Solute–solvent and solvent–solvent interactions in binary solvent mixtures. Part 7. Comparison of the enhancement of the water structure in alcohol–water mixtures measured by solvatochromic indicators

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ABSTRACT: A preferential solvation model that takes into account the enhancement of the structure of water when small amounts of alcohol are added was applied to solvatochromic data for binary mixtures of water with 2-methylpropan-2-ol, propan-2-ol, ethanol and methanol. Application of the model allows the calculation of the effect of the enhancement of the water structure on solvatochromic solvent properties. It is demonstrated that the enhancement of water structure increases the solvent dipolarity/polarizability and hydrogen-bond donor acidity and decreases the solvent hydrogen-bond acceptor basicity. The effect decreases in the order 2-methylpropan-2-ol–water, propan-2-ol–water, ethanol–water and methanol–water. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: solute–solvent interactions; solvent–solvent interactions; binary solvents; alcohol–water mixtures; water structure; solvatochromic indicators

INTRODUCTION

The thermodynamic and physical properties of alcohol–water mixtures exhibit peculiar behaviour.[1–12] These mixtures show a minimum in partial molar volume[3–5] and adiabatic compressibility,[6–9] a maximum in excess heat capacity[3,5] and ultrasonic speed[4,10] and a remarkable increase in light scattering[11] in the composition range between 0 and 0.2 mole fraction of alcohol. This maximum or minimum tends to move towards lower alcohol contents whith increase in the length of the alcohol carbon chain. These data suggest 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 living hydrogen bonds.[2,6,7] This rearrangement of the hydrogen bonds caused by the alcohol enhances the water structure and changes its properties.

In a previous study,[12] solvatochromic indicators were used to measure the dipolarity and hydrogen-bond properties of 2-methylpropan-2-ol–water and propan-2-ol–water mixtures. It was demonstrated that preferential solvation models can be applied to alcohol–water mixtures to describe the enhancement of the water structure. It was also shown that the enhancement of the water structure by 2-methylpropan-2-ol and propan-2-ol increases its dipolarity and hydrogen-bond donor acidity and decreases its hydrogen-bond acceptor basicity.

In the present study, we extended our analysis to mixtures of water with two other common alcohols, ethanol and methanol. Solvatochromic data for seven solvatochromic indicators in 25 different mixtures for each binary system were measured and analyzed by means of the previously developed model.[12] The indicators studied were 1-ethyl-4-nitrobenzene, 4-nitroanisole, 2-nitroanisole, 4-nitrophenol, 4-nitroaniline, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate (Reichardt's betaine dye) and sodium-{4-[4-(4-carboxylatophenyl)-2,6-diphenyl-1-pyridinio]-2,6-diphenylphenolate} (Reichardt's water-soluble betaine dye). The results obtained allow a comparison of the effect of the four studied alcohols on the enhancement of the water structure and of the polarity and hydrogen-bond properties of these four different enhanced water structures.
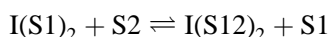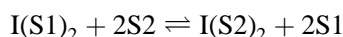
PREFERENTIAL SOLVATION MODEL

The basis of the preferential solvation model used has been described in previous papers,[12–17] and it agrees essentially with one of the models proposed by

Skwierczynski and Connors.[18] This previous model is based on two solvent exchange processes:

$$I(S1)_2 + 2S2 \rightleftharpoons I(S2)_2 + 2S1$$

$$I(S1)_2 + S2 \rightleftharpoons I(S12)_2 + S1$$

where S1 and S2 indicate the two pure solvents mixed (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 synergetic mixtures.[13,14] $I(S1)_2$, $I(S2)_2$, and $I(S12)_2$ represent the indicator solvated by solvents S1, S2, and S12, respectively.

The constants of the two processes are defined by the preferential solvation parameters $f_{2/1}$ and $f_{12/1}$ according to the equations

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

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{x_2^0/x_1^0} \tag{2}$$

where x_1^s, x_2^s, and x_{12}^s are the mole fractions of solvents S1, S2 and S12, respectively, in the microsphere of solvation of the indicator and x_1^0 and x_2^0 are the mole fractions of the two solvents in the bulk mixed solvent. The parameters $f_{2/1}$ and $f_{12/1}$ measure the tendency of the indicator to be solvated by solvents S2 and S12 with reference to solvent S1.

