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Thermo-solvatochromism in aqueous alcohols: effects of the molecular structures of the alcohol and the solvatochromic probe

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epoc ABSTRACT: Thermo-solvatochromism of 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)-1-phenolate, 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl) phenolate and 1-methylquinolinium-8-olate in the temperature range 10–45 °C was studied in mixtures of water with methanol, ethanol, 1-propanol, 2-propanol, 2-methyl-2-propanol, 2-methoxyethanol and 1,2-ethanediol. Plots of the solvent polarity parameter, E_T in kcal mol^{-1}, versus mole fraction of water in the binary mixture, χw, indicated that all probes are preferentially solvated by the alcohol. Thermo-solvatochromic data for aqueous methanol, 2-methoxyethanol and 1,2-ethanediol were fitted to a simple solvent-exchange model, in which water substitutes alcohol in the probe solvation micro-sphere. Data for the remaining alcohols required a more elaborate model, where water and water–alcohol complex substitute alcohol and/or water in the probe solvation micro-sphere. A temperature increase causes gradual desolvation of the probe, due to a decrease in the H-bonding abilities of both components of the binary mixture. Copyright © 2002 John Wiley & Sons, Ltd.
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KEYWORDS: thermo-solvatochromism; aqueous alcohols; molecular structure

INTRODUCTION

Binary mixtures of water and organic solvents are extensively employed in organic synthesis and in physical organic chemistry studies of, e.g., solvolysis, nucleophilic substitutions and acyl transfers. The reasons are partially practical and are often connected with solubility constraints. Additionally, there is increasing interest in understanding the effects of solvents and their mixtures on the rates and equilibria of chemical reactions.[1,2] In analyzing solvent effects, extensive use has been made of the empirical solvent polarity parameter, E_T, which is calculated by the following equation:

$$E_T(\text{kcal mol}^{-1}) = 28591.5/\lambda_{\max}(\text{nm}) \qquad (1)$$

which converts the wavelength of the electronic transition within the solvatochromic probe (hereafter called 'probe') into the corresponding intramolecular transition energy in kcal mol^{-1} (1 kcal = 4.184 kJ). Dipolarity/polarizability, H-bond donation and H-bond acceptance abilities of both probe and solvent contribute to E_T. Consequently, correlations between the latter property and rate or equilibrium data are complex, for both pure solvents and their binary mixtures. In the latter case, preferential solvation of the relevant species (e.g. probes, reactants and transition states) by one component of the binary mixture introduces additional complexity; this factor has recently been analyzed in some detail.[2–6]

A wealth of mechanistic information can be extracted from the dependence of activation enthalpy, $\Delta H^{\neq}$, and entropy, $\Delta S^{\neq}$, on the composition of binary solvent mixtures. For simple reactions, e.g. water-catalyzed hydrolyses, the $\Delta H^{\neq}$ and $T\Delta S^{\neq}$ terms were found to depend on the mole fraction of water, χw, in a complex, rather compensating manner.[1a,7] A thorough analysis of these data, and indeed the data of reactions that occur in any binary solvent mixture, should address the following questions: (i) what is the relationship between compositions of bulk solvent and solvation micro-sphere of the species of interest?; and (ii) how does the latter composition depend on the molecular structure of the relevant species, the nature of the binary solvent mixture and temperature?

Thermo-solvatochromism sheds light on the above questions because probes of different structures are convenient models for many reactants.[2] The term describes the effects of temperature on the solvatochro-

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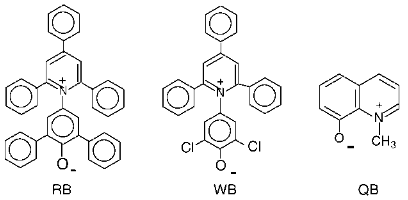

Figure 1. Solvatochromine probes studied

mic responses of probes, a phenomenon that has been studied in much less detail than solvatochromism (at room temperature), and only for a limited number of probes and binary solvent mixtures.[2,3,8] In this work, we studied thermo-solvatochromism of the following probes in aqueous solvents, in the temperature range 10–45 °C (probe name, acronym, E_T scale): 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)-1-phenolate, RB, $E_T(30)$; 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl) phenolate, WB, $E_T(33)$; and 1-methylquinolinium-8-olate, QB, $E_T(QB)$ (Fig. 1).

To our knowledge, there is no information on thermo-solvatochromism of WB and QB either in pure solvents or in binary solvent mixtures. The organic components employed included the alcohols methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH) and 2-methyl-2-propanol (2-Me-2-PrOH), an alkoxy alcohol, 2-methoxyethanol (MeOEtOH), and a diol, 1,2-ethanediol (ED). Thermo-solvatochromic responses to solvent composition were analyzed in terms of a solvent-exchange mechanism in which water and/or water–alcohol complexes substitute alcohol and/or water in the probe solvation microsphere. A temperature increase results in gradual desolvation of the probe, and the relevance of this result to solvolytic reactions is briefly discussed.

EXPERIMENTAL

Materials. The probes were available from previous studies.[4] Spectroscopy-grade organic solvents were purchased from Aldrich or Merck. They were purified by distillation from CaH_2, followed by storage over activated type 4A molecular sieves. Their purity was established from their densities (DMA 40 digital densimeter, Anton Paar, Graz, Austria) and from agreement between experimental and literature E_T values (see below).

Sample preparation. All binary mixtures (16 per set) were prepared at 25 °C. The probe solution in acetone was pipetted into 1 ml volumetric tubes. Acetone was removed under reduced pressure over P_4O_{10}, the binary solvent mixture was added and the probe was dissolved with the aid of a tube rotator (Labquake, Lab Industries, Berkeley, CA, USA). RB was insoluble in pure water and in mixed solvents of high water content, typically $\chi_W > 0.96$. The relatively high m.p. of 2-Me-2-PrOH, 25.5 °C, precluded carrying out the experiment at 10 °C. At 25.0 °C, the absorbances of the probes in this alcohol were stable, probably due to m.p. depression of the latter by the solute, and by the low atmospheric pressure in São Paulo.

