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Thermo-solvatochromism of betaine dyes in aqueous alcohols: explicit consideration of the water–alcohol complex

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ABSTRACT: Thermo-solvatochromism of 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)-phenolate, 1-methylquinolinium-8-olate and 4-[2-(1-methylpyridinium-4-yl)ethenyl]-phenolate, in the temperature ranges 10–45 °C (methanol) and 10–60 °C (1- and 2-propanol) was investigated in binary water–alcohol mixtures. Thermo-solvatochromic data were treated according to a modified model that explicitly considers the presence of 1:1 water–alcohol species in bulk solution, and its exchange reactions with water and alcohol in the solvation micro-sphere of the probe employed. Concentrations of these complex species were calculated from density data. Plots of the empirical solvent polarity parameter, E_T, versus effective mole fraction of water in the binary mixtures indicate that the probes are preferentially solvated by the alcohol, except for one case. A temperature increase causes gradual desolvation of the probe, due to a decrease in the H-bonding abilities of all components of the binary solvent mixture. Copyright © 2003 John Wiley & Sons, Ltd.

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KEYWORDS: aqueous alcohols; thermo-solvatochromism; solvation; betaine dyes

INTRODUCTION

The study of solvatochromism has contributed a great deal to our understanding of effects of solvation on chemical phenomena. The UV–vis spectra, absorption or emission, of certain solvatochromic substances (hereafter designated as 'probes') are measured in solvents, and/or solvent mixtures and the data therefrom are employed to analyze both solvent–probe and solvent–solvent interactions.[1,2] Extensive use has been made of an empirical solvent polarity scale, E_T, calculated by

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

which converts the electronic transition within the probe into the corresponding intramolecular energy transition in $\mathrm{kcal\,mol^{-1}}$ (1 kcal = 4184 kJ). Zwitterionic probes have been extensively employed because of their favorable UV–vis spectral properties. Examples include 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-y)-phenolate (RB), 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)-phenolate (WB), 1-methylquinolinium-8-olate (QB) and 4-[2-(1-methylpyridinium-4-yl)ethenyl]-phenolate (MC). Their molecular structures are shown in Fig. 1; the corresponding solvent polarity scales are referred to as $E_T(30)$, $E_T(33)$, $E_T(\mathrm{QB})$ and $E_T(\mathrm{MC})$, respectively.

Solvatochromic data in pure solvents have been successfully analyzed by the Kamlet–Taft–Abboud equation which, for a single probe in a series of solvents, is given by[3]

$$SDP = \text{constant} + s(\pi^*_{\text{solv}} + \mathrm{d}\delta) + a\alpha_{\text{solv}} + b\beta_{\text{solv}} + h(\delta^2_H) \qquad (2)$$

where the solvent-dependent property, *SDP*, such as a solvatochromic shift, is modeled as a combination of a dipolarity/polarizability term $[s(\pi^*_{\text{solv}} + \mathrm{d}\delta)]$, two hydrogen-bonding terms, in which the solvent is the hydrogen-bond donor ($a\alpha_{\text{solv}}$), or the hydrogen-bond acceptor ($b\beta_{\text{solv}}$), and a cavity term $[(h(\delta^2_{\mathrm{H}})]$.

In binary solvent mixtures, solvatochromism is further complicated by the so-called 'preferential solvation' of the probe by one component of the mixture. In principle, this phenomenon includes contributions from probe-independent 'dielectric enrichment,' and specific probe–solvent interactions, e.g. H-bonding. The most significant consequence of preferential solvation is that compositions of the solvation shells of most probes are different from those of the corresponding bulk solvents. It is worth noting that these composition differences are probe and temperature dependent.

The preceding discussion raises several important points:[1–4]

(i) Solvent 'polarity' is a deceptively simple term that cannot be adequately described by a single physical

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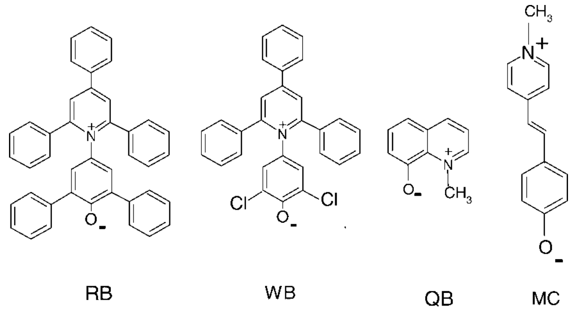

Figure 1. Molecular structures of solvatochromic probes

property of the medium, e.g. its dipole moment, dielectric constant, etc.

(ii) The regression coefficients of Eqn (2), i.e. *s*, *a* and *b*, are probe dependent. A clear understanding of probe–solvent interactions requires the study of probes of different structures, i.e. of different pK_a and hydrophobic/hydrophilic character. An example is that of RB and WB. Their pK_a values in water are very different, 8.65 and 4.78, but their regression coefficients *a* of Eqn (2) are similar, i.e. 14.45 and 15.30, respectively. This has been attributed to enhancement of coefficient (*a*) of WB [Eqn (2)], due to a combination of steric and inductive effects.[4b]

(iii) Thermo-solvatochromism describes the influence of temperature on solvatochromism. Its study adds another dimension, that of temperature, to solvent–solvent and solvent–solute interactions in pure and/or mixed solvents. Investigating temperature effects on solvation is important for understanding, *inter alia*, thermodynamic parameters of transfer of highly solvated ions, e.g. HO^- and F^-,[5] nucleophilic substitutions, including solvolytic reactions, and the quasi mirror-image behavior of the activation parameters of water-catalyzed, pH-independent reactions.[6]