Considering that the addition of all different mole fractions must be equal to unity:

$$x_1^s + x_2^s + x_{12}^s = 1 \tag{3}$$

the mole fractions in the sphere of solvation of the indicator can be easily calculated from the preferential solvation parameters and the solvent composition (x_2^0).[12]

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:

$$Y = x_1^s Y_1 + x_2^s Y_2 + x_{12}^s Y_{12} \tag{4}$$

and by substituting x_1^s, x_2^s and x_{12}^s into equation (4) the following general equation can be derived:

$$Y = \frac{Y_1(1-x_2^0)^2 + Y_2 f_{2/1}(x_2^0)^2 + Y_{12}f_{12/1}(1-x_2^0)x_2^0}{(1-x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0} \tag{5}$$

However, to take into account the enhancement of the water structure, a correction term (ΔY) proportional to the product of the mole fractions of alcohol and structured water [equation (6)] had to be added to equation (5):

$$\Delta Y = \frac{k f_{2/1}(x_2^0)^2[(1-x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0/2]}{[(1-x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0]^2} \tag{6}$$

where k is the proportionality constant.

Combination of equation (5) and (6) gives the following general equation:

$$Y = \frac{Y_1(1-x_2^0)^2 + Y_2 f_{2/1}(x_2^0)^2 + Y_{12}f_{12/1}(1-x_2^0)x_2^0}{(1-x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0} + \Delta Y \tag{7}$$

which we previously applied successfully to mixtures of water with 2-methylpropan-2-ol and propan-2-ol and that was also applied here to the mixtures with ethanol and methanol.

EXPERIMENTAL

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

Solvents and solvatochromic indicators. The solvents (ethanol, methanol and water) and solvatochromic indicators studied were the same as used in previous studies.[12,19]

Procedure. Indicator dye solutions of *ca* 5×10^{-5}–10^{-4} mol 1^{-1} were prepared in 25 binary solvent mixtures prepared by weight for each binary system, at intervals of *ca* 0.05 mole fraction. Narrower intervals were taken in the region between 0.80 and 1.00 mole fraction of water since the reinforcement of the structure of water is mainly observed in this region.[12]

The spectra of the indicator dyes in the solvent mixtures were 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 betaine dyes). All measurements were made in triplicate and averaged.

Computation of the wavenumbers of maximum absorption. The wavenumbers of maximum absorption of the indicators for the studied mixtures were obtained by numerical smoothing of the UV–visible spectra of the solvatochromic dyes.[16] These wavenumbers for the mixtures of water with ethanol and methanol are presented in Tables 1 and 2. The wavenumbers of the 2-methylpropan-2-ol–water and propan-2-ol–water mixtures were given in a previous paper.[12]

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

x_2^{0a}	Indicator[b]						
	A	B	C	D	E	F	G
0.000	36.65	32.85	31.23	32.09	26.90	18.13	18.11
0.050	36.61	32.78	31.14	32.02	26.81	18.19	18.19
0.100	36.52	32.72	31.10	31.95	26.73	18.23	18.21
0.150	36.48	32.65	30.99	31.91	26.66	18.30	18.25
0.200	36.41	32.59	30.92	31.86	26.59	18.37	18.29
0.250	36.39	32.53	30.83	31.82	26.52	18.42	18.34
0.300	36.32	32.48	30.78	31.78	26.47	18.50	18.38
0.350	36.28	32.43	30.71	31.76	26.44	18.57	18.45
0.400	36.21	32.37	30.65	31.74	26.38	18.62	18.50
0.450	36.13	32.32	30.61	31.70	26.35	18.68	18.53
0.500	36.09	32.26	30.55	31.66	26.29	18.76	18.62
0.550	36.02	32.21	30.50	31.66	26.26	18.86	18.67
0.600	35.97	32.15	30.43	31.63	26.20	18.92	18.78
0.650	35.91	32.08	30.40	31.59	26.16	19.03	18.83
0.700	35.77	32.01	30.25	31.56	26.11	19.15	18.99
0.750	35.61	31.93	30.16	31.51	26.07	19.30	19.06
0.800	35.48	31.82	30.01	31.47	26.06	19.52	19.26
0.825	35.42	31.76	29.93	31.47	25.99	19.70	19.36
0.850	35.32	31.71	29.88	31.46	25.96	19.90	19.63
0.875	35.19	31.65	29.82	31.46	25.97	20.17	19.85
0.900	35.14	31.63	29.76	31.46	25.99	20.49[c]	20.16
0.925	35.09	31.61	29.74	31.50	26.06	20.88[c]	20.50
0.950	35.09	31.62	29.72	31.51	26.17	21.28[c]	20.86
0.975	35.07	31.62	29.74	31.54	26.27	21.69[c]	21.22
0.990						21.80[c]	21.32
1.000	35.05	31.60	29.72	31.54	26.33	22.08[d]	21.61

[a] x_2^0 = mole fraction of water.
[b] A = 1-ethyl-4-nitrobenzene; B = 4-nitroanisole; C = 2-nitroanisole; D = 4-nitrophenol; E = 4-nitroaniline; F = Reichardt's betaine dye; G = Reichardt's water-soluble betaine dye.
[c] Calculated by equation (9).
[d] Literature value.[20,21]

RESULTS AND DISCUSSION

Preferential solvation of solvatochromic indicators

The wavenumbers of maximum absorption of the solvatochromic indicators were fitted to equation (7) and the parameters obtained are presented in Table 3.