Spectrophotometric determination of E_T. The final probe concentration in solution was $(2–5) \times 10^{-4}$ mol l^{-1}. The UV–Vis spectra of the probes employed showed no change in λ_{max} and/or spectrum shape as a function of probe concentration in the range 1×10^{-4}–1×10^{-3} mol l^{-1}. Therefore, no inter-probe interaction occurred under our experimental conditions. A Beckman DU-70 UV–Vis spectrophotometer was used. The temperature inside the thermostated cell holder was controlled to within ±0.05 °C with a digital thermometer (Model 4000A, Yellow Springs Instruments, Yellow Springs, OH, USA). Cuvettes of 1–4 cm pathlength were employed. Each spectrum was recorded twice at a rate of 300 nm min^{-1}. The value of λ_{max} was determined by two methods, peak-pick and first derivative of the spectrum. Measurements of λ_{max} in aqueous MeOH and aqueous 2-Me-2-PrOH, at different scan rates (120 and 300 nm min^{-1}), at 25 and 45 °C, showed that the uncertainties in E_T are 0.1 kcal mol^{-1} for QB and $\leq$0.2 kcal mol^{-1} for RB and WB. For RB, the uncertainty calculated is much smaller than that reported elsewhere (0.6 kcal mol^{-1}).[9]

RESULTS AND DISCUSSION

Choice of the probes and organic solvents

As shown in Fig. 1, the probes employed are betaines, and are sensitive to the same solute–solvent interactions, e.g. Coulombic, dispersion and H-bonding.[4] They differ, however, in several properties that bear on their solvatochromic response to variations of solvent composition and temperature (probe property, followed by values for RB, WB, and QB, respectively): solubility in water (7.2×10^{-6}, 3.7×10^{-4} and >0.2 mol l^{-1}), pK_a (8.60, 4.78 and 6.80), and volume of the hydrated species (0.631, 0.494, and 0.184 nm^3).[2,4] The organic solvents included linear alcohols, two branched-chain alcohols, one alkoxyethanol and a typical polyol.

Thermo-solvatochromism

Figure 2 shows representative plots of E_T(probe) versus χ_W at 25 and 45 °C. Rather than reporting extensive lists of E_T values, we calculated its (polynomial) dependence on χ_W and present the regression coefficients in supplementary Tables S1–S3 (available from the epoc

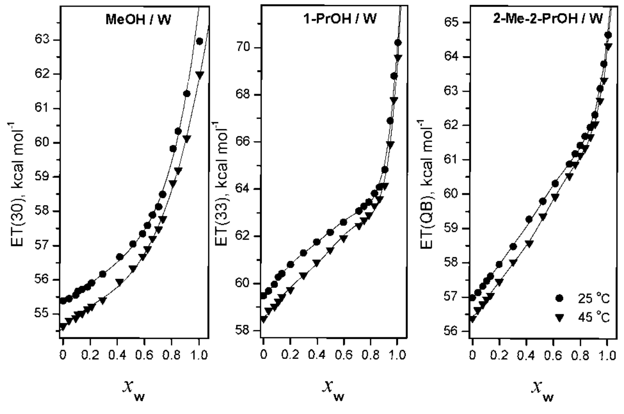

Figure 2. Representative plots showing the dependence of solvent polarity scale, E_T(probe), on mole fraction of water in the binary solvent mixture, χ_W, cat 25 and 45 °C. $E_T(30)$ in pure water was calculated from the data in Tables 1

website at http://www.wiley.com/epoc). The degree of the polynomial used is that which gave the best data fit, as indicated by the multiple correlation coefficients, r_{mult}, and the sums of the squares of the residues, ΣQ. Figures 3–5 show solvent polarity–temperature–solvent composition contours for MeOH/W and 2-Me-2-PrOH/W, for the three probes. These binary mixtures were chosen because they require different solvation schemes (see below).

Regarding these data, the following is relevant, where W and ROH refer to water, and the organic solvent, respectively:

(i) The quality of our data is shown by r_{mult}, ΣQ and the excellent agreement between experimental and calculated values of $E_T(\text{probe})_{\text{ROH}}$, and $E_T(\text{probe})_W$. At 25 °C, our $E_T(\text{probe})_{\text{ROH}}$ values agree with literature values, and this agreement was employed as another criterion for solvent purity. The two exceptions are RB and QB in 2-Me-2-PrOH, where the differences are 1.1 and 2.4 kcal mol^{-1}, respectively.

(ii) $E_T(\text{probe})_{\text{ROH}}$ decreases as a function of increasing T. This can be attributed to a decrease of solvent stabilization of the probe ground state, as a result of the concomitant decrease in solvent structure and H-bonding ability.[8b,e]

(iii) In the Onsager model of continuum dielectrics, the solute–solvent interaction energy, E, is given by

$$E = [-\mu^2 f(D)]/2r^3 \tag{2}$$

where μ and r are the dipole moment and radius, respectively, of the solute, and $f(D)$ is the Onsager dielectric function, given by $f(D) = 2(D - 1)/(2D + 1)$, where D is the solvent static dielectric constant. If the binary mixtures studied were ideal, then $f(D)$ of the mixture would be given by

$$f(D)_{\text{ROH/W}} = \chi_W f(D)_W + \chi_{\text{ROH}} f(D)_{\text{ROH}} \tag{3}$$

that is, $f(D)_{\text{ROH/W}}$ and the corresponding $E_T(\text{probe})_{\text{ROH/W}}$ are expected to be linear functions in χ_W.[2] Based on published dielectric constants of aqueous alcohols,[10] we correlated $f(D)$ with χ_W and obtained the following correlation coefficients: MeOH, 0.9977; EtOH, 0.9997; 1-PrOH, 0.9873; 2-Me-2-PrOH, 0.9951; ED, 0.9986; and MeOEtOH, 0.9943. That is, although Eqn. (3) applies satisfactorily to these binary mixtures, the dependence of E_T on χ_W is not linear in *all* cases, as shown in Figs 2–5. Specifically, the polarities of all ROH/W mixtures are lower than expected, based on the linear, i.e. ideal, relationship of $f(D)_{\text{ROH/W}}$ versus χ_W.