Thermo-solvatochromism has been studied much less than solvatochromism, especially in binary solvent mixtures. An important aspect is the model employed to treat the data obtained, e.g. in binary mixtures of water (W) and alcohol (ROH).[4b,7] For example, data for W and methanol (MeOH) were explained by a simple model, where only the exchange between W and MeOH in the probe solvation micro-sphere (hereafter designated as 'micro-sphere') was considered. Other alcohols, e.g. 1-propanol (1-PrOH) and 2-propanol (2-PrOH), required a more elaborate model, where the presence of ROH–W, H-bonded alcohol–water species, needed to be considered.[4c,7] An assumption in the latter model is that ROH–W forms *only* in the micro-sphere. The present work addresses problems associated with this assumption, and puts forward a modified model for solvatochromism where formation of ROH–W in bulk solvent, and its exchange with both W and ROH in the micro-sphere are explicitly considered. The present model has been applied to the thermo-solvatochromism of WB, QB and MC in mixtures of W with MeOH (*T* range = 10–45 °C) and 1-PrOH and 2-PrOH (*T* range = 10–60 °C). To our knowledge, this is the first study on the thermo-solvatochromism of MC. For WB and QB, the temperatures previously studied were 10, 25, 35 and 45 °C,[4a] whereas those in the present study were 10, 25, 40 and 60 °C. Therefore, we also determined the thermo-solvatochromism of these probes in aqueous 1-PrOH and/or 2-PrOH at 40 and 60 °C.

EXPERIMENTAL

Materials. The solvents were purchased from Aldrich or Merck, and were purified by distillation from CaH_2, followed by storage over activated type 4 Å molecular sieves. Their purity was established from their densities (DMA 40 digital densimeter, Anton Paar, Graz, Austria) and from agreement between experimental E_T and published data (see below). The same equipment was employed to determine the densities of 2-PrOH–W mixtures at 15, 25, 35, 40 and 50 °C. Glass-distilled, de-ionized water was used throughout.

WB and QB were available from previous studies.[4] MC was synthesized as described elsewhere,[8] by condensation of 1,4-dimethylpyridium iodide with 4-hydroxybenzaldehyde, followed by base-induced elimination of HI, dehydration and crystallization from hot water. The product gave satisfactory elemental analysis (the Microanalysis Laboratory, this Institute).

Sample preparation. Binary mixtures (16 per set) were prepared by weight at 25 °C. Probe solutions in acetone (WB and/or QB) or ethanol (MC) were pipetted into 1 ml volumetric tubes, followed by drying under reduced pressure, over P_4O_{10}. Pure solvents and/ or binary solvent mixtures were added and the probe was dissolved with the aid of a tube rotator (Labquake, Lab Industries, Berkeley, CA, USA).

Spectrophotometric determination of E_T. The final probe concentration was (2–5 $\times 10^{-4}$ mol l^{-1}. UV–vis spectra of probe solutions showed no changes 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}. This was taken to indicate that no intermolecular probe interactions 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 Instrument, Yellow Springs, OH, USA). Each spectrum was recorded twice at a rate of 120 nm min^{-1} at 10, 25, 35 and 45 °C for MeOH–W and 10, 25, 40 and 60 °C for 1-PrOH/W and 2-PrOH/W. λ_{max} was determined from the first derivative of the absorption spectrum; the uncertainties in E_T were 0.1 kcal mol^{-1} for QB and $\leq$0.2 kcal mol^{-1} for WB and MC.

RESULTS AND DISCUSSION

A modified model for solvatochromism

Consider solvatochromism in an alcohol–water mixture of a certain water mole fraction, χ_W. Plots of E_T versus χ_W usually show deviations from linearity, i.e. from ideal behavior, because of the above-mentioned preferential solvation. Therefore, it is important to determine the composition of the micro-sphere, and to compare it with the bulk solvent composition. An example of solvent-exchange equilibrium is given below where, for simplicity, we consider that the probe solvatochromic response is affected by only one solvent molecule in the micro-sphere:

$$\text{Probe(ROH)} + \text{W} \rightleftharpoons \text{Probe(W)} + \text{ROH} \qquad (3)$$

$$\varphi_{\text{W/ROH}} = \left(\chi_{\text{w}}^{\text{Probe}}\right)\left(\chi_{\text{ROH}}^{\text{Bk}}\right) / \left(\chi_{\text{ROH}}^{\text{Probe}}\right)\left(\chi_{\text{W}}^{\text{Bk}}\right) \qquad (4)$$

which can be readily rearranged to

$$\varphi_{\text{W/ROH}} = \frac{\left(\chi_{\text{w}}^{\text{Probe}}\right) / \left(\chi_{\text{ROH}}^{\text{Probe}}\right)}{\left(\chi_{\text{w}}^{\text{Bk}}\right) / \left(\chi_{\text{ROH}}^{\text{Bk}}\right)} \qquad (5)$$

where Bk refers to bulk solvent. The equilibrium constant for the exchange reaction (3) is given by the solvent 'fractionation factor,' $\varphi_{\text{W/ROH}}$, which describes the preference of W for solvation shell of the probe, relative to bulk solvent, Eqn (5). $\varphi_{\text{W/ROH}} > 1$ indicates that the probe solvation shell is richer in W than bulk solvent, the converse is true for $\varphi_{\text{W/ROH}} < 1$. For ideal behavior, $\varphi_{\text{W/ROH}}$ is unity, because the solvent composition in the micro-sphere is the same as that of the bulk solvent.