1-Ethyl-4-nitrobenzene, 4-nitroanisole and 2-nitroanisole are commonly considered to be sensitive only to the dipolarity/polarizability of the solvent,[20–22] although a recent study demonstrated that they may be capable of accepting hydrogen bonds.[23] Since they show positive solvatochromism, a decrease in the dipolarity/polarizability of the solvent increases the wavenumber of maximum absorption. Table 3 shows that the wavenumber of maximum absorption of the pure solvents increases in the order water (Y_2), methanol, ethanol, propan-2-ol and 2-methylpropan-2-ol (Y_1). The dipolarity/polarizability of the mixed 2-methylpropan-2-ol–water, propan-2-ol–water and ethanol–water S12 solvents must be very similar, since their wavenumbers of maximum absorption (Y_{12}) are very similar. However, the mixed methanol–water S12 solvent must have a higher dipolarity/polarizability because its Y_{12} values are markedly lower.

The $f_{2/1}$ values, which measure the preferential solvation of the indicator by water with reference to the alcohol, increase in the order 2-methylpropan-2-ol, propan-2-ol and ethanol. The $f_{12/2}$ values, which measure the preferential solvation of the indicator by the mixed alcohol–water S12 solvent with reference to the solvation by water, decrease in the order 2-methylpropan-2-ol, propan-2-ol, ethanol and methanol. The high $f_{12/1}$ and $f_{12/2}$ values demonstrate that the solvatochromic indicator is preferentially solvated by the mixed alcohol–water S12 solvent. This can be also observed in Fig. 1 which shows that S-shaped plots would be obtained if the enhancement of the water structure were not present (dashed lines).

The enhancement of the water structure produces a decrease of the wavenumber, especially at high water concentrations (Fig. 1). This effect is measured by the k parameter in Table 3, which increases, in absolute value, in the order methanol, ethanol, propan-2-ol and 2-methylpropan-2-ol. The effect of methanol on the enhancement of the water structure is almost meaningless.

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

x_2^{0a}	Indicator[b]						
	A	B	C	D	E	F	G
0.000	36.43	32.72	31.10	32.15	27.02	19.34	19.15
0.050	36.33	32.67	31.02	32.09	26.94	19.42	19.19
0.100	36.31	32.60	30.95	32.04	26.86	19.42	19.21
0.150	36.25	32.55	30.87	31.98	26.79	19.41	19.23
0.200	36.18	32.49	30.78	31.94	26.68	19.53	19.30
0.250	36.11	32.41	30.72	31.89	26.61	19.55	19.30
0.300	36.06	32.34	30.62	31.83	26.52	19.67	19.37
0.350	35.98	32.27	30.57	31.81	26.47	19.72	19.36
0.400	35.90	32.21	30.49	31.74	26.40	19.70	19.47
0.450	35.82	32.15	30.41	31.72	26.35	19.77	19.48
0.500	35.74	32.08	30.34	31.66	26.29	19.85	19.61
0.550	35.65	32.01	30.25	31.66	26.23	19.97	19.72
0.600	35.57	31.94	30.18	31.65	26.19	20.09	19.77
0.650	35.49	31.89	30.10	31.61	26.17	20.19	19.86
0.700	35.41	31.81	30.02	31.59	26.13	20.30	19.99
0.750	35.32	31.76	29.94	31.58	26.12	20.50	20.12
0.800	35.27	31.72	29.89	31.57	26.13	20.64	20.41
0.825	35.21	31.69	29.85	31.55	26.14	20.88	20.53
0.850	35.18	31.66	29.83	31.58	26.16	21.07[c]	20.67
0.875	35.17	31.66	29.81	31.58	26.19	21.25[c]	20.83
0.900	35.12	31.65	29.78	31.57	26.22	21.35[c]	20.92
0.925	35.10	31.64	29.77	31.57	26.26	21.55[c]	21.10
0.950	35.09	31.62	29.75	31.55	26.29	21.71[c]	21.24
0.975	35.11	31.59	29.74	31.53	26.32	21.89[c]	21.40
0.990						21.93[c]	21.43
1.000	35.04	31.57	29.73	31.54	26.36	22.08[d]	21.50