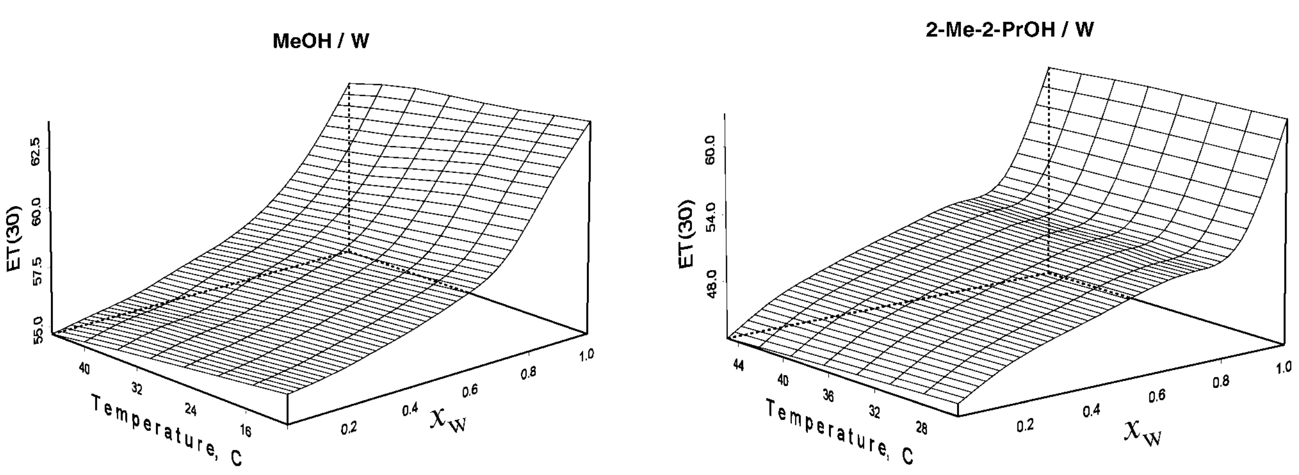

Figure 3. Solvent polarity–temperature–solvent composition contours for RB in MeOH/W and 2-Me-2-PrOH/W. $E_T(30)$ in pure water was calculated from the data of Tables 1. The following comments apply to this and subsequent figures: E_T(probe) is in kcal mol^{-1}; for better visualization of the contour, a larger number of intersections at the T and χ_W axes (than the number of data points) was employed

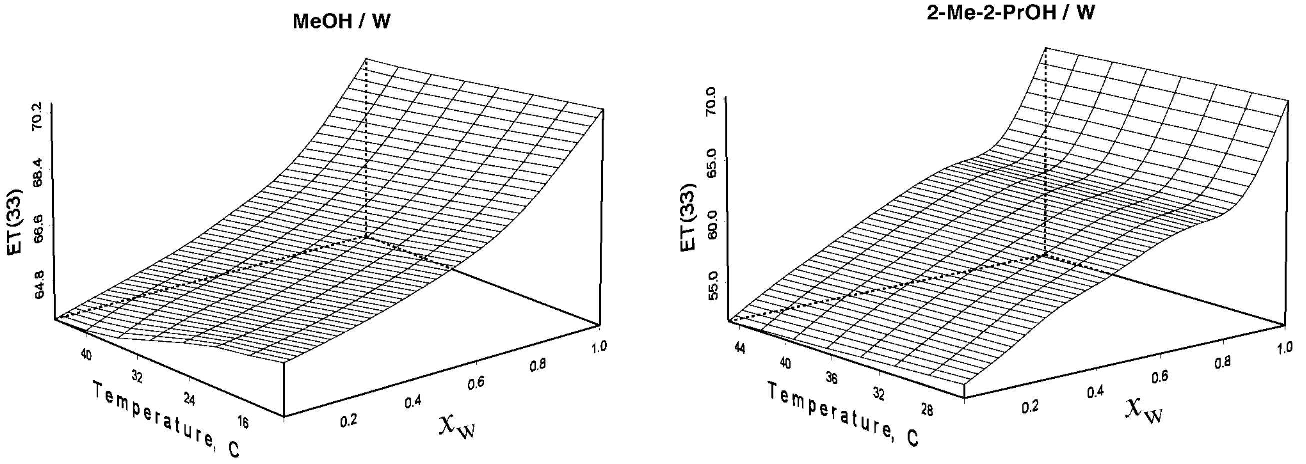

Figure 4. Solvent polarity–temperature–solvent composition contours for WB in MeOH/W and 2-Me-2-PrOH/W

(iv) As discussed elsewhere,[4–6,8,9,11] the reason for this non-ideal behavior is 'preferential solvation' of the probe by one component of the binary mixture. In principle, this phenomenon includes contributions from (a) 'dielectric enrichment' of the probe solvation micro-sphere in the solvent of higher dielectric constant, due to non-specific solute–solvent interactions, and (b) specific probe–solvent interactions, e.g. H-bonding. Non-linear behavior also results from solvent micro-heterogeneity, i.e. where one component of the mixed solvent prefers a molecule of the same type. This phenomenon leads to probe solvation by a cluster of one component of the mixture.

(v) Dielectric enrichment implies a positive deviation from ideality, i.e. the plot of $E_T(\text{probe})_{ROH/W}$ versus χ_W should lie above the straight line that connects $E_T(\text{probe})_{ROH}$ and E_T $(\text{probe})_W$. Since Figs 2–5 shows that this is not the case, the above-mentioned mechanism will not be considered any further. Probe–solvent interactions and solvent micro-heterogeneity should contribute to the observed non-ideality. Although there is some controversy with regard to cluster formation in aqueous MeOH and EtOH,[12a,b] we take the view that some clustering occurs in all aqueous ROH, the intensity of which increases as a function of increasing hydrophobic character of the alcohol.[8e,11,12c–f] In the next section, we quantify this preferential solvation by using different models, and discuss the dependence of the results obtained on the structure of the probe and temperature.

