Solvatochromism in pure and binary solvent mixtures: effects of the molecular structure of the zwitterionic probe

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ABSTRACT: The solvatochromic behavior of 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate (WB) was studied by UV–visible spectrophotometry in 32 pure solvents, in binary mixtures of 1-butanol–cyclohexane (BuOH–Cyhx), and of water with methanol, ethanol, 1-propanol, 2-butoxyethanol (2-BE), acetonitrile, 1,4-dioxane and THF. The solvent polarity, $E_T(33)$ in kcal mol^{-1}, was calculated from the position of the longest-wavelength intramolecular charge-transfer absorption band of WB and the results were compared with those for 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate [RB, $E_T(30)$] and of 1-methyl-8-oxyquinolinium betaine [QB, $E_T(QB)$]. For pure solvents, $E_T(33)$ is a linear function of $E_T(30)$, with a slope of practically unity. Steric crowding from the two *ortho* phenyl rings of RB hinders the formation of H-bonds with solvents, which results in similar susceptibilities of WB and RB to solvent acidity. For binary solvent mixtures, all plots of E_T versus the mole fraction of 1-butanol or water are nonlinear owing to preferential solvation of the probe by one component of the mixed solvent and, when applicable, to solvent micro-heterogeneity. Preferential solvation due to non-specific and specific probe–solvent interactions was calculated for BuOH–Cyhx and water–acetonitrile. Both solvation mechanisms contribute to the non-ideal behavior in the former binary mixture, whereas probe–solvent specific interactions dominate the solvatochromic behavior in the latter. The composition of the probe solvation shell was calculated. In aqueous alcohols, preferential solvation is by the alcohol. In water–aprotic solvent mixtures, preferential solvation of RB and WB is by the solvent which is present in lower concentration, whereas QB seems to form its own, water-rich solvation shell over a wide range of water concentration. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: solvatochromism; preferential solvation; binary mixtures; polarity
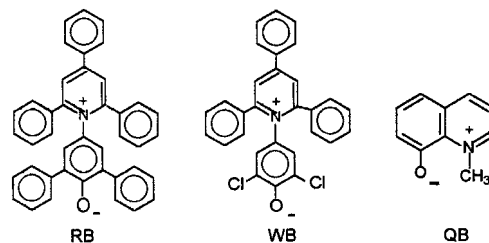
INTRODUCTION

Effects of organized assemblies on the rates and equilibria of chemical reactions have been rationalized in terms of 'medium' and, for ionic surfactants, electrostatic effects. The former originate from differences between the properties of interfacial and bulk water, whereas the latter account for effects of charged interfaces on the stability of, e.g., polar reactants and transition states. It is important, therefore, to determine the properties of interfacial water in order to separate the contribution of medium and electrostatic effects to micelle-mediated phenomena.[1–3] An important property of such water is its microscopic polarity, as measured by solvatochromic probes, e.g. 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate (RB), 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio) phenolate (WB) and 1-methyl-8-oxyquinolinium betaine (QB) (Scheme 1). The polarity

scale, E_T, is calculated from the position of the longest wavelength intramolecular charge-transfer (CT) absorption band of a solvatochromic probe (hereafter denoted 'probe') as shown in eqn (1).[4–6]

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

The corresponding polarity scales are denoted $E_T(30)$, $E_T(33)$ and $E_T(QB)$ for RB, WB and QB, respectively.

With regard to interfacial water, the following are relevant.[7,8]

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Scheme 1. Solvatochromic probes employed in the present work

(i) Calculation of its 'effective' concentration is based on comparing micellar solvatochromic data with those determined *outside* the micellar domain.

(ii) The dependence of the polarity measured on the charge and structure of the probe calls for an understanding of the relationship between the molecular structure of a probe and its solvatochromic behavior.

(iii) Although WB is structurally similar to RB, its pK_a in water is much lower owing to the inductive effect of the two *ortho*-chlorine atoms.[9] It is, therefore, the probe of choice when the micelle-induced pK_a increase is relatively large, e.g. as with RB in some cationic micelles (e.g. cetyltributylammonium chloride micelles; unpublished results).

WB, however, has been studied in much less detail than RB, and some of the data required for the micellar systems are not available. For example, published $E_T(33)$ values cover only 10 pure solvents. [Although WB has been studied in more solvents,[10] these data have never been published. Indeed, the correlation between $E_T(30)$ and $E_T(33)$, which has been reported in a recent study, is based on the same 10 solvents which were previously employed by Kessler and Wolfbeis![7,11]]. Except for aqueous ethanol,[9] solvatochromic data for WB in aqueous solvents do not cover the entire range of water mole fraction, χw.[10] Finally, no data are available for two important binary solvents, aqueous 1,4-dioxane and aqueous 1-propanol.[7,8,12,13]

The present study remedies the problems outlined in the preceding paragraph, and sheds light on the dependence of the solvatochromic behavior of these probes on their acidity (pK_a in water = 8.65, 6.80 and 4.78, for RB, QB, and WB, respectively)[4–6,9,14] and hydrophobicity (order RB >WB >QB; see below). Our results show that RB and WB have similar susceptibil-

ities to solvent dipolarity/polarizability and acidity. Preferential solvation and solvent microheterogeneity account for the observed non-linear dependence of E_T on solvent composition.

EXPERIMENTAL

Materials. The chemicals (including RB) were obtained from Aldrich and Merck. The solvents were purified by standard procedures[15] and kept over activated molecular sieves. QB was as used before,[14] and WB was synthesized as described elsewhere.[9,16] The deep purple product gave satisfactory microanalysis. Refractive indices of 1-butanol–cyclohexane (BuOH–Cyhx) mixtures were measured at $20.0 \pm 0.1\,°C$ with a Stanley and Billingham Model ED-60 precision Abbé refractometer. All-glass, doubly distilled water was used throughout.

Spectrophotometric determination of $E_T(33)$. The probe concentration range in the appropriate solvent was 2–5×10^{-4} M. A Beckman DU-70 UV–visible spectrophotometer, operating $25.0 \pm 0.1\,°C$ was used, and the value of λ_{max} was determined from the first derivative of the absorption spectrum. The uncertainties in E_T are 0.6, 0.3 and 0.1 kcal mol^{-1} for RB,[17] WB, and QB,[14] respectively. The solubility of WB in water, 3.7×10^{-4} M, was determined from the UV–visible absorption of its saturated solution and that of a solution of known concentration.