[a] x_2^0 = mole fraction of water.
[b] A = 1-ethyl-4-nitrobenzene; B = 4-nitroanisole; C = 2-nitroanisole; D = 4-nitrophenol; E = 4-nitroaniline; F = Reichardt's betaine dye; G = Reichardt's water-soluble betaine dye.
[c] Calculated by equation (9).
[d] Literature value.[20,21]

4-Nitrophenol and 4-nitroaniline are also positive solvatochromic indicators, but in addition to solvent dipolarity/polarizability they are also sensitive to solvent hydrogen-bond acceptor basicity. The combination of these two solvent properties determines that the order of the wavenumbers of the maximum absorption of these indicators (Y_1, Y_2 and Y_{12}) for the alcohols, water and alcohol–water S12 solvents is different to the order for 1-ethyl-4-nitrobenzene, 4-nitroanisole and 2-nitroanisole. However, the preferential solvation of the five indicators ($f_{2/1}$, $f_{12/1}$ and $f_{12/2}$) is very similar. The enhancement of the water structure measured by 4-nitrophenol and 4-nitroaniline (k) is similar for 2-methylpropan-2-ol, propan-2-ol and ethanol, and almost meaningless for methanol.

Reichardt's betaine dyes are negative solvatochromic indicators sensitive to solvent dipolarity/polarizability and hydrogen-bond donor acidity to almost the same extent.[20,21,24] The wavenumbers of maximum absorption of the pure solvents (Y_1 and Y_2) increase in the order 2-methylpropan-2-ol, propan-2-ol, ethanol, methanol and water. The wavenumbers of maximum absorption of the corresponding alcohol–water S12 solvents (Y_{12}) increase in the same order. The order of the preferential solvation parameters ($f_{2/1}$, $f_{12/1}$ and $f_{12/2}$) for these betaine dyes is

the same as for the other indicators studied. The effect of the enhancement of the water structure on the wavenumber of maximum absorption is greater for the betaine dyes than for the other indicators because they have a much higher sensitivity to solvent properties (compare the scales in Figs. 1 and 2). In contrast to the other indicators, k is positive because betaine dyes exhibit negative solvatochromism. However, the order of the absolute k values for the different alcohols is the same as the order for 1-ethyl-4-nitrobenzene, 4-nitroanisole and 2-nitroanisole.

For 2-methylpropan-2-ol–water and propan-2-ol–water mixtures, we reported an excellent correlation between the wavenumbers of maximum absorption of Reichardt's betaine dye (ν_F) and Reichardt's water-soluble betaine dye (ν_G):[12]

$$\nu_F = -2.70 + 1.15\nu_G \ (\text{SD} = 0.07, r^2 = 0.997, N = 42) \quad (8)$$

Inclusion of the data for ethanol–water and methanol–water gives almost the same correlation (Fig. 3):

$$\nu_F = -2.30 + 1.13\nu_G \ (\text{SD} = 0.07, r^2 = 0.997, N = 86) \quad (9)$$

As has been already reported[12] and can be easily observed in Fig. 3 the data for the mixtures richest in 2-methylpropan-2-ol drop out from the correlation.

Table 3. Parameters from equation (7) for mixtures of alcohols (S1) with water (S2)