Quantitative treatment of preferential solvation: the solvent fractionation factor, φ

Details of the calculation of all quantities discussed below are given in the Calculations section below. A simple way to express the *overall* preferential solvation is to use the solvent fractionation factor, φ. This concept has been discussed elsewhere,[2–5] so that only the essentials will be given here. Consider solvation of the probe by ROH, by W and by the solvent complex ROH–W. We focus on solvent molecules that constitute the probe solvation micro-sphere. For simplicity, we assume

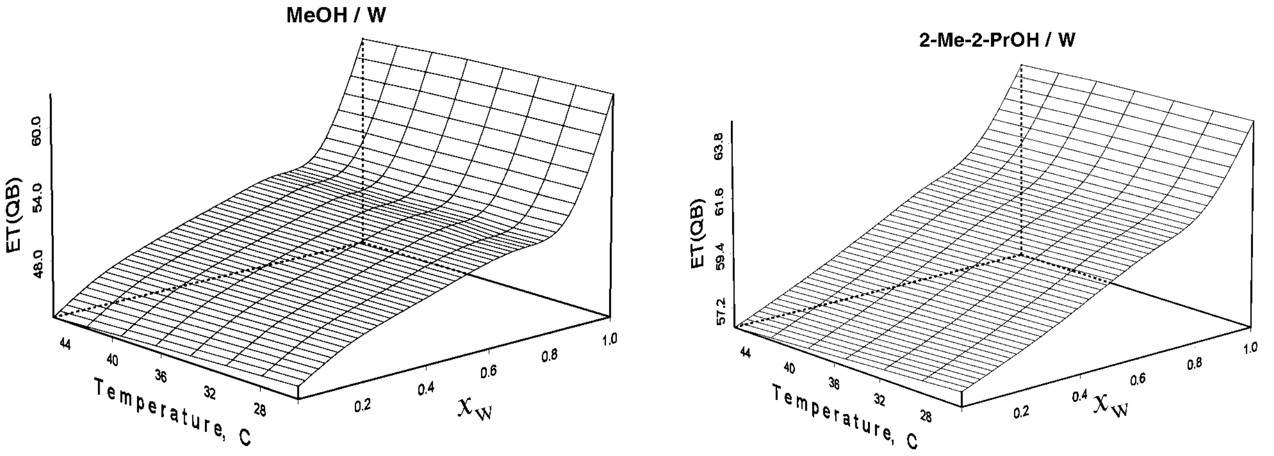

Figure 5. Solvent polarity–temperature–solvent composition contours for QB in MeOH/W and 2-Me-2-PrOH/W

Table 1. Results of application of Eqn. ((14)) to aqueous MeOH, 1-PrOH and 2-Me-2-PrOH at 25 °C

ROH	Probe	Range of χ_W	m	$\varphi_{W/ROH}$	$E_T(\text{Probe})_{ROH}$[a]	$E_T(\text{Probe})_W$[a]	SD[b]	$\sum Q$[b]
MeOH	RB	0–1.0	1.23	0.214	55.521 [−0.138]	63.029 [−0.063]	0.134	8.1×10^{-7}
	WB	0–1.0	1.03	0.349	64.540 [−0.021]	70.038 [−0.020]	0.031	1.1×10^{-5}
	QB	0–1.0	1.01	0.373	60.753 [0.340]	64.788 [0.016]	0.034	9.9×10^{-8}
1-PrOH	RB	0–1.0	0.54	0.166	50.831 [0.030]	62.977 [−0.100]	0.169	6.1×10^{-7}
	WB	0–0.5	1.10	2.444	59.460 [0.019]	63.287 [0.022]	0.043	7.5×10^{-5}
		0.5–1.0	1.52	0.0182	62.386 [−0.342]	70.298 [−0.083]	0.233	5.2×10^{-6}
	QB	0–1.0	0.73	0.362	58.995 [0.070]	64.920 [−0.067]	0.107	3.1×10^{-9}
2-Me-2-PrOH	RB	0–0.5	0.53	0.106	44.394 [−0.011]	49.644 [−0.110]	0.128	1.4×10^{-6}
		0.5–1.0	0.89	0.074	49.123 [−0.269]	63.585 [−0.014]	0.241	2.3×10^{-6}
2-Me-2-PrOH	WB	0–0.6	1.08	1.767	52.791 [0.059]	63.605 [0.102]	0.143	3.3×10^{-6}
		0.6–1.0	1.45	0.0224	60.857 [−0.321]	70.215 [−0.086]	0.279	1.6×10^{-5}
	QB	0–0.5	1.12	1.073	56.975 [−0.003]	62.230 [−0.017]	0.032	5.9×10^{-6}
		0.5–1.0	0.81	0.309	58.307 [−0.091]	64.695 [−0.038]	0.116	5.0×10^{-6}

[a] Calculated by regression. The values in brackets are $\Delta E_T(\text{Probe})_{ROH}$ = experimental $E_T(\text{Probe})_{ROH}$ − calculated $E_T(\text{Probe})_{ROH}$.

[b] SD = standard deviation; ΣQ = sum of the squares of the residues.

Table 2. Analysis of thermo-solvatochromic responses in binary solvent mixtures[a]