RESULTS AND DISCUSSION

Solvatochromism in pure solvents

Table 1 shows $E_T(33)$ values which we determined for 32 solvents. The relationship between $E_T(30)$ and $E_T(33)$ is

Table 1. Solvent polarities, E_T in kcal mol^{-1}, based on the solvatochromic probes RB, $E_T(30)$, WB, $E_T(33)$, and QB, $E_T(QB)$[a]

Solvent[b]	$E_T(30)$	$E_T(33)$	$E_T(QB)$	Solvent[b]	$E_T(30)$	$E_T(33)$	$E_T(QB)$
Water	63.1	70.2	64.5	*t*-Butanol	43.3	52.8	54.5
Glycerol	57.0	66.7	—	DMF	43.2	53.3	54.2
Ethylene glycol	56.3	65.7	61.9	DMAC	42.9	51.5	53.6
Formamide	55.8	64.3	—	Acetone	42.2	52.0	53.2
Methanol	55.4	64.6	60.7	NMePy	42.2	50.6	—
2-ME	52.0	59.8	59.6	1,2-Dichloroethane	41.3	51.1	—
Ethanol	51.9	60.7	59.5	Dichloromethane	41.1	49.7	—
1-Propanol	50.7	58.7	58.9	HMPT	40.9	49.3	—
Benzyl alcohol	50.4	58.8	59.0	Pyridine	40.5	48.8	52.4
1-Butanol	50.2	57.7	58.6	Chloroform	39.1	48.6	52.0
2-BE	50.1	57.6	58.6	EGDE	38.6	46.2	—
1-Octanol	48.1	56.1	—	Ethyl acetate	38.1	47.6	—
Cyclohexanol	47.2	54.7	—	THF	37.4	44.7	50.9
Isoamyl alcohol	45.7	56.1	—	Chlorobenzene	36.8	44.3	50.8
Acetonitrile	45.6	55.4	54.9	1,4-Dioxane	36.0	44.0	50.6
DMSO	45.1	55.1	54.7	Benzene	34.3	41.4	49.8

[a] Measurements at 25 °C for WB, QB and at 30 °C for RB. $E_T(30)$ and $E_T(QB)$ are from Refs 6 and 14, respectively.
[b] Abbreviations: 2-ME, 2-methoxyethanol; 2-BE, 2-butoxyethanol; NMePy, 1-methyl-2-pyrrolidinone; DMAC, *N,N*-dimethylacetamide; HMPT, hexamethylphosphorotriamide; EGDE: ethylene glycol dimethyl ether.

Table 2. Results of the application of Eqn. (4): E_T (probe) = constant + $s(\pi^*_{solv} + d\delta) + a\alpha_{solv} + b\beta_{solv}$[a]

Probe	Constant	$s(\pi^*_{solv})$	$s(d\delta)$	a	b	r_{mult}	$F_{4,95}$
RB	30.2	12.99 (±0.54)	−2.74 (±0.36)	14.45 (±0.34)	2.13 (±0.51)	0.9867	876
WB	38.64 (±1.79)	14.71 (±1.96)	−4.02 (±1.20)	15.30 (±0.97)	0.20 (±1.61)	0.9490	94
QB	46.8	7.10 (±0.51)	−1.20 (±0.27)	8.54 (±0.23)	1.44 (±0.38)	0.9941	470

[a] Data for RB and QB were taken from Ref. 14

given in Eqn. (2), and Eqn. (3) has been published previously,[14] where N is the number of solvents employed and r is the correlation coefficient:

$$E_T(30) = 0.979 E_T(33) - 7.461 \quad N = 32; r = 0.9905 \quad (2)$$

$$E_T(30) = 1.761 E_T(QB) - 52.415 \quad N = 28; r = 0.9935 \quad (3)$$

We employed RB as a reference probe because there are extensive data on its solvatochromic behavior both in pure solvents and in binary solvent mixtures.[4–6,18–20] The linear correlations expressed by Eqns (2) and (3) arise because all probes are betaines and solvatochromic shifts involve $\pi \rightarrow \pi^*$ transitions in the UV–visible region. That is, all are sensitive to the same solute–solvent interactions, e.g. coulombic, dispersion and hydrogen bonding. In Eqn. (2), the slope is practically unity, i.e. the structurally related dyes RB and WB have similar *overall* response to the properties of the solvent, a result which has been observed for other classes of compounds, e.g. substituted phenols and anilines.[4–6,18–20]

A widely employed equation to quantify probe–solvent interactions is the Kamlet–Taft–Abboud equation, which for a single solute in a series of solvents is[21]

$$SDP = \text{constant} + s(\pi^*_{solv} + d\delta) + a\alpha_{solv} + b\beta_{solv} + h(\delta^2_H) \quad (4)$$

The solvent-dependent property, SDP, such as a solvatochromic shift, is modeled as a linear combination of a dipolarity/polarizability term [$s(\pi^*_{solv} + d\delta)$], two hydrogen-bonding terms, in which the solvent is the hydrogen-bond donor ($a\alpha_{solv}$), or the hydrogen-bond acceptor ($b\beta_{solv}$), and a cavity term [$h(\delta^2_H)$]. The last term is not considered when the Frank–Condon principle is obeyed. The parameters π^*_{solv}, α_{solv} and β_{solv} are known as solvatochromic parameters; we have used the subscript (solv) so that they are not confused with other known quantities, e.g. α and β of the Brønsted equation. We applied Eqn. (4) to the data for WB, taking into account conditions that should be met in order to obtain meaningful statistical correlations.[14,21] Table 2 shows the regression coefficients obtained for WB and the data for RB and QB have been published elsewhere.[4–6,14,20]

Regarding these equations, the following are relevant:

(i) The number of solvents employed in Eqn. (4) is smaller than that used in Eqn. (2) because solvatochromic parameters for some of the solvents are not available.