Equation (3) describes one possible solvent-exchange reaction, that between W and ROH. Several pieces of evidence indicate, however, the formation of H-bonded ROH–W complexes. Examples are the observed non-ideal, i.e. non-linear, relationships between compositions and physico-chemical properties of binary mixtures, including densities, dielectric constants, NMR chemical shifts and relaxation times, dielectric relaxations and fluorescence lifetimes of dissolved probes.[9] Theoretical calculations, the Kirkwood–Buff integral functions (that describe W–W, ROH–ROH and ROH–W interactions) and mass spectrometry support the formation of ROH–W complexes.[10] Consequently, the presence and solvent exchange reactions of the species ROH–W should be also considered, along with those between W and ROH. The appropriate set of equations is as follows:[7]

$$\text{Probe(ROH)}_m + m\text{W} \rightleftharpoons \text{Probe(W)}m + m\text{ROH} \qquad (6)$$

$$\text{Probe(ROH)}_m + \frac{m}{2}\text{W} \rightleftharpoons \text{Probe(ROH–W)}_m + \frac{m}{2}\text{ROH} \qquad (7)$$

$$\text{Probe(W)}_m + \frac{m}{2}\text{ROH} \rightleftharpoons \text{Probe(ROH–W)}_m + \frac{m}{2}\text{W} \qquad (8)$$

where m represents the number of solvent molecules whose exchange in the micro-sphere affects E_T, usually ≤ 2. This model focuses on the formation of ROH–W in the micro-sphere, according to the equilibrium $\text{W} + \text{ROH} \rightleftharpoons 2\ \text{ROH–W}$. The coefficient 2 in the right-hand side of the equilibrium 'is necessary to keep the number of solvent molecules constant. This equilibrium should be considered an equilibrium between solvent structures more than between individual solvent molecules.'[7a] The convenience of this approach is that bulk [ROH–W] is not considered in the calculations, so that solvent fractionation factors are based on analytical concentrations of W and/or ROH.

This model has been successfully employed to fit E_T versus χ_W data.[4c,7] We would like to discuss, however, the following (chemical) aspects that are important, along with statistical criteria,[11] for accepting a model: (i) deviations from ideality of macroscopic properties of these mixtures have been explained on the basis of the presence of ROH–W complexes in bulk solution; (ii) at equilibrium, ROH–W in the micro-sphere should be in equilibrium with the same species in bulk solvent, and consequently, the concentration of ROH–W should be incorporated in the model; (iii) if, on the other hand, the (micro-sphere) assumption is maintained, then the model cannot describe the ideal case, i.e. where the micro-sphere composition is equal to the bulk solvent composition, because the former contains an additional species (ROH–W); (iv) although inclusion of the coefficient 2 in Eqns (6) and (7) leads to mathematically consistent equations,[7a] the (chemical) rationale for its use is not obvious.

What is required, therefore, is a model that considers explicitly the presence of ROH–W in bulk solution and takes into account its solvent-exchange reactions. A corollary is that E_T versus composition plots should be based on 'effective' not analytical [W] and [ROH], respectively. Equation (6), plus the following ones, describe the modified model:

$$\text{ROH} + \text{W} \rightleftharpoons \text{ROH–W} \qquad (9)$$

$$\text{Probe(ROH)}_m + m\text{(ROH–W)} \rightleftharpoons \text{Probe(ROH–W)}_m + m\text{ROH} \qquad (10)$$

$$\text{Probe(W)}_m + m\text{(ROH–W)} \rightleftharpoons \text{Probe(ROH–W)}_m + m\text{W} \qquad (11)$$

where m has its usual meaning. The resulting solvent-fractionation factors refer to the following solvent exchanges in the micro-spheres: $\varphi_{\text{W/ROH}}$ (water substituting alcohol), $\varphi_{\text{ROH-W/ROH}}$ (bulk solvent complex substituting alcohol) and $\varphi_{\mathrm{ROH\text{-}W/W}}$ (bulk solvent complex substituting water). In terms of mole fraction, they are given by the equations

$$\varphi_{\mathrm{W/ROH}} = \frac{\chi_w^{\mathrm{Probe}}/\chi_{\mathrm{ROH}}^{\mathrm{Probe}}}{\left(\chi_{\mathrm{W}}^{\mathrm{Bk;Effective}}/\chi_{\mathrm{ROH}}^{\mathrm{Bk;Effective}}\right)^m} \tag{12}$$

$$\varphi_{\mathrm{ROH-W/ROH}} = \frac{\chi_{\mathrm{ROH-W}}^{\mathrm{Probe}}/\chi_{\mathrm{ROH}}^{\mathrm{Probe}}}{\left(\chi_{\mathrm{ROH-W}}^{\mathrm{Bk;Effective}}/\chi_{\mathrm{ROH}}^{\mathrm{Bk;Effective}}\right)^m} \tag{13}$$

$$\varphi_{\mathrm{ROH-W/W}} = \frac{\chi_{\mathrm{ROH-W}}^{\mathrm{Probe}}/\chi_{\mathrm{W}}^{\mathrm{Probe}}}{\left(\chi_{\mathrm{ROH-W}}^{\mathrm{Bk;Effective}}/\chi_{\mathrm{W}}^{\mathrm{Bk;Effective}}\right)^m} \tag{14}$$

Regarding the application of this model to ROH–W mixtures, the following are relevant:

(i) Use of 1:1 stoichiometry for ROH–W, according to Eqn (9), is a practical and convenient assumption that has been employed elsewhere.[4c,7] Mixed solvents with a structure stoichiometry other than 1:1 can be regarded, to a good approximation, as mixtures of the 1:1 structure plus excess of a pure solvent. Additionally, the 1:1 model has been successfully employed in fitting results of spectroscopic techniques that are particularly suitable to determine the stoichiometry of ROH–W aggregates, e.g. ^{1}H NMR[12a,b] and FTIR.[12c]

(ii) Dependence of density and viscosity of binary mixtures can be used to probe the formation of ROH–W species. As given in Calculations section, we employed the first property in order to calculate the ROH–W association constant, K_{assoc}, of Eqn (9). Except for one temperature, the order is MeOH > 1-PrOH > 2-PrOH. The resulting species distribution, at 25 °C, is shown in Fig. 2. For MeOH–W mixtures, the concentration of the mixed species is appreciable; its maximum concentration is at $\chi_{\mathrm{W}} \approx 0.5$, in agreement with the maximum excess Gibbs free energy of mixing of these two solvents.[13]