ROH	Probe	T (°C)	m	$\varphi_{W/ROH}$	$\varphi_{ROH\text{–}W/ROH}$	$\varphi_{ROH\text{–}W/W}$	E_T (Probe)$_{ROH}$[b]	E_T (Probe)$_W$[b]	SD[c]	ΣQ[c]
MeOH	RB	10	1.34	0.187			56.074 [−0.196]	63.588 [−0.017]	0.144	5.0×10^{-6}
		25	1.23	0.214			55.521 [−0.138]	63.029 [−0.063]	0.134	8.1×10^{-7}
		35	1.07	0.239			55.141 [−0.099]	62.701 [−0.018]	0.079	4.1×10^{-8}
		45	1.06	0.260			54.745 [−0.093]	62.019 [−0.013]	0.068	1.7×10^{-8}
	WB	10	1.07	0.340			65.265 [−0.055]	70.502 [−0.023]	0.039	2.1×10^{-8}
		25	1.03	0.349			64.540 [−0.021]	70.038 [−0.020]	0.031	1.1×10^{-5}
		35	1.01	0.357			64.083 [0.009]	69.712 [−0.010]	0.040	1.6×10^{-5}
		45	0.96	0.369			63.581 [−0.052]	69.516 [−0.043]	0.041	
	QB	10	1.20	0.353			61.168 [−0.066]	64.827 [0.169]	0.071	4.3×10^{-7}
		25	1.03	0.361			60.791 [−0.022]	64.777 [0.045]	0.041	4.2×10^{-6}
		35	1.00	0.368			60.559 [0.0017]	64.584 [0.023]	0.044	-4.1×10^{-7}
		45	0.98	0.368			60.398 [−0.028]	64.360 [−0.008]	0.054	-4.3×10^{-7}
MeOEtOH/W	RB	10	1.17	0.088			53.049 [−0.180]	63.592 [−0.21]	0.144	2.3×10^{-7}
		25	1.07	0.115			52.338 [−0.164]	62.664 [−0.024]	0.138	1.0×10^{-5}
		35	1.00	0.132			51.826 [−0.184]	62.727 [−0.44]	0.134	8.4×10^{-6}
		45	0.97	0.156			51.305 [−0.139]	62.067 [−0.061]	0.146	4.6×10^{-6}
	WB	10	1.03	0.216			60.829 [−0.177]	70.755 [−0.071]	0.111	2.0×10^{-6}
		25	0.97	0.245			60.017 [−0.064]	70.325 [−0.101]	0.097	4.8×10^{-7}
		35	0.94	0.262			59.520 [−0.078]	69.980 [−0.082]	0.071	1.2×10^{-7}
		45	0.93	0.268			59.086 [−0.074]	69.627 [−0.044]	0.052	6.2×10^{-9}
	QB	10	1.14	0.177			60.077 [−0.017]	65.044 [0.048]	0.037	7.0×10^{-8}
		25	1.08	0.199			59.634 [0]	64.828 [0.350]	0.039	1.1×10^{-6}
		35	1.06	0.203			59.401 [−0.020]	64.676 [0.032]	0.052	4.5×10^{-7}
		45	1.03	0.224			59.094 [−0.057]	64.428 [0.025]	0.062	1.7×10^{-7}
ED/W	RB	10	1.18	0.221			56.790 [−0.061]	63.459 [0.112]	0.086	6.6×10^{-8}
		25	1.13	0.230			56.394 [−0.034]	62.940 [0.026]	0.074	2.4×10^{-6}
		35	1.08	0.233			56.048 [−0.025]	62.687 [−0.003]	0.062	4.2×10^{-6}
		45	1.08	0.244			55.780 [−0.024]	62.003 [0.003]	0.046	2.8×10^{-6}
	WB	10	1.05	0.312			66.381 [−0.039]	70.662 [−0.036]	0.053	4.7×10^{-6}
		25	1.05	0.318			65.822 [−0.033]	70.129 [0.009]	0.036	5.5×10^{-8}
		35	0.99	0.321			65.446 [−0.019]	69.915 [−0.009]	0.025	1.2×10^{-8}
		45	0.98	0.324			65.067 [0.010] ;	69.616 [−0.050]	0.043	2.4×10^{-7}
	QB	10	1.18	0.258			62.321 [−0.017]	65.087 [0.020]	0.047	6.4×10^{-6}
	QB	25	1.11	0.263			62.066 [−0.004]	64.878 [0.022]	0.031	1.1×10^{-6}
		35	1.07	0.271			61.894 [−0.014]	64.6874 [0.007]	0.034	1.2×10^{-8}
		45	1.06	0.280			61.700 [0.007]	64.476 [0.021]	0.032	4.8×10^{-6}
EtOH	RB	10	3.88	0.207	11.230	54.251	52.541 [−0.080]	63.379 [−0.192]	0.121	1.7×10^{-6}
		25	3.35	0.219	7.116	32.493	52.434 [−0.083]	62.879 [0.087]	0.171	1.8×10^{-5}
		35	3.30	0.371	11.008	29.671	51.911 [−0.105]	62.946 [−0.163]	0.204	1.2×10^{-5}
		45	3.26	0.428	10.872	25.402	51.463 [−0.120]	62.021 [−0.015]	0.203	3.0×10^{-5}
	WB	10	3.36	0.175	3.947	22.554	61.819 [0.008]	70.018 [0.088]	0.097	1.3×10^{-6}
		25	2.74	0.227	3.297	14.524	61.111 [−0.039]	69.939 [−0.083]	0.072	1.1×10^{-5}
		35	2.40	0.240	2.683	11.179	60.397 [−0.017]	69.768 [−0.063]	0.131	1.8×10^{-5}
		45	2.38	0.327	3.239	9.905	59.995 [0.040]	69.415 [−0.035]	0.117	1.9×10^{-4}
	QB	10	2.74	0.163	2.119	13.000	59.676 [−0.004]	65.049 [0.013]	0.032	4.6×10^{-7}
		25	2.50	0.114	1.404	12.316	59.333 [0.004]	64.881 [−0.003]	0.025	5.1×10^{-5}
		35	2.28	0.104	1.118	10.750	59.096 [−0.011]	64.758 [−0.006]	0.025	3.0×10^{-6}
		45	2.26	0.109	1.168	12.716	58.883 [−0.017]	64.516 [−0.012]	0.038	5.3×10^{-5}

Table 2. Continued.[a]