(ii) The regression coefficients indicate that all probes are much more sensitive to the solvent dipolarity/polarizability and H-bond donation than to its H-bond acceptance ability, probably because they do not carry groups that act as H-bond donors, e.g. OH.

(iii) At first glance, the similarity of the regression coefficients (a) of RB and WB is surprising, because the latter is a stronger acid. Additionally, we have previously obtained a Brønsted-type correlation between $\log|a|$ and the pK_a of 17 solvatochromic compounds [Eqn. (5)], including the structurally related probes shown in Scheme 2:[14]

$$\log|a| = 0.1 pK_a + 0.24 \qquad r = 0.972 \qquad (5)$$
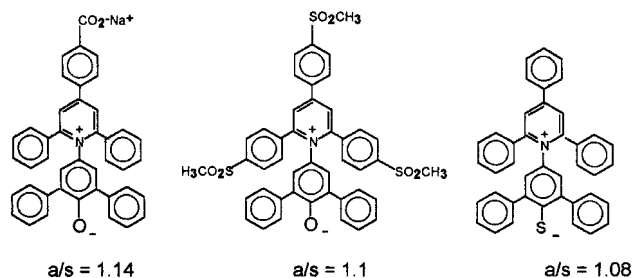
Scheme 2. Solvatochromic probes structurally related to RB and the corresponding *a/s* values of Eqn. 4

The following discussion shows that the regression coefficient (a) for WB may be enhanced owing to a combination of steric and inductive effects. X-ray diffraction of the parent phenols (2,6-dichloro- and 2,6-diphenylphenol) has shown that the two *ortho*-chlorine atoms lie in plane of the phenol ring,[22] whereas the corresponding *ortho*-phenyl rings are twisted in opposite directions with respect to the plane of the phenol ring, by 52° and 44°, respectively.[23] Therefore, the *free* solid angle around the oxygen atom of the phenoxide ion of RB (a measure of its accessibility to H-bonding) should be smaller than the corresponding angle for WB.[24] Indeed, the H-bonding ability of RB depends on the acidity and steric hindrance of the proton donor, e.g. it does not form an H-bond to 2,6-di-*tert*-butyl-4-methylphenol.[25] Finally, the C—Cl bond of chlorophenols is

Table 3. Polynomial dependence of E_T (33) in kcal mol^{-1} on the mole fraction of water or 1-butanol in binary solvent mixtures, calculated according to the equation, e.g. for aqueous solutions $E_T(33) = A + B(\chi_w) + C(\chi_w)^2 + D(\chi_w)^3 + E(\chi_w)^4 + F(\chi_w)^5 + G(\chi_w)^6$

Mixture	A	B	C	D	E	F	G	r_{mult}[a]	ΣQ[a]
Water–methanol	64.61	2.81	−2.42	5.24				0.9996	0.029
Water–ethanol	60.65	2.01	22.96	−52.42	37.26			0.9985	0.30
Water–1-propanol	58.71	7.09	35.01	−250.02	653.2	−752.65	319.11	0.9974	0.093
Water–2-BE	57.69	5.02	4.78	−11.30	9.86			0.9890	1.27
Water–acetonitrile	55.81	61.19	−224.47	442.15	−426.83	162.55		0.9991	0.26
Water–1,4-dioxane	44.21	59.36	−96.36	62.77				0.9991	0.99
Water–THF	47.07	68.60	−236.88	493.89	−526.41	223.97		0.9987	0.78
BuOH–Cyhx	52.25	6.72	−1.26					0.9963	0.071

[a] r_{mult} = Correlation coefficient for the polynomial; ΣQ = sum of the squares of the residues.

appreciably polarized, so that the chlorine atom forms H-bonds with suitable donors, e.g. the solvent or, for *ortho*-chlorophenols, the neighboring OH group.[26] Therefore, the regression coefficient (*a*) for WB is enhanced with respect to its RB counterpart because of lower steric hindrance to H-bond formation with the solvent, and the additional ability of the two *ortho*-chlorine atoms to form H-bonds. Both factors appear to compensate for the lower basicity of this probe;

(iv) Although the regression coefficients of QB are very different from those of the other two probes, the *a/s* values are almost the same, 1.11, 1.04 and 1.20 for RB, WB and QB, respectively. This is also the case for the structurally similar indicators shown in Scheme 2.
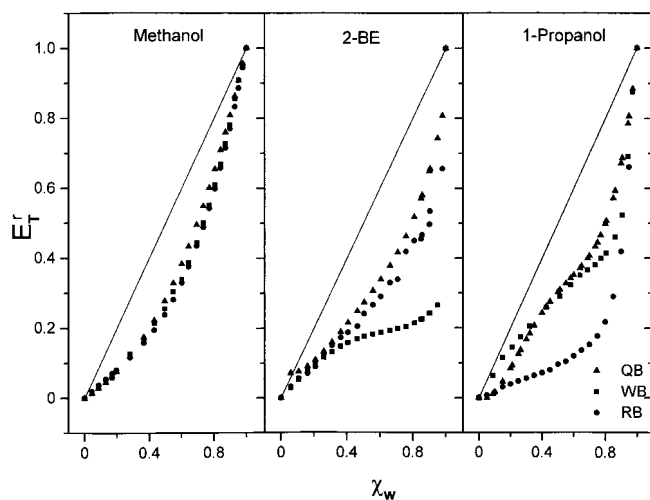
Solvatochromism in aqueous and non-aqueous binary solvent mixtures

We have studied the solvatochromism of WB in a series of organic solvent–water mixtures which are most commonly used, e.g. in colloid and physical organic chemistry studies.[1,4–8,27] In order to present the extensive solvatochromic data comprehensively, we calculated the polynomial dependence of $E_T(33)$ on χ_{Wa} (Table 3). The degree of the polynomial used was that which gave the best data fit, as indicated by *r* and the sum of the squares of the residues, ΣQ. That is, our main concern is to make it feasible to calculate $E_T(33)$ as close as possible to the experimental value. Table 3 also includes one non-aqueous solvent mixture; this will be discussed later.