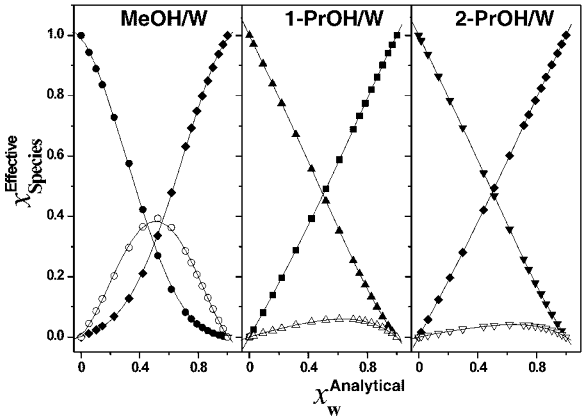

Figure 2. Species distribution for MeOH–W, 1-PrOH–W and 2-PrOH–W mixtures at 25 °C. W (◆); ROH (●, ▲, ▼); and ROH–W (○, △, ▽)

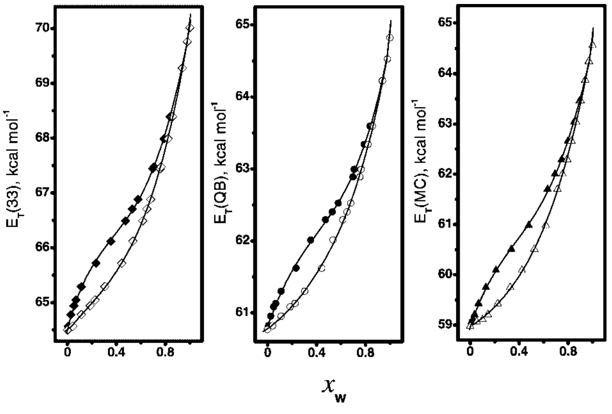

Figure 3. Dependence of solvent polarity scale, E_T(probe), on analytical, $\chi_{\mathrm{W}}^{\mathrm{Analytical}}$ (open symbols), and 'effective,' $\chi_{\mathrm{W}}^{\mathrm{Effective}}$ (solid symbols) water mole fraction for MeOH–W mixture at 25 °C

(iii) Figure 3 shows plots of E_T versus composition, where the latter is given as analytical, $\chi_{\mathrm{W}}^{\mathrm{Analytical}}$, and/or 'effective,' $\chi_{\mathrm{W}}^{\mathrm{effective}}$, water mole fractions (MeOH–W, 25 °C). The curves are visibly different, as can be seen, e.g., from the following regression analysis of E_T (33):

$$\begin{aligned} E_T(33) &= 64.456 + 2.982\chi_{\mathrm{W}}^{\mathrm{Analytical}} \\ &\quad - 2.788(\chi_{\mathrm{W}}^{\mathrm{Analytical}})^2 + 5.354(\chi_{\mathrm{W}}^{\mathrm{Analytical}})^3, \\ r &= 0.9998 \end{aligned}$$

$$\begin{aligned} E_T(33) &= 64.564 + 7.018\chi_{\mathrm{W}}^{\mathrm{Effective}} \\ &\quad - 10.237(\chi_{\mathrm{W}}^{\mathrm{Effective}})^2 + 8.676(\chi_{\mathrm{W}}^{\mathrm{Effective}})^3, \\ &= 0.9996 \end{aligned}$$

(iv) Rather than reporting extensive lists of E_T, we calculated its (polynomial) dependence on $\chi_{\mathrm{W}}^{\mathrm{Analytical}}$ and present the regression coefficients in Tables S1–S3 (see Supplementary Material, available at the epoc website at http://www.wiley.com/epoc). The degree of polynomial employed is that which gave the best data fit, as indicated by the multiple correlation coefficients, r_{mult}, and sums of the squares of the residuals, ΣQ. From the data in Tables S1–S3, K_{assoc} and the densities of W and ROH at different temperatures, the dependence of E_T on the 'effective' mole fractions of each species can be readily calculated, as given in the Calculations section.

Figures 4–6 show solvent polarity–temperature–solvent composition contours for the indicators studied in MeOH–W and 2-PrOH–W.

Based on Tables S1–S3 and the above-discussed modified model, we calculated the appropriate solvent fractionation factors, as given in the Calculations section. The results are given in Table 1, from which the following can be deduced.

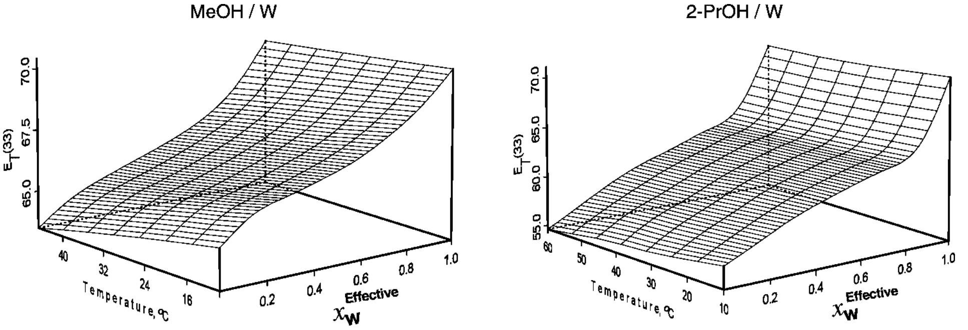

Figure 4. Solvent polarity–temperature–solvent composition contours for WB in MeOH–W and 2-PrOH–W