ROH	Probe	T (°C)	m	$\varphi_{W/ROH}$	$\varphi_{ROH-W/ROH}$	$\varphi_{ROH-W/W}$	E_T (Probe)$_{ROH}$[b]	E_T (Probe)$_W$[b]	SD[c]	ΣQ[c]
1-PrOH	RB	10	2.47	0.083	4.582	55.205	51.385 [−0.044]	63.571 [0.001]	0.079	7×10^{-6}
		25	2.40	0.052	2.972	57.154	50.905 [−0.044]	62.965 [0.001]	0.081	8×10^{-5}
		35	2.32	0.044	2.438	55.409	50.532 [0.001]	62.682 [0.001]	0.058	3×10^{-5}
		45	2.23	0.053	2.352	44.377	50.086 [0.027]	62.005 [0.001]	0.066	7.6×10^{-7}
	WB	10	3.51	0.065	6.175	95.000	60.601 [−0.220]	70.807 [−0.060]	0.170	5.2×10^{-6}
		25	3.24	0.059	4.947	83.847	59.654 [−0.175]	70.308 [−0.093]	0.146	1.5×10^{-6}
		35	3.14	0.046	3.776	82.087	59.195 [−0.160]	69.981 [−0.070]	0.120	1.5×10^{-6}
		45	2.97	0.042	2.953	70.310	58.746 [−0.220]	69.667 [−0.060]	0.120	1.2×10^{-5}
	QB	10	2.54	0.142	2.387	16.810	59.399 [−0.044]	64.928 [−0.036]	0.056	1.2×10^{-6}
		25	2.24	0.083	1.354	16.313	59.135 [0.030]	64.811 [−0.058]	0.058	2.8×10^{-8}
		35	2.90	0.090	1.051	12.663	58.874 [0.053]	64.653 [−0.047]	0.059	2.6×10^{-6}
		45	1.84	0.146	1.303	8.925	58.410 [0.098]	64.460 [−0.057]	0.0840	8.9×10^{-6}
2-PrOH	RB	10	2.52	0.066	2.660	40.303	48.815 [0.002]	63.997 [−0.007]	0.127	7.6×10^{-8}
		25	2.36	0.052	2.011	38.673	48.265 [0.011]	62.966 [0]	0.064	2.1×10^{-6}
		35	2.29	0.042	1.598	38.048	47.926 [−0.018]	62.681 [0.002]	0.059	1×10^{-6}
		45	2.26	0.047	1.490	31.702	47.554 [−0.028]	62.006 [0]	0.053	6.6×10^{-8}
	WB	10	3.19	0.163	6.657	40.840	56.761 [0.142]	70.472 [−0.031]	0.183	-6.1×10^{-5}
		25	3.01	0.115	4.690	40.783	56.087 [−0.187]	70.027 [−0.025]	0.126	4.9×10^{-6}
		35	2.93	0.090	3.649	40.544	55.714 [−0.059]	69.770 [−0.043]	0.087	2.5×10^{-7}
		45	2.78	0.069	2.780	40.290	55.346 [−0.140]	69.469 [−0.006]	0.118	-2.5×10^{-7}
	QB	10	2.77	0.169	4.197	24.834	58.146 [−0.015]	64.934 [−0.036]	0.077	2.8×10^{-7}
		25	2.68	0.117	2.881	24.624	57.768 [0.014]	64.662 [0.014]	0.044	2.9×10^{-7}
		35	2.54	0.099	2.389	24.131	57.600 [0.032]	64.532 [0.016]	0.077	1.1×10^{-5}
		45	2.46	0.087	2.084	23.954	57.345 [−0.007]	64.330 [−0.015]	0.109	4.1×10^{-6}
2-Me-2-PrOH	RB	25	2.24	0.120	3.506	29.217	44.062 [−0.153]	62.986 [−0.020]	0.161	1.5×10^{-4}
		35	2.12	0.106	3.077	29.028	43.517 [−0.130]	62.688 [−0.005]	0.108	4.8×10^{-5}
		45	2.06	0.098	2.827	28.847	42.909 [−0.101]	62.010 [−0.004]	0.094	1.7×10^{-5}
	WB	25	2.84	0.073	3.501	47.959	53.039 [−0.190]	70.286 [−0.160]	0.230	4×10^{-6}
		35	2.75	0.066	3.091	46.833	52.715 [−0.450]	70.033 [−0.200]	0.280	2.9×10^{-6}
		45	2.62	0.059	2.687	45.542	52.023 [−0.255]	69.551 [−0.096]	0.224	5.9×10^{-7}
	QB	25	2.50	0.056	1.556	27.786	57.015 [−0.040]	64.680 [−0.023]	0.047	2.5×10^{-6}
		35	2.34	0.058	1.390	23.966	56.697 [−0.018]	64.561 [−0.006]	0.026	3.8×10^{-7}
		45	2.25	0.047	1.173	21.957	56.446 [−0.058]	64.348 [−0.011]	0.058	1.3×10^{-5}

[a] Regression analysis was carried out by using Eqn. ((14)) for MeOH, MeOEtOH and ED and Eqn. ((11)) for the remaining alcohols.

[b] Calculated by regression. The values in brackets are $\Delta E_T(\text{Probe})_{\text{solvent}}$ = experimental $E_T(\text{Probe})_{\text{Solvent}}$ − calculated $E_T(\text{Probe})_{\text{Solvent}}$.

[c] SD = standard deviation; ΣQ = sum of the squares of the residues.

that ROH–W only forms *within* this micro-sphere, by interaction of its two components, and that these are present in equal numbers. One can write the following solvent-exchange equilibria:

$$\text{Probe(ROH)}_m + m\text{W} \rightleftharpoons \text{Probe(W)}_m + m\ \text{ROH} \tag{4}$$

$$\text{Probe(ROH)}_m + \frac{m}{2}\text{W} \rightleftharpoons \text{Probe(ROH-W)}_m + \frac{m}{2}\text{ROH} \tag{5}$$

$$\text{Probe(W)}_m + \frac{m}{2}\text{ROH} \rightleftharpoons \text{Probe(ROH-W)}_m + \frac{m}{2}\text{W} \tag{6}$$

where *m* represents the number of solvent molecules whose exchange in the probe solvation micro-sphere affects its E_T. The equilibrium constant for each of the above solvent-exchange reactions is its solvent fractionation factor, φ. Equations ((4)–(6)) yield three fractionation factors, $\varphi_{\text{W/ROH}}$ (water substituting alcohol in the solvation shell), $\varphi_{\text{ROH–W/ROH}}$ (solvent complex, (ROH–W)$_m$, substituting alcohol in the solvation shell), and $\varphi_{\text{ROH–W/W}}$ [solvent complex, (ROH–W)$_m$, substituting water in the solvation shell]. These fractionation factors are given by

$$\varphi_{\text{W/ROH}} = \frac{\text{Probe(W)/Probe(ROH)}}{\text{(W)/(ROH)}} \tag{7}$$

$$\varphi_{\text{ROH--W/ROH}} = \frac{\text{Probe(ROH}-\text{W)}_m\text{/Probe(ROH)}}{\sqrt{(\text{W/ROH})^m}} \tag{8}$$

$$\varphi_{\text{ROH--W/W}} = \frac{[\text{Probe(ROH}-\text{W)}_m\text{/Probe(W)}]}{\sqrt{(\text{ROH/W})^m}} \tag{9}$$

