78	0.78
0.350	0.58	0.67	0.73	0.66	0.77	0.93	0.85	0.79	0.79	0.79
0.400	0.61	0.69	0.74	0.68	0.76	0.93	0.85	0.79	0.79	0.79
0.451	0.62	0.70	0.76	0.69	0.77	0.92	0.84	0.80	0.79	0.79
0.501	0.64	0.73	0.78	0.72	0.76	0.90	0.83	0.81	0.81	0.81
0.550	0.66	0.74	0.80	0.73	0.75	0.89	0.82	0.81	0.79	0.80
0.600	0.68	0.76	0.82	0.75	0.74	0.88	0.81	0.81	0.80	0.81
0.650	0.70	0.77	0.84	0.77	0.74	0.86	0.80	0.82	0.78	0.80
0.700	0.71	0.79	0.87	0.79	0.74	0.85	0.79	0.82	0.81	0.82
0.750	0.75	0.82	0.89	0.82	0.73	0.83	0.78	0.82	0.81	0.82
0.800	0.79	0.87	0.94	0.86	0.71	0.79	0.75	0.82	0.81	0.82
0.825	0.83	0.88	0.97	0.89	0.70	0.77	0.73	0.82	0.82	0.82
0.850	0.87	0.91	1.00	0.93	0.69	0.75	0.72	0.84	0.82	0.83
0.874	0.92	0.95	1.05	0.97	0.68	0.71	0.70	0.83	0.81	0.82
0.900	1.01	1.00	1.09	1.03	0.66	0.67	0.67	0.85	0.83	0.84
0.925	1.12	1.07	1.15	1.12	0.64	0.59	0.62	0.88	0.88	0.88
0.950	1.16	1.08	1.19	1.14	0.60	0.53	0.57	—	0.99	0.99
0.975	1.18	1.08	1.18	1.15	0.57	0.47	0.52	—	1.13	1.13
1.000	1.16	1.08	1.17	1.14	0.58	0.43	0.50	1.26	1.25	1.25
				1.09[b,c]			0.18[b] 0.47[c]			1.17[b,c]

[a] x_2^0 = Mole fraction of water. *A–G* as in Table 1. [b] Literature values from ref. 31. [c] Literature values from ref. 32.

prisingly, very similar, since both indicators are very similar and the correlation equation for Reichardt's water-soluble dye [eqn. (22)] has been obtained from the correlation for Reichardt's dye [eqn. (21)].

This disparity of values for the same parameters reflects the different sensitivity of the indicators to solute–solvent interactions, which is not only solute dependent, but also solvent dependent.[32] This is particularly important in solvent mixtures because the solvent–solvent interactions affect the solute–solvent interactions.

Regardless of this disparity of values for π^* and β parameters, the trend in the variation of each one of these parameters, as measured by one indicator or another, is similar. Moreover, the averaged values obtained for the pure solvents 2-methylpropan-2-ol, propan-2-ol, and water agree very well with the most recent compilation of solvatochromic parameter values, which have been obtained by a variety of indicators and measuring techniques (spectroscopic, kinetic and equilibria techniques). Therefore, the average of the values obtained by different indicators should give a good estimate of the solvatochromic property of the mixture, and it is a more meaningful quantity than the value obtained from any single indicator.[32]

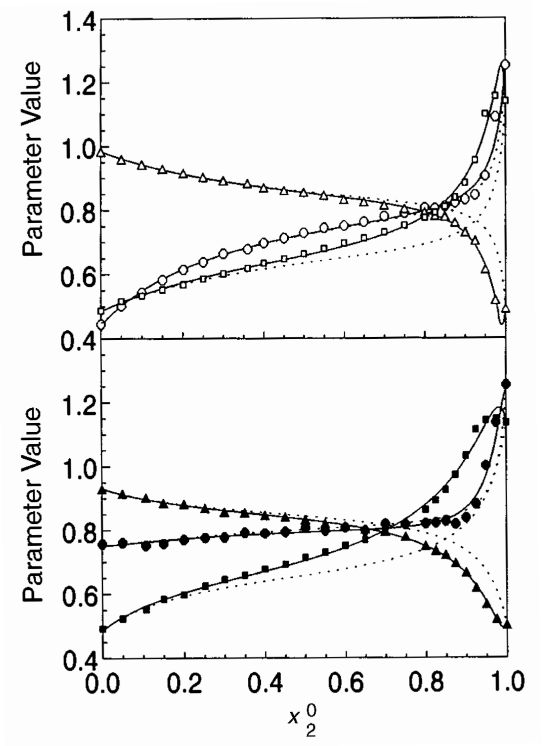

Fig. 6 Solvatochromic parameters in aqueous binary solvents: π^* (□), β (△) and α (○) in 2-methylpropan-2-ol–water and π^* (■), β (▲) and α (●) in propan-2-ol–water. Continuous lines calculated using eqn. (11), (16)–(22) from the parameters of Table 3, dashed lines calculated using the same eqns. but neglecting the ΔY term.