Indicator	Alcohol	Y_1	Y_2	Y_{12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$[a]	k	SD
1-Ethyl-4-nitrobenzene	2-Methylpropan-2-ol	36.71	35.04	36.38	0.061	4.0	66	−8.2	0.05
	Propan-2-ol	36.69	35.06	36.39	0.39	8.2	21	−5.3	0.05
	Ethanol	36.66	35.08	36.49	1.6	11	6.9	−4.1	0.03
	Methanol	36.41	35.06	35.43	0.37	1.0	2.7	−0.5	0.02
4-Nitroanisole	2-Methylpropan-2-ol	32.96	31.58	32.53	0.088	3.5	40	−4.2	0.03
	Propan-2-ol	32.95	31.60	32.52	0.33	5.1	15	−3.4	0.03
	Ethanol	32.86	31.62	32.53	1.03	5.5	5.3	−2.7	0.02
	Methanol	32.72	31.58	31.91	0.72	1.4	1.9	−0.2	0.01
2-Nitroanisole	2-Methylpropan-2-ol	31.25	29.71	30.71	0.080	2.7	34	−4.4	0.03
	Propan-2-ol	31.27	29.73	30.77	0.32	4.7	15	−3.9	0.03
	Ethanol	31.25	29.75	30.82	0.87	5.7	6.6	−3.4	0.03
	Methanol	31.10	29.74	30.08	0.40	1.5	3.8	−0.7	0.01
4-Nitrophenol	2-Methylpropan-2-ol	31.82	31.53	31.69	0.20	6.9	34	−1.4	0.02
	Propan-2-ol	31.99	31.53	31.72	0.55	7.1	13	−1.5	0.03
	Ethanol	32.10	31.56	31.84	2.15	8.4	3.8	−1.7	0.02
	Methanol	32.14	31.55	31.70	2.81	2.1	0.8	−0.1	0.01
4-Nitroaniline	2-Methylpropan-2-ol	26.43	26.37	26.56	0.30	5.3	18	−2.9	0.03
	Propan-2-ol	26.54	26.36	26.45	0.36	4.1	11	−3.0	0.03
	Ethanol	26.91	26.37	26.55	1.5	7.1	4.7	−3.6	0.03
	Methanol	27.02	26.37	25.86	0.55	1.4	2.5	−0.6	0.01
Reichardt's betaine	2-Methylpropan-2-ol	15.31	22.00	17.68	0.063	3.4	54	11.7	0.13
	Propan-2-ol	16.85	22.03	17.93	0.10	3.5	35	10.0	0.10
	Ethanol	18.11	22.01	18.40	0.40	7.0	18	7.5	0.06
	Methanol	19.38	22.03	21.55	0.027	0.25	9.3	0.1	0.05
Reichardt's water-soluble betaine	2-Methylpropan-2-ol	15.29	21.55	17.73	0.084	4.4	52	9.7	0.11
	Propan-2-ol	16.92	21.51	17.82	0.14	4.7	34	8.9	0.10
	Ethanol	18.11	21.54	18.26	0.69	12	17	6.6	0.06
	Methanol	19.16	21.48	20.98	0.032	0.25	7.8	0.3	0.03

[a] $f_{12/2} = f_{12/1}/f_{2/1}$.

Enhancement of the water structure measured by solvatochromic parameters

The Kamlet–Taft parameters[22,25–27] of dipolarity/polarizability (π^*), hydrogen-bond acceptor basicity (β) and hydrogen-bond donor acidity (α) of the studied mixtures were calculated from the wavenumbers of maximum absorption (ν) of the studied solvatochromic indicators by linear free-energy relationships:

$$\nu = \nu_0 + s\pi^* + b\beta + a\alpha \tag{10}$$

The ν_0, s, b and a coefficients for the different solvatochromic indicators are given in Table 4.[12,22,28]

The solvatochromic parameters obtained for the same solvent mixture from different indicators were averaged and the means and standard deviations obtained are presented in Table 5 and Fig. 4 for ethanol–water and methanol–water mixtures. The averaged π^* values were used for the calculation of the β and α parameters. The α parameter was calculated only from Reichardt's water-soluble betaine data, because the other α-sensitive indicator (Reichardt's betaine) is not soluble over the whole composition range studied. Anyway, the wavenumbers of both indicators are linearly related [equation (9)] and the α values calculated from the data on the solubility range of both indicators agree to 0.01 or less. The solvatochromic parameters for 2-methylpropan-2-ol–water and propan-2-ol–water mixtures have already been reported.[12]

The variation of the solvatochromic parameters for the

Table 4. Parameters for the sensitivity of solvatochromic indicators to solvent properties according to equation (10)

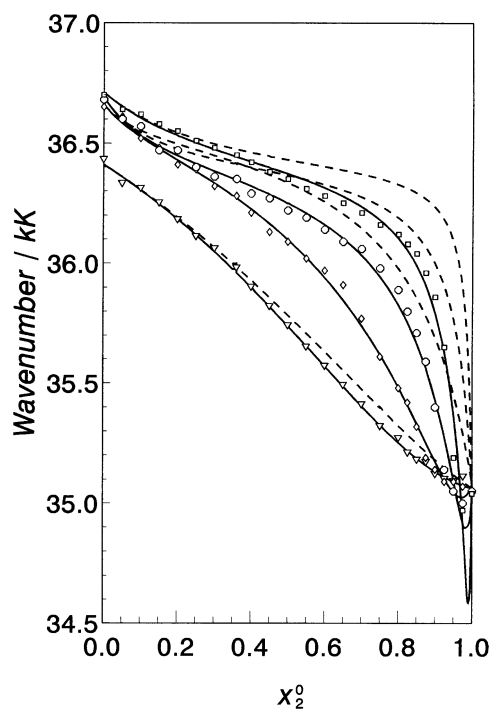| Indicator	ν_0	s	b	a
1-Ethyl-4-nitrobenzene	37.67	−2.26	—	—
4-Nitroanisole	34.12	−2.34	—	—
2-Nitroanisole	32.56	−2.43	—	—
4-Nitrophenol	35.045	−1.65	−2.89	—
4-Nitroaniline	31.10	−3.14	−2.79	—
Reichardt's betaine	10.91	3.87	—	5.38
Reichardt's water-soluble betaine	11.63	3.46	—	4.81