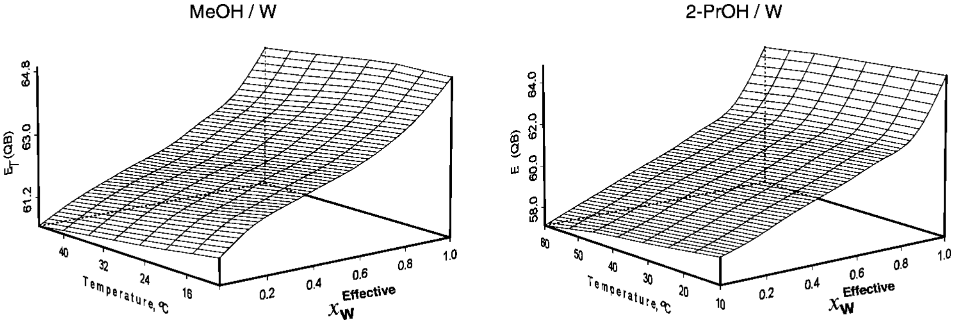

Figure 5. Solvent polarity–temperature–solvent composition contours for QB in MeOH–W and 2-PrOH–W

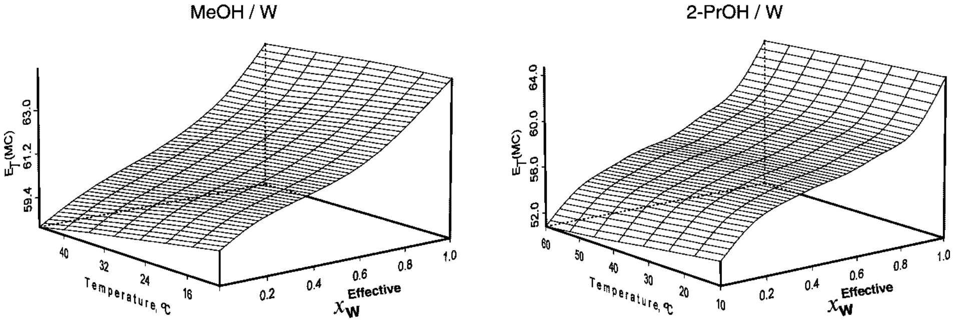

Figure 6. Solvent polarity–temperature–solvent composition contours for MC in MeOH–W and 2-PrOH–W

(i) The quality of our data is shown by the standard deviation, SD, ΣQ and the excellent agreement between experimental and calculated $E_T(\text{probe})_{\text{ROH}}$ and $E_T(\text{probe})_{\text{W}}$. At 25 °C, our $E_T(\text{probe})_{\text{ROH}}$ values agree with literature values, and this agreement was employed as another criterion for alcohol purity.

(ii) As a function of increasing temperature, $E_T(\text{probe})_{\text{ROH}}$, $E_T(\text{probe})_{\text{W}}$, $\varphi_{\text{ROH–W/ROH}}$ and $\varphi_{\text{ROH–W/W}}$ decrease, whereas $\varphi_{\text{W/ROH}}$ increases. The decrease in polarities of pure solvents can be attributed to a decrease in solvent stabilization of the probe ground state, as a result of the concomitant decrease in solvent structure and H-bonding ability.[14] Plots (not shown) of $E_T(\text{probe})_{\text{Solvent}}$ versus T gave excellent straight lines ($r \geq 0.995$ for 83% of the data), the (negative) slopes of which are given by $\Delta E_T(\text{probe})_{\text{Solvent}}$/degree ($\text{cal mol}^{-1}\,\text{K}^{-1}$). These were calculated for pure solvents; the order is $\Delta E_T(\text{probe})_{\text{ROH}} > \Delta E_T(\text{probe})_{\text{W}}$, reflecting the greater effect of temperature on the structure of ROH. Consequently, H-bonding of water with probe ground state is less susceptible to temperature increase than its ROH counterpart. The average $\Delta E_T(\text{probe})$ depends on the probe as shown by the following data [$\Delta E_T(\text{probe})_{\text{ROH}}$, $\Delta E_T(\text{probe})_{\text{W}}$, $\text{cal mol}^{-1}\,\text{K}^{-1}$]: -48 ± 3 and -28 ± 7 (WB); -23 ± 2 and -18 ± 3 (QB); -45 ± 4 and -16 ± 2 (MC). These data highlight the noticeable effect of temperature on solvation. This is relevant, e.g., for reactions where reagents and activated complexes have different polarities. If these probes are taken as models for polar activated complexes, provided that the reagents are not strongly solvated, then desolvation of the former complexes (in the temperature range 10–60 °C) may contribute as much as 1–2 kcal mol^{-1}, a sizeable amount relative to typical enthalpies of activation of organic reactions.

Table 1. Analysis of thermo-solvatochromic responses in binary water–alcohol mixtures