That is, $\varphi_{\text{W/ROH}}$ describes the preference of W for the probe solvation micro-sphere, relative to bulk solvent. Note that $\varphi_{\text{W/ROH}} > 1$ means that the solvation shell of the probe is richer in W than bulk solvent. The converse of this argument shows that $\varphi_{\text{W/ROH}} < 1$ means that the probe is preferentially solvated by ROH. Finally, a solvent fractionation factor of unity is expected for an ideal binary mixture, provided that there are no specific or non-specific probe–solvent interactions. The same line of reasoning applies to $\varphi_{\text{ROH–W/ROH}}$ and $\varphi_{\text{ROH–W/W}}$. Two special cases will also be considered, namely the probe solvation micro-sphere is adequately described by Eqn. (4), and the solvation shell composition is described by Eqns ((4)–(6)), with $m = 2$.[5]

The model to choose should fit the data accurately (i.e. with the smallest error), and agree with chemistry. The latter point has been stressed, e.g. in fitting spectroscopic and rate data to particular models.[13] We analyze the simplest scheme, i.e. that based on Eqn. (4), for aqueous MeOH, 1-PrOH and 2-Me-2-PrOH. The reason is that these alcohols give different types of E_T versus χ_W plots for all probes, as shown in Fig. 2. The other ROH studied showed plots similar to one of these three alcohols.

Table 1 shows the results of application of the simple model to the above-mentioned binary mixtures at 25 °C. This model applies satisfactorily to aqueous MeOH, i.e. the *whole* E_T versus χ_W plot can be calculated by using a *single* $\varphi_{\text{W/ROH}}$. As can be seen, the value of *m* for MeOH is practically unity for all probes investigated, and the same conclusion applies to aqueous MeOEtOH and ED (results not shown). For the other two alcohols (and the remaining ROH), no single $\varphi_{\text{W/ROH}}$ describes satisfactorily the whole χ_W range, i.e. the latter should be (arbitrarily) divided into two ranges. This division, however, results in $\varphi_{\text{W/ROH}}$ that is noticeably larger in the lower range of χ_W (0–0.5) than in the corresponding upper range. That is, the probe is solubilized by the solvent component, which is present in lower concentration, W in the water-poor region and ROH in the alcohol-poor region. This anomaly, and the abrupt decrease in $\varphi_{\text{W/ROH}}$ that occurs at $\chi_W \approx 0.5$, may indicate that the description of solvation in terms of Eqn. (4) is an over-simplification for some alcohols.

Equations ((4)–(6)) were applied to solvatochromic data in aqueous EtOH, 1-PrOH and 2-Me-2-PrOH, at 25 °C. Calculations were carried out by considering that *m* is either fixed at 2, or variable. The results obtained (not listed) have shown that both models can be conveniently employed. We subscribe to the latter, however, because it represents a more general solvation scheme; the results of calculations are given in Table 2.

Before addressing Table 2, it is worthwhile to summarize some points that bear on effects of increasing *T* on the binary mixtures studied. Alcohol molecules associate with water, and with each other through H-bonds and hydrophobic interactions.[14a] Simple (i.e. unsubstituted) alcohols are more basic than water, and can only participate in two H-bonds (water participates in four H-bonds). Therefore, W–ROH H-bonds are stronger but more disordered than water–water H-bonds.[14b] Several experimental techniques, including fluoresence,[8e,12f] NMR,[12d,14c] dielectric relaxation[14a] and calculations of the Kirkwood–Buff integral functions,[12e,14b,d] have indicated that the tendency of the binary mixture to segregate into 'clusters' of water and alcohol increases as a function of increasing *T*, a consequence of the decreased water–alcohol interactions.

Examination of Table 2 yields the following pieces of information:

(i) As discussed above, solvatochromic data in aqueous MeOH, MeOEtOH and ED are conveniently described by Eqn. (4), with $m \approx 1$, this being the reason for the absence in Table 2 of $\varphi_{\text{ROH–W/ROH}}$ and $\varphi_{\text{ROH–W/W}}$. LogP_{oct} {the partition coefficient of a substance between 1-octanol and water, i.e. log([substance]$_{\text{octanol}}$/[substance]$_{\text{water}}$)} is a quantitative measure of the hydrophilic character of a substance. LogP_{oct} values are −0.77, −0.77, −1.36, −0.31, 0.25, 0.05, and 0.35 for MeOH, 2-MeOEtOH, ED, EtOH, 1-PrOH, 2-PrOH and 2-Me-2-

PrOH, respectively,[15] that is, MeOH, MeOEtOH and ED are more hydrophilic than the remaining alcohols. Whether the adequacy of the simple model is due to the ‘water-like’ character of these alcohols is an open question, and calls for more work on the solvatochromism of structurally different probes in their binary mixtures.

(ii) The following trends are observed as a function of increasing T: a decrease in m, an increase in $\varphi_{\mathrm{W/ROH}}$ for binary mixtures where solvation is described by Eqn. (4) and a decrease in $\varphi_{\mathrm{ROH\text{–}W/ROH}}$ and $\varphi_{\mathrm{ROH\text{–}W/W}}$ for solvents where solvation is described by Eqns ((4)–(6)).