Figure 1. Wavenumbers of the maximum of absorption of 1-ethyl-4-nitrobenzene in mixtures of water with 2-methylpropan-2-ol ($\square$), propan-2-ol ($\bigcirc$), ethanol ($\lozenge$) and methanol ($\triangledown$). Continuous lines calculated using equation (7) from the parameters in Table 3; dashed lines calculated using equation (7) from the parameters in Table 3 but neglecting the ΔY term. x_2^0 is the mole fraction of water

Figure 2. Wavenumbers of the maximum of absorption of Reichardt's water-soluble betaine dye in mixtures of water with alcohols. Symbols and lines as in Fig. 1

four binary systems studied shows that the dipolarity/polarizability (π^*) of the mixtures increases with the content of water with a maximum at a mole fraction of water around 0.99 for 2-methylpropan-2-ol–water mixtures, caused by the enhancement of the water structure. However, this maximum decreases and flattens out for propan-2-ol–water and ethanol–water, and disappears for methanol–water mixtures. The hydrogen-bond donor basicity (β) of the mixtures decreases with the water content. 2-Methylpropan-2-ol–water mixtures present a minimum for β at a mole fraction of water of 0.99. This minimum decreases for propan-2-ol–water mixtures and it is not observed for ethanol–water and methanol–water. The solvent hydrogen-bond donor acidity (α) of the pure alcohols decreases markedly in the order methanol ($\alpha = 1.14$), ethanol ($\alpha = 0.98$), propan-2-ol ($\alpha = 0.76$) and 2-methylpropan-2-ol ($\alpha = 0.44$). This indicates that α increases with the water content for 2-methylpropan-2-ol–and propan-2-ol–water, but minima for mole fractions of water around 0.7 are obtained for mixtures with ethanol and methanol.

The effect of the enhancement of the water structure on the solvent properties can be easily calculated from the variation of the wavenumbers of maximum absorption of the solvatochromic indicators caused by this effect. This variation of the wavenumbers ($\Delta\nu = \Delta Y$) can be calcu-
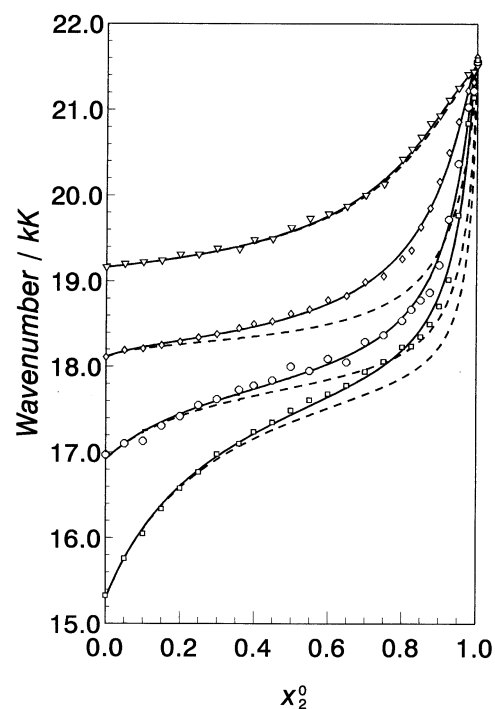
lated from the parameters in Table 3 through equation (6) and related to the change in solvent properties ($\Delta\pi^*$, $\Delta\beta$ and $\Delta\alpha$) by means of an equation similar to equation (10):

$$\Delta\nu = s\Delta\pi^* + b\Delta\beta + a\Delta\alpha \qquad (11)$$

where the s, b and a coefficients are given in Table 4.

These excess quantities were calculated and are plotted in Fig. 5 for the four solvent systems studied. The enhancement of the water structure produces an increase
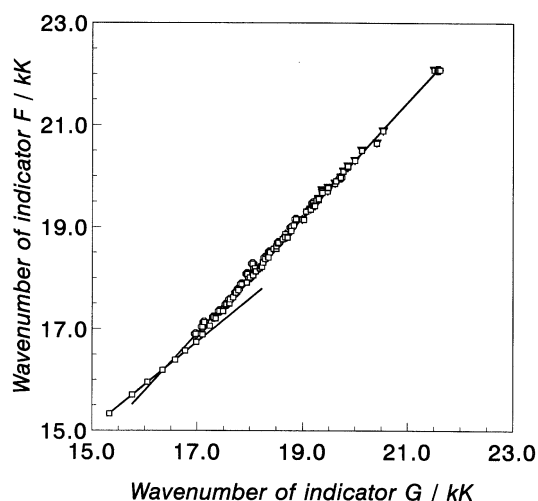