Solvent	Probe	T (°C)	m	$\varphi_{\mathrm{W/ROH}}$	$\varphi_{\mathrm{ROH-W/ROH}}$	$\varphi_{\mathrm{ROH-W/W}}$	E_{T} (probe)$_{\mathrm{ROH}}$[a]	E_{T} (probe)$_{\mathrm{W}}$[a]	SD[b]	ΣQ[b]
MeOH–W	WB	10	1.114	0.582	2.223	3.820	65.209 [−0.040]	70.439 [−0.012]	0.033	3.4×10^{-6}
		25	1.060	0.601	2.212	3.681	64.499 [0.001]	70.012 [0.016]	0.017	8.4×10^{-7}
		35	1.008	0.617	2.142	3.472	64.021 [−0.011]	69.771 [−0.001]	0.017	5.6×10^{-6}
		45	0.909	0.638	1.931	3.027	63.509 [−0.039]	69.526 [−0.004]	0.044	4.0×10^{-6}
	QB	10	1.066	0.360	1.262	3.506	61.129 [− 0.009]	64.903 [0.017]	0.023	1.4×10^{-7}
		25	0.950	0.381	1.172	3.076	60.770 [0.001]	64.800 [0.023]	0.034	-7.4×10^{-7}
		35	0.892	0.410	1.080	2.634	60.575 [0]	64.589 [0.018]	0.032	1.1×10^{-5}
		45	0.844	0.430	0.986	2.295	60.389 [−0.019]	64.415 [−0.005]	0.031	2.9×10^{-5}
	MC	10	1.247	0.339	1.431	4.221	59.549 [0.011]	64.660 [0.030]	0.029	1.9×10^{-6}
		25	1.092	0.375	1.416	3.776	58.968 [0.012]	64.558 [0.002]	0.023	4.5×10^{-6}
		35	1.039	0.392	1.370	3.460	58.621 [−0.021]	64.409 [−0.029]	0.037	4.5×10^{-6}
		45	0.974	0.403	1.227	3.045	58.170 [0]	64.185 [0.015]	0.039	5.4×10^{-6}
1-PrOH–W	WB	10	1.855	0.256	172.026	671.977	60.016 [−0.136]	70.877 [−0.027]	0.142	2.0×10^{-6}
		25	1.700	0.265	149.208	563.049	59.085 [−0.078]	70.323 [−0.043]	0.096	1.5×10^{-6}
		40	1.571	0.271	135.138	498.664	58.381 [−0.141]	69.885 [−0.035]	0.084	-4.4×10^{-5}
		60	1.451	0.282	125.024	443.348	57.408 [−0.087]	69.119 [−0.069]	0.139	1.8×10^{-5}
	QB	10	1.481	0.289	30.352	105.352	59.141 [−0.034]	64.766 [−0.006]	0.040	1.1×10^{-5}
		25	1.360	0.305	29.599	97.046	58.650 [−0.060]	64.546 [−0.016]	0.032	2.0×10^{-7}
		40	1.218	0.319	20.001	62.699	58.491 [−0.046]	64.250 [0]	0.032	9.9×10^{-7}
		60	1.019	0.324	9.963	30.750	58.043 [−0.045]	64.034 [−0.017]	0.049	5.7×10^{-5}
	MC	10	1.450	0.261	28.868	110.605	55.391 [−0.099]	64.775 [−0.025]	0.073	4.1×10^{-7}
		25	1.310	0.274	23.279	84.960	54.631 [−0.078]	64.577 [−0.032]	0.077	-7.9×10^{-8}
		40	1.191	0.282	18.629	66.060	53.809 [−0.035]	64.264 [−0.028]	0.010	$- 1.5 \times 10^{-6}$
		60	1.123	0.300	17.908	59.693	52.849 [−0.019]	63.873 [−0.006]	0.085	3.8×10^{-5}
2-PrOH–W	WB	10	1.657	0.544	224.216	412.162	57.049 [−0.196]	71.067 [0.023]	0.161	-2.1×10^{-5}
		25	1.573	0.551	192.625	349.592	56.173 [−0.003]	70.433 [−0.053]	0.137	8.8×10^{-7}
		40	1.464	0.579	120.650	208.377	55.623 [−0.103]	69.880 [−0.068]	0.164	2.9×10^{-6}
		60	1.380	0.598	102.535	171.463	54.654 [−0.104]	69.434 [−0.033]	0.099	5.5×10^{-6}
	QB	10	1.291	0.392	30.621	78.115	58.420 [−0.020]	64.785 [0.015]	0.045	2.0×10^{-5}
		25	1.258	0.428	26.418	61.724	58.062 [−0.042]	64.574 [−0.014]	0.036	-6.3×10^{-8}
		40	1.216	0.444	23.708	53.396	57.724 [−0.014]	64.325 [−0.005]	0.029	9.0×10^{-6}

Continues

Table 1. Continued

Solvent	Probe	T (°C)	m	$\varphi_{W/ROH}$	$\varphi_{ROH–W/ROH}$	$\varphi_{ROH–W/W}$	E_T (probe)$_{ROH}$[a]	E_T (probe)$_W$[a]	SD[b]	ΣQ[b]
		60	1.185	0.461	23.403	50.766	57.162 [−0.052]	63.902 [−0.022]	0.035	3.3×10^{-7}
	MC	10	1.243	2.837	120.360	42.425	52.874 [−0.044]	64.722 [−0.046]	0.093	-1.7×10^{-4}
		25	1.207	2.918	105.188	36.048	52.167 [0.033]	64.481 [−0.021]	0.094	-3.6×10^{-6}
		40	1.141	3.034	73.402	24.193	51.512 [0.019]	64.217 [−0.045]	0.098	-1.6×10^{-7}
		60	1.071	3.181	45.249	14.225	50.797 [−0.017]	63.810 [−0.040]	0.107	-2.6×10^{-4}

[a] Calculated by regression. The values in brackets are $\Delta E_T(\text{probe})_{\text{Solvent}}$ (ROH and/or W) = experimental $\Delta E_T(\text{probe})_{\text{Solvent}}$ − calculated $\Delta E_T(\text{probe})_{\text{Solvent}}$.
[b] SD = standard deviation; ΣQ = sum of the squares of the residuals.

(iii) As stated above, an increase in temperature affects ROH more than W, and this leads to a measurable 'depletion' of ROH in the probe solvation microsphere, so that $\varphi_{W/ROH}$ increases. Except for one case, all $\varphi_{W/ROH}$ are smaller than unity, i.e. the probes are preferentially solvated by ROH in the temperature range studied. The exception is MC in 2-PrOH/W, where the deviation from ideality is positive in the water-poor region ($\chi_w^{\text{Analytical}} \leq 0.34$). This means that the preferential solvation is by water, which results in a $\varphi_{W/ROH}$ of ca 3. The pK_a of the probes are 4.78, 6.80 and 8.37 for WB, QB and MC, respectively,[4,8] and the corresponding values for the alcohols are 15.5, 16.1 and 17.1 for MeOH, 1-PrOH and 2-PrOH, respectively.[15] Since H-bonding is a dominant factor in probe–solvent interactions, it is plausible that the tendency of the most basic, most hydrophilic probe, MC, to discriminate between W and ROH increases with increasing ΔpK_a [$= pK_a$ (ROH)$-pK_a$ (W)], giving rise to the observed preferential solvation by water in a certain composition range.