(iii) For the former series of binary mixtures, the increase of $\varphi_{\mathrm{W/ROH}}$ may be attributed to the fact that temperature increase affects the structure of ROH more than that of water. Consequently, water–probe H-bonding is less susceptible to temperature increase than its alcohol–probe counterpart. This leads to a measurable ‘depletion’ of ROH in the probe solvation micro-sphere, so that $\varphi_{\mathrm{W/ROH}}$ increases. It is relevant, however, that all $\varphi_{\mathrm{W/ROH}}$ are smaller than unity, i.e. the probes are preferentially solvated by ROH in the temperature range studied.

(iv) For the remaining binary mixtures, we address the response (a small but persistent decrease) of $\varphi_{\mathrm{ROH\text{–}W/ROH}}$ and $\varphi_{\mathrm{ROH\text{–}W/W}}$ to increasing temperature, since both fractionation factors are much larger than $\varphi_{\mathrm{W/ROH}}$. Preferential ‘clustering’ of water and alcohol as a function of increasing T means that the strength of W–ROH interactions also decreases in the same direction,[12e,14b,d,e] with a concomitant decrease in the ability of the mixed solvent to displace both water and alcohol.

(v) We note that m decreases as a function of increasing T, independent of the nature of the probe and the solvation model employed. That is, a temperature increase leads to gradual desolvation of the probe. This is an important result because the solvatochomic response of these probes to an experimental variable (e.g. composition of the binary mixture) has been employed to gain insight into the mechanisms of, *inter alia*, solvolytic reactions.[2,7] The transition states of these reactions contain several solvent molecules,[1,16] the number of which may vary as a result of changing T. This fact should be considered when kinetic-based data (e.g. activation parameters and solvent kinetic isotope effects) are employed to probe reaction mechanisms.

CONCLUSIONS

The solvatochromic response of the probes studied can be described in terms of a general solvent-exchange mechanism in which water and/or water–alcohol complexes displace the alcohol and/or water present in the probe solvation microsphere. Temperature effects on solvent fractionation factors have been rationalized in terms of structures of water and alcohol, and their mutual interactions. A temperature increase results in gradual desolvation of *every* probe, in *all* binary mixtures. This is relevant to reactions whose transition states are highly solvated.

CALCULATIONS

Preferential solvation parameters

Consider a probe whose solvation shell is composed of W, ROH and the solvent complex ROH–W. E_{T} is given by the polarities of these components, $E_{\mathrm{T}}^{\mathrm{W}}$, $E_{\mathrm{T}}^{\mathrm{ROH}}$ and $E_{\mathrm{T}}^{\mathrm{ROH\text{--}W}}$, respectively, multiplied by the corresponding mole fractions in the probe solvation micro-sphere, $\chi_{\mathrm{Probe(W)}}$, $\chi_{\mathrm{Probe(ROH)}}$ and $\chi_{\mathrm{Probe(ROH\text{–}W)}}$, respectively:

$$E_{\mathrm{T}} = \chi_{\mathrm{Probe(W)}} E_{\mathrm{T}}^{\mathrm{W}} + \chi_{\mathrm{Probe(ROH)}} E_{\mathrm{T}}^{\mathrm{ROH}} + \chi_{\mathrm{Probe(ROH\text{--}W)}} E_{\mathrm{T}}^{\mathrm{ROH\text{--}W}} \qquad (10)$$

Substituting Eqn. (7) and (8) into Eqn. (10) gives

$$E_{\mathrm{T}} = E_{\mathrm{T}}^{\mathrm{ROH}} + \frac{a(\chi_{\mathrm{W}})^m + b\sqrt{[(1-\chi_{\mathrm{W}})\chi_{\mathrm{W}}]^m}}{(1-\chi_{\mathrm{W}})^m + \varphi_{\mathrm{W/ROH}}(\chi_{\mathrm{W}})^m + \varphi_{\mathrm{ROH\text{--}W/ROH}}\sqrt{[(1-\chi_{\mathrm{W}})_{\mathrm{W}}]^m}} \qquad (11)$$

where m is the number of solvent molecules in the probe solvation shell that affect its transition energy, and a and b are given by

$$a = \varphi_{\mathrm{W/ROH}}(E_{\mathrm{T}}^{\mathrm{W}} - E_{\mathrm{T}}^{\mathrm{ROH}}) \qquad (12)$$

$$b = \varphi_{\mathrm{ROH\text{--}W/ROH}}(E_{\mathrm{T}}^{\mathrm{ROH\text{--}W}} - E_{\mathrm{T}}^{\mathrm{ROH}}) \qquad (13)$$

A program in BASIC that relies on the S-Plus 2000 program package (MathSoft, Seattle, WA, USA) was written and employed to solve Eqn. ((11)). The input data included χ_{W}, the corresponding E_{T}, initial estimates for m, E_{T}(W), E_{T}(ROH), E_{T}(ROH–W), $\varphi_{\mathrm{(W/ROH)}}$ and $\varphi_{\mathrm{(ROH\text{–}W/ROH)}}$. The following are typical initial values for these parameters: $m = 2$, experimental values of E_{T}(W) and E_{T}(ROH) and $E_{\mathrm{T}}(\mathrm{ROH\text{–}W}) = [E_{\mathrm{T}}(\mathrm{ROH}) + E_{\mathrm{T}}(\mathrm{W})]/2$. The following equation was employed to calculate the remaining fractionation factor:

$$\varphi_{\mathrm{(ROH\text{–}W/W)}} = \varphi_{\mathrm{(ROH\text{–}W/ROH)}}/\varphi_{\mathrm{(W/ROH)}}$$

For MeOH/W, MeOEtOH/W and ED/W, solvation by ROH–W can be neglected, i.e. $\varphi_{\mathrm{ROH-W/ROH}} \rightarrow 0$, and Eqn. ((11)) is reduced to

$$E_{\mathrm{T}} = E_{\mathrm{T}}^{\mathrm{ROH}} + \frac{a(\chi_{\mathrm{W}})^m}{(1-\chi_{\mathrm{W}})^m + \varphi_{\mathrm{W/ROH}}(\chi_{\mathrm{W}})^m} \qquad (14)$$

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