In order to compare the dependences of $E_T(30)$, $E_T(33)$ and $E_T(QB)$ on χ_w, we used Eqn. (6) to convert each polarity scale into a reduced scale; the results are shown in Figs 1 and 2:
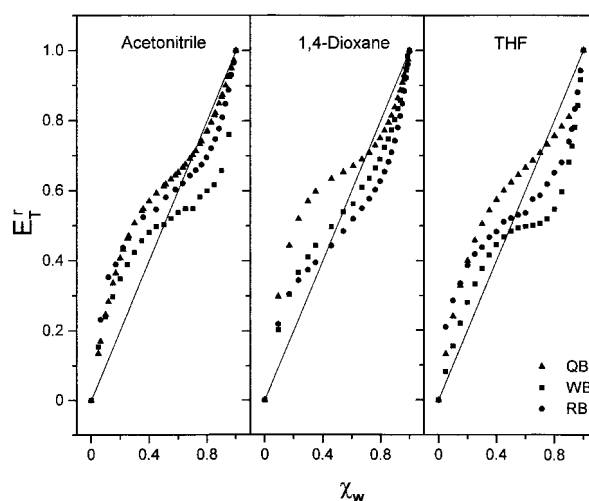

Figure 1. Dependence of E_T^r on χ_{water} for RB, WB and QB for three aqueous alcohols. In this and all subsequent figures, the diagonal line represents the expected behavior if solvatochromism were ideal, i.e. if there were no preferential solvation of the probe by one component of the binary mixture (see text for explanation)

Figure 2. Dependence of E_T^r on χ_{water} for RB, WB and QB, for three mixtures of water with dipolar aprotic solvents

$$E_T^r = \frac{E_T(\text{aqueous organic solvent}) - E_T(\text{pure organic solvent})}{E_T(\text{water}) - E_T(\text{pure organic solvent})} \tag{6}$$

We begin our discussion of Figs 1 and 2 by considering the expected solvatochromic behaviour of a probe in a binary mixture of solvents, S1 and S2, where the latter is more polar and has a higher dielectric constant. As discussed elsewhere, E_T for an ideal binary solvent mixture is given by[12,13,18]

$$E_T(\text{mixture}) = \chi_{s1} E_T S1 + \chi_{s2} E_T S2 \tag{7}$$

That is, a plot of E_T (mixture) versus χ_{s2} should be a straight line connecting the E_T values of the two pure solvents, provided that the composition of the solvation shell of the probe is the same as that of bulk solvent. Figures 1 and 2 show that this is not the case for the probes under study.

The observed deviations from linearity result, in part, from the so-called 'preferential solvation' of the probe by one of the components of the mixture. In principle, this phenomenon includes contributions from the following: (i) 'dielectric enrichment', which denotes enrichment of the solvation shell of the probe in S2, due to probe dipole–solvent dipole interactions; this interaction, if it occurs, implies a *positive* deviation in the E_T^r versus χ_{s2} plot as shown, e.g., in Fig. 2; (ii) specific probe–solvent interactions, e.g. H-bonding.[18,28]

Note that the regression coefficient (B) in Table 3 refers to the limiting value of $[d(E_T)/d(\chi_{s2})]$ for $\chi_{s2} \to 0$. Therefore, B should be unity if there were no preferential solvation, and not far from unity for mixtures of solvents of similar nature.[29d] Indeed, B values for aqueous alcohols are much smaller than their counterparts for water–aprotic solvent mixtures (see Table 3). QB and RB show a similar behavior.[12,13]

Non-ideal behavior also results from solvent microheterogeneity, i.e. when one component of the mixed solvent prefers a molecule of the same kind. Interactions (i) and (ii) are probe-induced, whereas solvent microheterogeneity is not.[10,20,29]

We included BuOH–Cyhx in the present study, because the Onsager dielectric function of their mixtures, $f(D)$, is linear in χ_{s2} within experimental error $[f(D) = 2(D-1)/(2D+1)$, where D is the solvent dielectric constant].[18] Accordingly, solvent microheterogeneity does not contribute to the observed (positive) deviation from ideality. In the Calculations section we show how this deviation can be partitioned into contributing dielectric enrichment and specific probe–solvent interactions. The results are shown in Figs 3 (BuOH–Cyhx) and 4 (aqueous acetonitrile), where (i) the energy difference between the diagonal line (ideal behavior, no preferential solvation) and the curve defined by the symbol ◆ represents *total* preferential solvation of the probe by the binary solvent mixture, (ii) the energy difference between the diagonal line and the curve defined by the symbol ∗ represents the contribution to preferential solvation by dielectric enrichment and (iii) the energy difference between the curves defined by the symbols ∗ and ◆ represents the contribution to preferential solvation by specific solute–solvent interactions, e.g. H-bonding.

It is clear from Fig. 3 that both solvation mechanisms contribute to the deviation of E_T^r from ideality. The
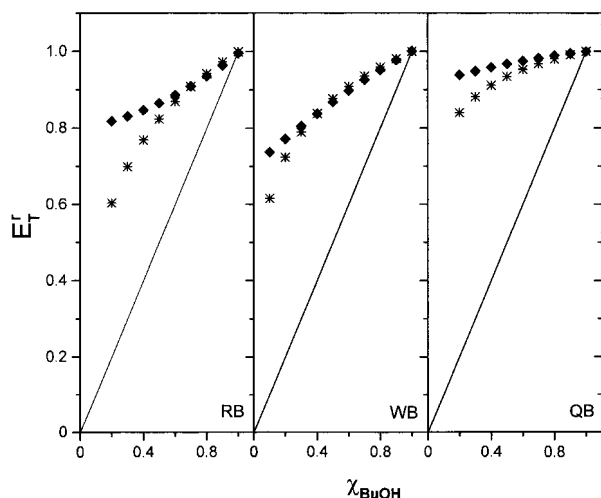

Figure 3. Dependence of E_T^r on χ_{BuOH} (BuOH–Cyhx) for RB, WB, and QB. (◆) Experimental results; (∗) calculated contribution to experimental E_T^r by preferential solvation of the probe by dielectric enrichment (see Calculations section)