Figure 3. Correlations between the wavenumbers of the maximum of absorption of Reichardt's betaine dye (F) and Reichardt's water-soluble betaine dye (G) indicators in mixtures of water with alcohols. Symbols as in Fig. 1

Table 5. Averaged solvatochromic parameters for binary solvent mixtures of ethanol and methanol with water calculated from the wavenumbers in Tables 1 and 2 and equation (10) with the coefficients in Table 4

	Ethanol–water			Methanol–water		
x_2^{0a}	$\pi^* \pm SD$	$\beta \pm SD$	α	$\pi^* \pm SD$	$\beta \pm SD$	α
0.000	0.51 ± 0.04	0.83 ± 0.10	0.98	0.58 ± 0.02	0.74 ± 0.07	1.14
0.050	0.54 ± 0.05	0.83 ± 0.09	0.97	0.61 ± 0.02	0.74 ± 0.06	1.13
0.100	0.57 ± 0.04	0.84 ± 0.09	0.96	0.64 ± 0.02	0.74 ± 0.06	1.12
0.150	0.60 ± 0.05	0.83 ± 0.09	0.94	0.66 ± 0.03	0.74 ± 0.06	1.10
0.200	0.63 ± 0.05	0.83 ± 0.08	0.93	0.70 ± 0.03	0.74 ± 0.06	1.09
0.250	0.65 ± 0.06	0.83 ± 0.08	0.93	0.73 ± 0.03	0.74 ± 0.06	1.07
0.300	0.68 ± 0.06	0.82 ± 0.08	0.92	0.76 ± 0.03	0.74 ± 0.05	1.06
0.350	0.70 ± 0.06	0.81 ± 0.07	0.91	0.78 ± 0.03	0.72 ± 0.05	1.04
0.400	0.73 ± 0.06	0.80 ± 0.07	0.91	0.82 ± 0.03	0.72 ± 0.04	1.04
0.450	0.75 ± 0.05	0.79 ± 0.06	0.89	0.85 ± 0.03	0.71 ± 0.04	1.02
0.500	0.77 ± 0.05	0.79 ± 0.06	0.90	0.88 ± 0.02	0.70 ± 0.03	1.03
0.550	0.80 ± 0.05	0.78 ± 0.06	0.89	0.91 ± 0.02	0.68 ± 0.03	1.02
0.600	0.82 ± 0.05	0.77 ± 0.06	0.89	0.95 ± 0.02	0.66 ± 0.03	1.01
0.650	0.85 ± 0.05	0.77 ± 0.05	0.89	0.98 ± 0.02	0.65 ± 0.02	1.01
0.700	0.90 ± 0.04	0.74 ± 0.04	0.88	1.01 ± 0.02	0.63 ± 0.01	1.01
0.750	0.94 ± 0.03	0.71 ± 0.03	0.86	1.04 ± 0.03	0.61 ± 0.00	1.02
0.800	1.00 ± 0.03	0.67 ± 0.01	0.87	1.06 ± 0.03	0.59 ± 0.01	1.06
0.825	1.03 ± 0.04	0.66 ± 0.01	0.87	1.08 ± 0.03	0.58 ± 0.02	1.07
0.850	1.06 ± 0.03	0.64 ± 0.01	0.90	1.09 ± 0.03	0.56 ± 0.02	1.09
0.875	1.09 ± 0.03	0.61 ± 0.01	0.92	1.10 ± 0.03	0.55 ± 0.02	1.12
0.900	1.11 ± 0.04	0.59 ± 0.01	0.97	1.11 ± 0.04	0.54 ± 0.04	1.13
0.925	1.12 ± 0.04	0.56 ± 0.02	1.03	1.11 ± 0.04	0.52 ± 0.04	1.17
0.950	1.13 ± 0.04	0.54 ± 0.04	1.11	1.12 ± 0.04	0.52 ± 0.05	1.19
0.975	1.13 ± 0.04	0.52 ± 0.05	1.18	1.12 ± 0.03	0.51 ± 0.06	1.22
1.000	1.13 ± 0.04	0.50 ± 0.07	1.26	1.14 ± 0.04	0.49 ± 0.07	1.23

[a] x_1^0 = Mole fraction of water.