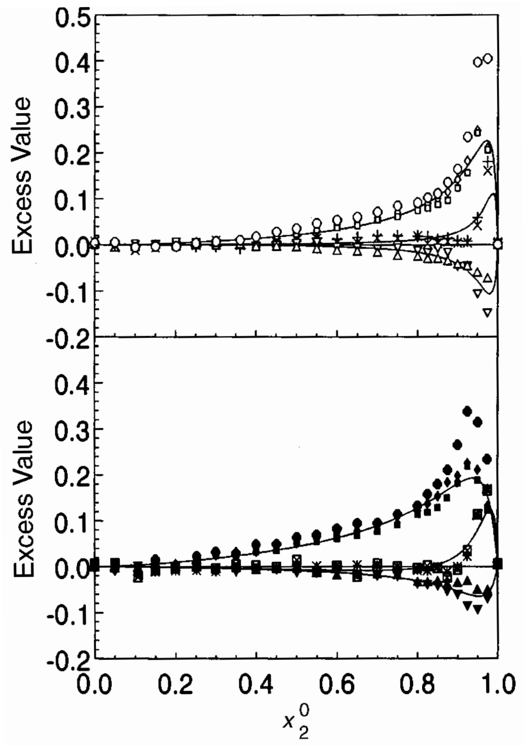

Fig. 7 Excess solvatochromic parameters in aqueous binary solvents caused by the reinforcement of the structure of water. Symbols as in Fig. 6.

In Tables 4 and 5, we have also included the original values given by Kamlet and Taft,[31] which were later revised.[32] The revision affected significantly some of the pure solvents studied here. Thus, the original β value for water was almost trebled and the original α value for 2-methylpropan-2-ol was decreased by about one third. The original β values for the pure alcohols were also slightly reduced, although the new values we present here agree better with the original Kamlet–Taft ones.

The averaged π^*, β and α values for the studied mixtures are presented in Fig. 6. The dipolarity/polarizability of the mixtures (π^*) increases with the water content, with a maximum at mole fractions of water of 0.98 (propan-2-ol) or 0.99 (2-methylpropan-2-ol) caused by the reinforcement of the structure of water in the presence of small quantities of alcohol. The hydrogen-bond acceptor capability of the medium decreases with the mole fraction of water, with a minimum at $x_2^0 = 0.99$ for both systems caused also by the properties of enhanced water structure. The maxima for π^* and the minima for β are larger for the 2-methylpropan-2-ol–water mixtures than for the propan-2-ol–water system, which shows that the enhancement of the water structure is more important in the first system. The hydrogen-bond donor capability (α) increases with the mole fraction of water, but it does not show any partial maximum or minimum.

In Fig. 6, we have also plotted as dashed lines the variation in solvent properties that would be obtained if the enhancement of the water structure were not present. In this instance, S-shaped or reversed S-shaped variations, without maxima or minima, would be obtained for the three parameters.

The differences between the continuous and dashed lines of Fig. 6 are a measure of the effect of the enhancement of the structure of water on the solvent properties, and these differences are plotted in Fig. 7 for all indicators studied. These differences can be also calculated from the ΔY values calculated from eqn. (9) and the correlations between the solvatochromic parameters and indicator wavenumbers [eqn. (16)–(22)]. For an indicator which is sensitive only to solvent dipolarity/polarizability, which follows a correlation equation of the kind in eqn. (23) [similar to eqn. (16)–(18)], we can calculate the

$$\pi^* = a_{\pi^*}(Y_0 - Y) \qquad (23)$$

variation in dipolarity/polarizability caused by the reinforcement of the structure of water ($\Delta\pi^*$) from eqn. (24).

$$\Delta\pi^* = a_{\pi^*}\,\Delta Y \qquad (24)$$

For an indicator sensitive to solvent dipolarity/polarizability and also to hydrogen-bond acceptor basicity or hydrogen-bond donor acidity, which should follow a correlation equation similar to eqn. (25) or (26), we can calculate the $\Delta\beta$ and $\Delta\alpha$ terms as eqn. (27) and (28).

$$\beta = a_\beta (Y_0 - Y) - b_\beta \pi^* \qquad (25)$$

$$\alpha = a_\alpha (Y_0 - Y) - b_\alpha \pi^* \qquad (26)$$

$$\Delta\beta = a_\beta \Delta Y - b_\beta \Delta\pi^* \qquad (27)$$

$$\Delta\alpha = a_\alpha \Delta Y - b_\alpha \Delta\pi^* \qquad (28)$$

These excess quantities are plotted in Fig. 7 for the indicators studied. 4-Nitroanisole and 2-nitroanisole give very similar $\Delta\pi^*$ values and we have used the average of these two $\Delta\pi^*$ values to calculate the $\Delta\beta$ and $\Delta\alpha$ terms by eqn. (27) and (28). However, the $\Delta\pi^*$ values computed from 1-ethyl-4-nitrobenzene are *ca.* 50% larger than the ones calculated from the nitroanisoles. The reason is the higher k value obtained for this indicator (Table 3).

The $\Delta\alpha$ values obtained from both Reichardt's dyes are very similar, and the $\Delta\beta$ values calculated from 4-nitrophenol or 4-nitroaniline are not very different. Consequently, the two pairs of values for each solvent system can be averaged to obtain a good estimate of the variation in solvent hydrogen-bond donor acidity and hydrogen-bond acceptor basicity caused by the reinforcement of the structure of water. Fig. 7 shows that the reinforcement of the structure of water by small additions of alcohols causes a decrease in the hydrogen-bond acceptor ability of the solvent and an increase in the polarity and hydrogen-bond acceptor capability. The variation in polarity is about twice the variation in the hydrogen-bond acidity or basicity and all the variations seem to be slightly larger for 2-methylpropan-2-ol–water than for propan-2-ol–water.

Conclusions

Solvatochromic indicators are very appropriate to study the solute–solvent and solvent–solvent interactions in binary aqueous mixtures. They allow us to quantify the different interactions, including the effect of the reinforcement of the structure of water when alcohols are added to water. The preferential model proposed, even though it is very simple and only approximate, allows a quantitative description of this effect. Application of this model to the solvatochromic shifts of different indicators in 2-methylpropan-2-ol–water and propan-2-ol–water systems shows that the enhanced water structure is more polar and hydrogen-bond acidic and less hydrogen-bond basic than the pure water structure.

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