Figure 4. Dependence of E_T^r on χ_w (aqueous acetonitrile) for RB, WB and QB. (◆) Experimental results; (∗) calculated contribution to experimental E_T^r by preferential solvation of the probe by dielectric enrichment (see Calculations section)
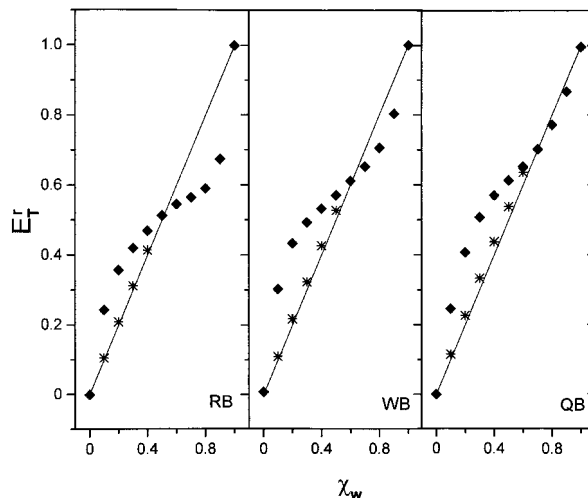
Table 4. Solvent fractionation factors, φ_s, calculated for the probes in aqueous organic solvents[a]

Binary solvent	Probe	φ_s	Range of χ_w
Water–methanol	RB	0.26 ± 0.01	$0.0 - 1.0$
	WB	0.36 ± 0.01	$0.0 - 1.0$
	QB	0.41 ± 0.02	$0 - 1.0$
Water–ethanol	RB	0.15 ± 0.01	$0.0 - 1.0$
	WB	0.23 ± 0.02	$0.0 - 1.0$
	QB	0.31 ± 0.01	$0.0 - 1.0$
Water–1-propanol	RB	0.05 ± 0.01	$0.5 - 1.0$
	WB	0.07 ± 0.01	$0.5 - 1.0$
	QB	0.31 ± 0.01	$0 - 1.0$
Water–2-BE	WB	0.11 ± 0.03	$0.3 - 1.0$
	QB	0.38 ± 0.02	$0 - 0.96$
Water–acetonitrile	RB	6.26 ± 0.07	$0 - 0.5$
	RB	0.06 ± 0.01	$0.65 - 1.0$
	WB	8.3 ± 0.6	$0 - 0.5$
	WB	0.16 ± 0.01	$0.5 - 1.0$
	QB	4.6 ± 0.2	$0 - 0.7$
Water–1,4-dioxane	RB	5.5 ± 0.3	$0 - 0.55$
	RB	0.15 ± 0.01	$0.55 - 1.0$
	WB	4.75 ± 0.08	$0 - 0.5$
	WB	0.23 ± 0.01	$0.5 - 1.0$
	QB	7.4 ± 0.4	$0 - 0.7$
Water–THF	RB	2.87 ± 0.01	$0 - 0.5$
	RB	0.10 ± 0.01	$0.65 - 1.0$
	WB	8.8 ± 0.9	$0 - 0.5$
	WB	0.13 ± 0.01	$0.5 - 1.0$
	QB	4.3 ± 0.1	$0 - 0.7$

[a] Values of φ_s for RB and QB are based on data from Refs 12 and 13, for aqueous alcohols, and mixtures of water and aprotic solvents, respectively. Some φ_s for RB were recalculated so that the χ_w ranges for RB and WB are as close as possible.

contribution of H-bonding is more important at lower χ_{BuOH}, i.e. when auto-association of the alcohol is not extensive. In aqueous acetonitrile (Fig. 4), the solvatochromic behavior is almost entirely due to specific probe–solvent interactions, although it is not trivial to divide this deviation into contributions from H-bonding and solvent microheterogeneity.[12]

The deviation from linearity of the E_T^r versus χ_w plots can be discussed in terms of the relationship between solvent composition in the solvation shell of the probe and in bulk solvent, as given by the so called solvent 'fractionation factor', φ_s. This is the equilibrium constant of the following solvent exchange reaction for a probe solvated by a mixture of S1 and S2 (for simplicity we represent the probe as being solvated by a single solvent molecule):

$$\text{probe(S1)} + \text{S2} \rightleftharpoons \text{Probe(S2)} + \text{S1} \qquad (8)$$
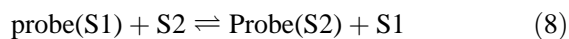
$$K = \varphi_s = [\text{probe(S2)}][\text{S1}]/[\text{probe(S1)}][\text{S2}] \qquad (9)$$

$$\varphi_s = ([\text{S2}]/[\text{S1}])_{\text{probe}}/([\text{S2}]/[\text{S1}])_{\text{bulk solvent}} \qquad (10)$$

i.e. φ_s describes the preference of S2 for the solvation

shell of the probe, relative to bulk solvent. When $\varphi_s > 1$, the solvation shell of the probe is richer in S2 than bulk solvent and when φ_s is <1, the solvation shell is richer in S1 than bulk solvent, whereas when $\varphi_s = 1$, the solvent composition in the solvation shell is the same as that of bulk solvent, and the appropriate E_T depends linearly on χ_{s2}. Using the procedure outlined elsewhere,[12,30] we calculated φ_s from the dependence of E_T^N (dimensionless, normalized polarity scale) on χ_w, and the results are given in Table 4. E_T^N is defined by Eqn. (11),[4–6] where TMS refers to tetramethylsilane:

$$E_T^N = \frac{E_T(\text{pure organic solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} \qquad (11)$$

Considering first solvatochromism in aqueous alcohols, the following are relevant:

(i) A plot E_T^r or E_T^N versus χ_w should be either linear (no preferential solvation), curve downwards (preferential solvation by the alcohol) or curve upwards (preferential solvation by water). All plots curve downwards, although positive and negative deviations from ideal behavior have been observed previously, e.g. for QB in aqueous 2-methyl-2-propanol.[12]