(iv) Preferential 'clustering' of water and alcohol as a function of increasing temperature means that the strength of ROH–W interactions also decreases in the same direction,[9d,10a,16] with a concomitant decrease in the ability of the mixed solvent to displace both water and alcohol. This explains the decrease of $\varphi_{ROH–W/ROH}$ and $\varphi_{ROH–W/W}$ as a function of increasing temperature.

(v) Table 1 shows that m decreases as a function of increasing temperature; its value is close to unity for all probes in MeOH, and for QB and MC in the other two solvents. This gives credence to the suggestion that solvatochromism is affected by a relatively small number of molecules, e.g. those H-bonded to the probe phenolate oxygen.

(vi) Thermo-solvatochromism of WB and QB has been studied in these aqueous alcohols at 10, 25, 35 and 45 °C.[4c] It is interesting to examine the results of the application to the previously employed model in aqueous 1-PrOH and/or 2-PrOH at 10 and 25 °C. The reason for not including MeOH is that Eqn (3) described E_T versus χ_W satisfactorily, at least statistically. Compared with the results of the present model, previous treatment of thermo-solvatochromic data resulted in larger values of m, 3.25 ± 0.25 (WB) and 2.5 ± 0.3 (QB), smaller values of $\varphi_{W/ROH}$, 0.39 ± 0.27 (WB) and 0.12 ± 0.04 (QB), and much smaller $\varphi_{ROH–W/ROH}$ and/or $\varphi_{ROH–W/W}$, 5.7 ± 0.9 (WB) and 2.8 ± 0.14 (QB), 68 ± 27 (WB) and 20.8 ± 4.0 (QB), respectively. The equations that were employed previously to calculate m and the appropriate φ are as follows:[4c,7a]

$$E_T^{\text{obs}} = E_T^{\text{ROH}} + \frac{a(\chi_w^{\text{Bk}})^m + b\sqrt{[(1-\chi_w^{\text{Bk}})\chi_w^{\text{Bk}}]^m}}{(1-\chi_w^{\text{Bk}})^m + \varphi_{W/ROH}(\chi_w^{\text{Bk}})^m + \varphi_{ROH-W/ROH}\sqrt{[(1-\chi_w^{\text{Bk}})\chi_w^{\text{Bk}}]^m}} \tag{15}$$

$$a = \varphi_{W/ROH} \times \left(E_T^{W} - E_T^{\text{ROH}}\right) \tag{16}$$

$$b = \varphi_{ROH-W/ROH} \times \left(E_T^{\text{ROH-W}} - E_T^{\text{ROH}}\right) \tag{17}$$

where the symbols have their usual meanings. The mathematical forms of Eqns (15)[7a] and (26) (see later: dependence of E_T on solution composition; see *Calculations* section) are different; they are based on bulk and effective solvent concentrations, respectively. Therefore, direct comparison between the data for the two models is rendered difficult, although both models point to the same trend, namely thermo-solvatochromism depends on the structure of the probe, and an increase in temperature causes gradual desolvation of the latter.

CONCLUSIONS

Solvatochromic response can be described by a solvent-exchange mechanism in which W and ROH–W complexes exchange with alcohol and/or water present in the probe solvation micro-sphere. The temperature effect on solvent fractionation factors is rationalized in terms of the structures of W and ROH and their mutual interactions. A temperature increase results in gradual desolvation of every probe, in all binary mixtures. This is relevant to the analysis of activation parameters of reactions carried out in pure and/or mixed solvents, especially when the difference between polarities of reagents and activated complexes is relatively large.

CALCULATIONS

Determination of K_{assoc} and $\chi_{\text{Species}}^{\text{Effective}}$ from density data

The model discussed by Katz and co-workers[17] was employed to determine the association constant of W and ROH from density data. The model is based on the formation of a 1:1 W–ROH complex, Eqn (9), whose dissociation constant, K_{dissoc}, is given by

$$K_{\text{dissoc}} = \frac{[\text{ROH}][\text{W}]}{[\text{ROH–W}]} \tag{18}$$

where the required K_{assoc} is the reciprocal of K_{dissoc}. In a mixture of W, ROH and ROH–W, the solution density is given by

$$d = \frac{[\text{W}]M_{\text{w}} + [\text{ROH}]M_{\text{ROH}} + [\text{ROH}-\text{W}]M_{\text{ROH}-\text{W}}}{[\text{W}]V_{\text{w}} + [\text{ROH}]V_{\text{ROH}} + [\text{ROH}-\text{W}]V_{\text{ROH}-\text{W}}} \tag{19}$$

where [W], [ROH], [ROH–W], M and V refer to molar concentration, molecular mass and molar volume of the appropriate species, respectively. [W], [ROH] and [ROH–W] are given by

$$[\text{W}] = \frac{-b + (b^2 + 4c)^{0.5}}{2} \tag{20}$$

$$[\text{ROH}] = \frac{\alpha}{V_{\text{ROH}}} - [\text{ROH–W}] \tag{21}$$

$$[\text{ROH–W}] = \frac{1-\alpha}{V_{\text{W}}} - [\text{W}] \tag{22}$$

Where α is the analytical volume fraction of ROH and the coefficients b and c in Eqn (20) are given by

$$b = K_{\text{dissoc}} + \frac{\alpha}{V_{\text{ROH}}} + \frac{\alpha}{V_{\text{W}}} - \frac{1}{V_{\text{W}}} \tag{23}$$

$$c = K_{\text{dissoc}}\left(\frac{1}{V_{\text{W}}} - \frac{\alpha}{V_{\text{W}}}\right) \tag{24}$$