in the solvent dipolarity/polarizability and hydrogen-bond donor acidity and a decrease in the solvent hydrogen-bond donor basicity. In general, the largest effect is observed for 2-methylpropan-2-ol–water mixtures and decreases in the order 2-methylpropan-2-ol–water, propan-2-ol–water, ethanol-water and methanol–water mixtures. The mole fraction of water at which the effect is maximum decreases in the same solvent order. The effect of the enhancement of water structure on solvent properties is appreciable for the systems of the three alcohols with the longest carbon chains, and almost meaningless for methanol–water. It can also be observed that the effect on the solvent dipolarity/polarizability ($\Delta\pi^*$) is almost the double that on solvent hydrogen-bond properties ($\Delta\beta$ and $\Delta\alpha$).
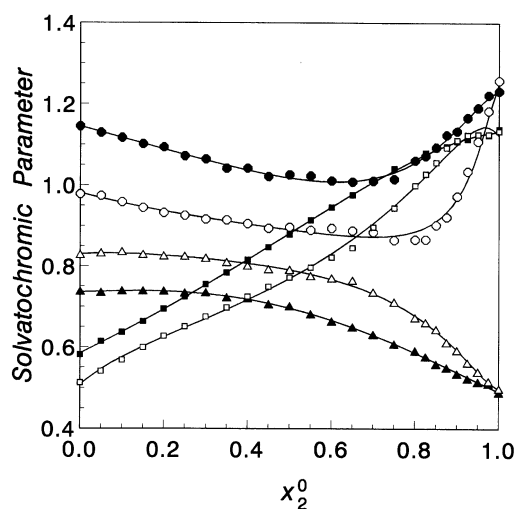
CONCLUSIONS

The enhancement of the water structure caused by the addition of small amounts of alcohols to water can easily be studied by application of preferential solvation models to solvatochromic indicator data. A comparison of this effects for aqueous mixtures of 2-methylpropan-2-ol, propan-2-ol, ethanol and methanol shows that the effect decreases on going from the longest to the shortest carbon chain alcohols. The enhancement of the water structure produces an important increase in solvent dipolarity/polarizability ($\Delta\pi^* \approx 0.20 \pm 0.03$) for 2-methylpropan-2-ol–water, propan-2-ol–water and ethanol–water mixtures. The same effect produces a minor increase in hydrogen-bond donor acidity ($\Delta\alpha \approx 0.11 \pm 0.01$) and even a minor decrease in hydrogen-bond acceptor
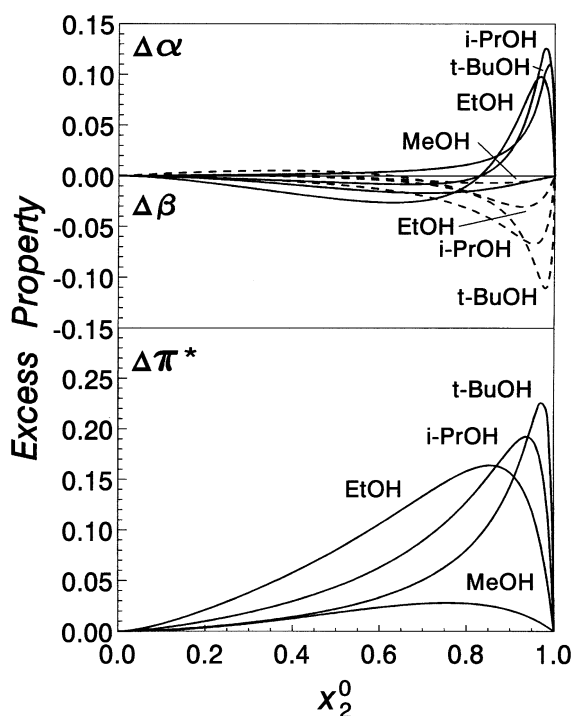

Figure 4. Solvatochromic parameters in aqueous binary solvent mixtures: π^* ($\square$), β ($\triangle$) and α ($\bigcirc$) in ethanol–water and π^* ($\blacksquare$), β ($\blacktriangle$) and α ($\bullet$) in methanol–water

Figure 5. Excess solvatochromic parameters in mixtures of water with alcohols caused by the enhancement of the structure of water. Excess dipolarity/polarizability ($\Delta\pi^*$) and hydrogen-bond donor acidity ($\Delta\alpha$) as continuous lines and excess hydrogen-bond acceptor basicity ($\Delta\beta$) as dashed lines. t-BuOH = 2-methylpropan-2-ol–water mixtures, i-PrOH = propan-2-ol–water mixtures, EtOH = ethanol–water mixtures and MeOH = methanol–water mixtures

basicity ($\Delta\beta \approx 0.07 \pm 0.05$) for these three solvent systems. The effect for methanol–water mixtures is very small.

Acknowledgments

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