(ii) For the same alcohol, the value of φ_s decreases in the order QB $>$WB $>$RB, which can be explained by considering their hydrophobicity, as indicated by their solubility in water, 7.2×10^{-6},[4] 3.7×10^{-4} and >0.2 M[14] for RB, WB and QB, respectively. Thus, the solvation shell of RB, the most hydrophobic probe, contains the highest concentration of alcohol because of its high energy of hydrophobic hydration.[17,31] For the same probe in different alcohols, φ_s decreases in the order methanol $>$ethanol, 2-BE $>$1-propanol (the reason for not reporting φ_s of RB in 2-BE has been discussed elsewhere).[12] The pK_a values of these alcohols are 15.5, 15.9, 15.8 and 16.1, respectively.[32] It seems, therefore, that φ_s of the same probe in aqueous alcohols is determined, in part, by the basicity of the alcohol;

(iii) The dependence of E_T^r on χ_w is identical for the three probes only in water–methanol mixtures because these two solvents are similar.[17,31,33] Additionally, among the alcohols studied, methanol and ethanol do not form clusters in aqueous solutions.[34] The steep increase in E_T^r of WB in 2-BE and of RB in 1-propanol in the water-rich region is a clear manifestation of the susceptibility of the solvatochromic behavior of hydrophobic probes to changes in solvent structure. The microheterogeneity of 2-BE–water mixtures has been discussed previously.[35] In the χ_w range 1–0.98 there is sufficient water for the formation of complete hydration spheres around the alcohol molecules. At

$\chi_w \approx 0.95$, the 'magic mole fraction,'[36] hydrophobic interactions between the solvated alcohol molecules have reached their maximum, and at still smaller χ_w unhydrated alcohol molecules exist. The abrupt increase in E_T^r over a narrow range of χ_w is, therefore, the result of solvation of RB by highly polar alcohol hydrates.[31a]

We now turn our attention to solvatochromism in mixtures of water and dipolar aprotic solvents (Fig. 2).

The relationship between E_T^r or E_T^N and χ_w is sigmoidal, with both positive and negative deviations from linearity, and is clearly probe-dependent. It was not feasible to fit the solvatochromic data for RB and WB to a single curve, so we divided the plots into two sections, and obtained two φ_s for the water-poor and the water-rich region. The calculated φ_s depend somewhat on the range of χ_w employed and this, in part, accounts for the observation that there is no systematic correlation between φ_s and the probe hydrophobic character;

In discussing φ_s, one has to keep in mind the probe response to the microheterogeneity of the binary solvent mixture. In the ensuing discussion, we concentrate on solvatochromism in aqueous acetonitrile because there is enough information on the structure of this binary mixture,[18,20,29,34,37,38] and it serves as a model for the other solvents used.[18,29,34] When acetonitrile is added to water, it replaces the uncoordinated water molecules and the polarity of the mixture decreases since uncoordinated water molecules are considerably more polar than coordinated molecules.[39] The limit of χ_w beyond which acetonitrile cannot be accommodated within the cavities of water is $\chi_w \approx 0.85$. Below this χ_w limit solvent microheterogeneity sets in, and there exist two 'micro-phases,' one highly structured consisting predominantly of coordinated water molecules, and a relatively disordered micro-phase containing mostly acetonitrile molecules.[39] Addition of more acetonitrile leads to a change in the relative concentrations of the two microphases but their compositions do not vary appreciably. Consequently, the calculated E_T values may vary little in the χ_w range 0.3–0.7,[38a] as shown for RB and WB (Fig. 2). At $\chi_w \leq 0.3$, water–acetonitrile association becomes important, resulting in the formation of

complexes, e.g. $(CH_3CN)_m$–H_2O, where $m = 1$–4.[29b,37a,38c] At still lower χ_w, the structure of acetonitrile dominates, and species such as $(CH_3CN)_m$ and CH_3CN are abundant.[38c]

From the preceding discussion, it is clear that the solvatochromic behavior of RB and WB follows the structural changes that occur within water–acetonitrile mixtures more closely than QB. As a first approximation, one expects that RB and WB are solubilized in the range $0.3 \geq \chi_w \geq 0.8$ by the solvent species which are present in higher concentration, that is, by acetonitrile–water complexes which are either rich in acetonitrile (for $\chi_w \leq 0.3$), or rich in water (for $\chi_w \geq 0.8$). Alternatively, it is solubilized by the acetonitrile clusters in the region of microheterogeneity ($0.3 \leq \chi_w \leq 0.8$), that is, φ_s for RB and WB should be <1 in the water-poor region and >1 in the water-rich region. This expectation does not agree with the calculated results, which indicate the contrary, i.e. preferential solvation is by the solvent present in smaller concentration! Therefore, φ_s values should be treated with reserve: they may not be valid for probes whose solvatochromism closely follows the variation in the structure of microheterogeneous solvent mixtures because the probe is solvated by clusters whose composition is not related in a simple way to the overall solvent composition.

On the other hand, the composition of the solvation sphere of QB, the more hydrophilic probe, is less affected by solvent microheterogeneity. It is rich in water until the end of the microheterogeneous region, i.e. until $\chi_w \approx 0.8$, after which solvatochromism is not far from ideal, especially in aqueous acetonitrile.

CONCLUSIONS

Solvatochromism in mixed binary solvents is a complex phenomenon because of preferential solvation and, when applicable, of solvent microheterogeneity.

Non-linear plots of E_T^r versus χ_{s2} can be rationalized in terms of non-specific and specific probe–solvent interactions. The relative importance of each type can be quantified, and is clearly probe- and solvent-dependent.

Table 5. Polynomial dependence of μ_g on the mole fraction of water or 1-butanol in binary solvent mixtures according to the equation, e.g. for aqueous solutions, $10^{29}\,\mu_g\,(C\,m) = A + B\chi_w + C(\chi_w)^2 + D(\chi_w)^3 + E(\chi_w)^4 + F(\chi_w)^5 + G(\chi_w)^6$ [a]

Probe	Binary mixture	A	B	C	D	E	F	G	r_{mult}
RB	BuOH–Cyhx	5.8757	4.2037	−2.4419	0.4673				0.9997
	Water–acetonitrile	8.2594	0.2666	−0.5059	−1.4823	6.5767	−7.5939	2.8194	0.9990
WB	BuOH–Cyhx	6.3848	5.2611	−4.7797	1.7599				0.9993
	Water–acetonitrile	3.8310	0.0943	0.0449	0.0408				0.9987
QB	BuOH–Cyhx	2.3475	1.5131	0.4015	−0.5653				0.9999
	Water–acetonitrile	3.8310	0.0943	−0.0449	0.0408				0.9949

[a] μ_g refers to the dipole moment of the ground state of the *solvated* probe, calculated by the Amsol program.