The input data to solve Eqn (19) include M_{W}, M_{ROH}, $M_{\text{ROH–W}}$, V_{M} and V_{ROH}, along with initial estimates for K_{dissoc} and $V_{\text{ROH–W}}$. The densities were calculated by iteration until ΣQ was $\leq 10^{-3}$. In order to reduce the number of iterations, the following constraint was employed: $V_{\text{ROH–W}} \geq$ sum of the molar volumes of W and ROH, calculated with commercial software (Spartan-Pro program package, version 5.1; Wave Function, Irvine, CA, USA), corrected for T. Densities were taken from the literature, MeOH, 25–45 °C,[17b,c] and 1-PrOH, 25–50 °C.[18] We have determined densities of 2-PrOH–W in the range 15–50 °C. As shown by the following regression analysis, the van't Hoff equation applied satisfactorily to the data and was employed, when required, to obtain K_{assoc} at the desired temperature (see Table 2). Figure 7 shows typical results, where the densities are experimental and the curve was obtained by iteration:

$$\text{MeOH–W}: \quad \log K_{\text{assoc}} = +995.972T^{-1} + 1.098, \quad r = 0.9958$$

$$\text{1-PrOH–W}: \quad \log K_{\text{assoc}} = +757.094T^{-1} + 1.451, \quad r = 0.9920$$

Table 2. Calculated K_{assoc} at different temperatures for MeOH–W, 1-PrOH–W and 2-PrOH–W

Binary mixture	Temperature (°C)	K_{assoc} (l mol^{-1})
MeOH–W[a]	10	263.9
	25	173.3
	35	140.3
	45	106.7
1-PrOH–W[b]	10	16.8
	25	12.3
	40	9.3
	60	6.7
2-PrOH–W	10	8.6
	25	8.1
	40	7.7
	60	7.2

[a] Densities at 25–45 °C were taken from Refs 17a and b and were calculated at the desired temperatures by applying the van't Hoff equation.
[b] Densities at 25–50 °C were taken from Ref. 18 and were calculated at the desired temperatures as indicated for MeOH–W.

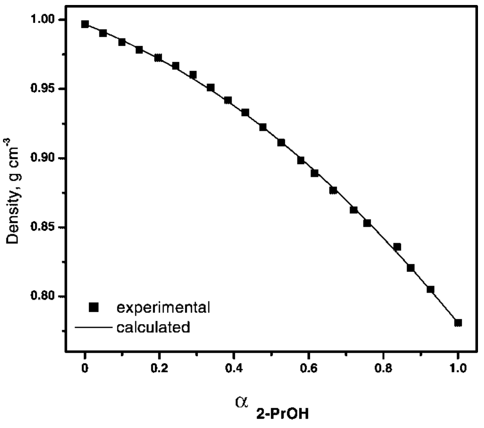

Figure 7. Representative plot showing the dependence of calculated and experimental solution density on the volume fraction, α, of 2-PrOH in ROH–W mixture at 25 °C

$$2-\text{PrOH–W}: \quad \log K_{\text{assoc}} = +144.404T^{-1} - 0.425, \quad r = 0.9975$$

Modified preferential solvation model: explicit consideration of ROH–W in bulk solvent

The probe solvation micro-sphere is composed of W, ROH and ROH–W. The observed E_T, E_T^{obs}, is the sum of the polarity of each component, E_T^{W}, E_T^{ROH}, and $E_T{}^{\text{ROH–W}}$, respectively, multiplied by the corresponding mole fraction in the micro-sphere, $\chi_{\text{w}}^{\text{Probe}}$, $\chi_{\text{ROH}}^{\text{Probe}}$ and $\chi_{\text{ROH–W}}^{\text{Probe}}$, respectively:

$$E_T^{\text{obs}} = \chi_{\text{w}}^{\text{Probe}} E_T^{\text{W}} + \chi_{\text{ROH}}^{\text{Probe}} E_T^{\text{ROH}} + \chi_{\text{ROH-W}}^{\text{Probe}} E_T^{\text{ROH-W}} \tag{25}$$

Substitution of Eqns (12) and (13) in Eqn (25) gives (where $\chi_{\text{w}}^{\text{Probe}} + \chi_{\text{ROH}}^{\text{Probe}} + \chi_{\text{ROH-W}}^{\text{Probe}} = 1$):

$$E_T^{\text{obs}} = \frac{\left(\chi_{\text{ROH}}^{\text{Bk;Effective}}\right)^m E_T^{\text{ROH}} + \varphi_{\text{W/ROH}}\left(\chi_{\text{W}}^{\text{Bk;Effective}}\right)^m E_T^{\text{W}} + \varphi_{\text{ROH-W/ROH}}\left(\chi_{\text{ROH-W}}^{\text{Bk;Effective}}\right)^m E_T^{\text{ROH-W}}}{\left(\chi_{\text{ROH}}^{\text{Bk;Effective}}\right)^m + \varphi_{\text{W/ROH}}\left(\chi_{\text{W}}^{\text{Bk;Effective}}\right)^m + \varphi_{\text{ROH-W/ROH}}\left(\chi_{\text{ROH-W}}^{\text{Bk;Effective}}\right)^m} \tag{26}$$

where m, $\chi_{\text{ROH}}^{\text{Bk;Effective}}$, $\chi_{\text{w}}^{\text{Bk;Effective}}$ and $\chi_{\text{ROH-W}}^{\text{Bk;Effective}}$ refer to the number of molecules in the micro-sphere that affect solvatochromic response and effective mole fractions of the appropriate species in bulk solvent, respectively. The input data to solve Eqn (26) include E_T^{obs}, E_T^{W}, E_T^{ROH} and $\chi_{\text{Species}}^{\text{Effective}}$, along with initial estimates of m, $E_T^{\text{ROH-W}}$ and the appropriate solvent fractionation factors. E_T^{obs} was calculated by iteration until ΣQ was $\leq 10^{-3}$.

Consider solvatochromism in the absence of dielectric enrichment and/or preferential solvation, i.e. when all solvent fractionation factors are unity. Under these conditions, Eqn (26) is reduced to Eqn (25), provided that $m = 1$, a plausible and experimentally sound assumption. In other words, Eqn (26) is a general equation, capable of describing ideal and non-ideal solvation schemes.

All calculations were based on a laboratory-developed BASIC script that relies on the S-Plus 2000 program package (MathSoft, Seattle, WA, USA).

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