Preferential solvation is discussed in terms of φ_s, the magnitude of which can be explained in terms of bulk solvent properties, and probe hydrophobicity. Care should be exercised when considering φ_s of very hydrophobic probes in microheterogeneous mixtures.

Judicious choice of a solvatochromic probe as a model for, e.g., rates and equilibria of reactions should consider the properties of the probe, e.g. its hydrophobic/hydrophilic character, and pK_a. Chemical processes involving small reactants are probably best correlated with $E_T(QB)$, whereas those involving large, hydrophobic reactants are probably best correlated with $E_T(30)$ or $E_T(33)$.

CALCULATIONS

$E_T(33)_{TMS}$ (39.0 kcal mol^{-1}), which is required to calculate E_T^N from Eqn. (11), was been obtained from $E_T(30)_{TMS}$ (30.7 kcal mol^{-1})[6] by the use of Eqn. (2).

The electronic transition energy associated with dielectric enrichment at the coordinates (r, θ) of the probe solvation shell, E_{enrich}, is given by Eqn. (12).[12,18,30]

$$E_{enrich} = \frac{-\chi_{S1}\chi_{S2}\Delta E_{S2-S1}}{8} \int_{-1}^{1} d\rho$$

$$\times \int_{-1}^{1} du \frac{G(u)\{1 - \exp[-G(u)Z\rho^2]\}}{\chi_{S2} + \chi_{S1} \exp[-G(u)Z\rho^2]} \quad (12)$$

where χ_{S1} and χ_{S2} are those defined before and R and T have their usual meanings ΔE_{S2-S1} is the difference between the E_T values of the two pure solvents, $\rho = (a/r)^3$ where a is the radius of the cavity that should be created in the solvent in order to accommodate the probe molecule and r is a distance from the center of the probe dipole, $r \geq a$, and $G(u) = 3u^2 + 1$, where $u = \cos \theta$. The 'index of preferential solvation,' Z, is given by

$$Z = \frac{3\mu_g^2 M \Delta f}{8\pi RT \delta a^6} \quad (13)$$

where μ_g is the dipole moment of the ground state of the probe, δ and M refer to the mean density and the mean molecular mass of the two solvents, respectively, and Δf is given by $\Delta f = f(D)_{S2} - f(D)_{S1}$, where $f(D)$ is the above-mentioned Onsager dielectric function. The cavity radius ($a = 5.58 \times 10^{-10}$, 5.13×10^{-10} and 3.67×10^{-10} m for RB, WB and QB, respectively) was taken as equal to the radius of the probe molecule; the latter was calculated from the probe volume, V, by the relationship $a = \mathscr{R} = (3V/4\pi)^{1/3}$, where V was calculated as given elsewhere.[40]

In Eqn. (13), the μ_g employed was calculated for

solvated RB, WB and QB, respectively, by using the Amsol 6.6 program package, which employs the CM2/PM3 charge models for calculating partial atomic charges and the SM5.4 P solvation model for calculating the free energies of solvation.[41] The inputs for calculating μ_g include the solvatochromic parameters, α_{solv}, β_{solv} of Eqn. (4), and the dielectric constant, the refractive index and the surface tension at each χ_{s2}, i.e. at each mole fraction of BuOH and/or water. These data were taken from Refs 18 and 42 for BuOH–Cyhx and Refs 29b and 43 for water–acetonitrile. We found that the dependence of the refractive indices of BuOH–Cyhx mixtures (n) on χ_{BuOH} is given by $n_D^{20} = 1.359 + 0.06697e^{-(\chi_{BuOH})/1.9467}$, $\Sigma Q = 2.6 \times 10^{-8}$. The calculated μ_g depends on the solvent composition; this dependence ($\chi_{s2} = 0$–1) is shown in Table 5. Again, the degree of polynomial employed is that which gave the best fit.

Equation (13) was solved numerically by varying u from 1 to -1 in intervals of 0.02, the ratio a/r from 0 (infinity distance from the probe dipole) to 1 (at the surface of the probe) using 100 intervals and χ_{s2} from 0.1 to 0.9 using 0.1 intervals.

REFERENCES

1. Bunton CA. *J. Mol. Liq.* 1997; **72**:231.
2. El Seoud OA. *Adv. Colloid Interface Sci.* 1989; **30**:1, and references cited therein.
3. Fendler JH. *Membrane Mimetic Chemistry*. Wiley: New York, 1982.
4. Reichardt C. *Solvents and Solvent Effects in Organic Chemistry* (2nd edn). VCH: Weinheim, 1988, and references cited therein.
5. Reichardt C. *Chem. Soc. Rev.* 1992; **21**:147.
6. Reichardt C. *Chem. Rev.* 1994; **94**:2319.
7. Grieser F, Drummond CJ. *J. Phys. Chem.* 1988; **92**:5580, and references cited therein.
8. (a) Novaki LP, El Seoud OA. *Phys. Chem. Chem. Phys.* 1999; **1**:1957; (b) Novaki LP, El Seoud OA. *Langmuir* 2000; **16**:35.
9. Kessler MA, Wolfbeis OS. *Chem. Phys. Lipids* 1989; **50**:51.
10. Park JH, Dallas AJ, Chau P, Carr PW. *J. Phys. Org. Chem.* 1994; **7**:757.
11. Spange S, Reuter A, Lubda D. *Langmuir* 1999; **15**:2103.
12. Novaki LP, El Seoud OA. *Ber. Bunsenges. Phys. Chem.* 1997; **101**:105.
13. Novaki LP, El Seoud OA. *Ber. Bunsenges. Phys. Chem.* 1997; **101**:902.
14. Novaki LP, El Seoud OA. *Ber. Bunsenges. Phys. Chem.* 1996; **100**:648.
15. Perrin DD, Armarego WLF. *Purification of Laboratory Chemicals* (3rd edn). Pergamon Press: New York, 1988.

16. Osterby BR, McKelvey RD. *J. Chem. Educ.*, 1996; **73**:260.
17. Dawber JG, Ward J, Williams RA. *J. Chem. Soc., Faraday Trans. 1* 1988; **84**:713.
18. Suppan P, Ghoneim N. *Solvatochromism*. Royal Society of Chemistry: Cambridge, 1997, and references cited therein.
19. Pytela O. *Collect. Czech. Chem. Commun.* 1988; **53**:1333, and references cited therein.
20. (a) Marcus Y. *J. Solution Chem.*, 1991; **20**:9; (b) Marcus Y. *Chem. Soc. Rev.* 1993; **22**:409.
21. (a) Kamlet MJ, Abboud J-LM, Taft RW. *Prog. Phys. Org. Chem.* 1981; **13**:485; (b) Abraham MH, Grellier PL, Abboud J-LM, Doherty RM, Taft RW. *Can. J. Chem.* 1988; **66**:2673; (c) Laurence C, Nicolet P, Dalati MT, Abboud J-LM, Notario R. *J. Phys. Chem.* 1994; **98**:5807.
22. Bavoux PC, Michel P. *Acta Crystallogr., Sect. B* 1974; **30**:2043.
23. Nakatsu K, Yoshiioka H, Kunimoto K. *Acta Crystallogr., Sect. B* 1978; **34**:2357.
24. Seeman JI, Viers JW, Schung JC, Stovall MD. *J. Am. Chem. Soc.* 1984; **106**:143.
25. Coleman CA, Murray CJ. *J. Org. Chem.* 1992; **57**:3578.
26. Chandramani R, Devaraj N. *J. Chem. Soc., Faraday Trans. 2* 1980; **76**:1055.
27. (a) Engberts JBFN. *Pure Appl. Chem.* 1982; **54**:1797, and references cited therein; (b) Isaacs NS. *Physical Organic Chemistry*. Longman: London, 1987.
28. (a) Toselli NB, Silber JJ, Anunziata JD. *Spectrochim. Acta, Part A* 1988; **44**:829; (b) Boggetti H, Anunziata JD, Cattana R, Silber JJ. *Spectrochim. Acta* 1994; **50**:719; (c) Cattana R, Silber JJ, Anunziata J. *Can. J. Chem.* 1992; **70**:2677.
29. (a) Migron Y, Marcus Y. *J. Chem. Soc., Faraday Trans.* 1991; **87**:1339; (b) Marcus Y, Migron Y. *J. Phys. Chem.* 1991; **95**:400; (c) Marcus Y. *J. Chem. Soc., Faraday Trans.* 1995; **91**:427; (d) Alemany MT, Díez MT, Arín MJ, Abboud J-LM. *J. Phys. Chem.* 1990; **94**:4491.
30. (a) Bosch E, Rosés M. *J. Chem. Soc., Faraday Trans.* 1992; **88**:3541; (b) Rosés M, Ràfols C, Ortega J, Bosch E. *J. Chem. Soc., Perkin Trans. 2* 1995; 1607.
31. (a) Haak JR, Engberts JBFN. *Recl. Trav. Chim. Pays-Bas* 1986; **105**:307. (b) Ben-Naim A. *Hydrophobic Hydration*. Plenum Press: New York, 1980.
32. Barlin GB, Perrin DD. *Q. Rev. Chem. Soc.* 1966; **20**:75.
33. (a) Dawber JG. *J. Chem. Soc., Faraday Trans 1* 1978; **74**:1702; (b) Zelano V, Mirti P. *Z. Phys. Chem., N.F.* 1983; **138**:31.
34. Shulgin I, Ruckenstein E. *J. Phys. Chem. B* 1999; **103**:872.
35. (a) Iwasaki K, Fujiyama T. *J. Phys. Chem.* 1977; **81**:1908; (b) Roux G, Perron G, Desnoyers JE. *J. Solution Chem.* 1978; **7**:639; (c) Holterman HAJ, Engberts JBFN. *J. Org. Chem.* 1983; **48**:4025; (d) Koga Y, Siu WWY, Wong TYH. *J. Phys. Chem.* 1990; **94**:7700.
36. Engberts JBFN. In *Water, a Comprehensive Treatise*, vol. 6, Franks F (ed). Plenum Press: New York, 1979; 139.
37. (a) Wakisaka A, Shimizu Y, Nishi N, Tokumaru K, Sakuragi H. *J. Chem. Soc., Faraday Trans.* 1992; **88**:1129; (b) Wakisaka A, Takahashi S, Nishi N. *J. Chem. Soc., Faraday Trans.* 1995; **91**:4063.
38. (a) Matteoli E, Lepori L. *J. Phys. Chem.*, 1984; **80**:2856; (b) Blandamer MJ, Blundell NJ, Burgess J, Cowles HJ, Horn IM. *J. Chem. Soc., Faraday Trans.* 1990; **86**:277; (c) Rowlen KL, Harris JM. *Anal. Chem.* 1991; **63**:964.
39. (a) Easteal AJ. *Aust. J. Chem.* 1979; **32**:1379; (b) Balakrishnan S, Easteal AJ. *Aust. J. Chem.* 1981; **34**:943; (c) Easteal AJ, Woolf LA. *J. Chem. Thermodyn.* 1982; **14**:755; (d) Davis MI, Douhéret G. *Thermochim. Acta* 1986; **104**:203.
40. Abraham MH, McGowan JC. *Chromatographia* 1987; **23**:243.
41. Hawkins GD, Giesen DJ, Lynch GC, Chambers CC, Rossi I, Storer JW, Li J, Zhu T, Rinaldi D, Liotard DA, Cramer CJ, Truhlar DG. AMSOL-version 6.6. University of Minnesota: Minneapolis, MN, 1998; based in part on Liotard DA, Healy EF, Ruiz JM, Dewar MJS. *AMPAC-version 2.1*.
42. Bhardwaj U, Singh KC, Maken S. *Indian J. Chem., Sect. A* 1997; **36**:1046.
43. Horvath C, Melander W. *J. Chromatogr. Sci.* 1977; **15**:393.