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A novel, convenient, quinoline-based merocyanine dye: probing solvation in pure and mixed solvents and in the interfacial region of an anionic micelle

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ABSTRACT: A novel solvatochromic probe—2,6-dibromo-4-[(*E*)-2-(1-butylquinolinium-4-yl)ethenyl] phenolate, $BuQMBr_2$—has been synthesized and its properties examined. The quinoline-based probe is soluble in more organic solvents than the parent merocyanine dye, 4-[2-(1-methylpyridinium-4-yl)ethenyl] phenolate, and its pK_a is lower by 3.7 units. Its solvatochromic data in binary mixtures of cyclohexane–*n*-butanol showed that the deviation from ideal behavior is due to a combination of non-specific and specific solvent–probe interactions. Its thermo-solvatochromism has been studied in mixtures of water with methanol, ethanol, 1-propanol, 2-propanol and 2-methyl-2-propanol, respectively. The data obtained were analyzed according to a recently introduced model that explicitly considers the presence of 1:1 alcohol–water hydrogen-bonded species, ROH–W, *in bulk solution*, and its exchange equilibria with water and alcohol in the probe solvation microsphere. The composition of the latter is given in terms of the appropriate set of solvent fractionation factors. These indicate that the probe is more solvated by alcohol than by water. Additionally, solvation by ROH–W is favored over solvation by either W or ROH. Solvation by alcohols is more affected by probe–ROH hydrophobic interactions than by hydrogen bonding of ROH to the probe phenolate oxygen. Temperature increase results in a gradual desolvation of the probe, due to a decrease in the hydrogen bonding of all components of the binary solvent mixture. The probe has been employed to calculate the effective concentration of interfacial water of sodium dodecyl sulfate micelles, which is 38.9 mol l^{-1}. Copyright © 2005 John Wiley & Sons, Ltd.

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KEYWORDS: thermo-solvatochromism; aqueous alcohols; solvation mechanisms; anionic micelles

INTRODUCTION

Effects of solvents on reaction rates and equilibria are rationalized in terms of the physicochemical properties of the solvent and its interactions with the species of interest, reactants, activated complexes and products.[1–3] Information on the effects of medium polarity is obtained most conveniently by studying the spectra (absorption or emission) of certain solvatochromic indicators (hereafter designated as 'probes') in solvents and/or in solvent mixtures. Zwitterionic probes have been employed extensively because of their favorable UV–Vis spectral properties. Examples include 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (Reichardt Betaine, RB), 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (Wolfbeis betaine, WB), 1-methylquinolinium-8-olate (QB) and 4-[2-(1-methylpyridinium-4-yl)ethenyl] phenolate (MePM) (see Fig. 1).[2b,4]

The impetus for studying the solvatochromic behavior of these probes is that their ground and excited states differ greatly in polarity, i.e. they serve as models for reactions where there are relatively large differences in polarities between the species of interest, e.g. reactants and activated complexes. Solvatochromic data give information on solvent–probe interactions. For binary solvent mixtures, they shed light on solvent–solvent interactions and on the relationship between the compositions of the probe solvation microsphere and that of the bulk solvent. Finally, thermo-solvatochromic data, derived from effects of temperature on solvatochromism, provide information on the susceptibilities of these interactions to changes in temperature.[4]

Extensive use has been made of an empirical solvent polarity scale, E_T, calculated by Eqn (1):[2b]

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

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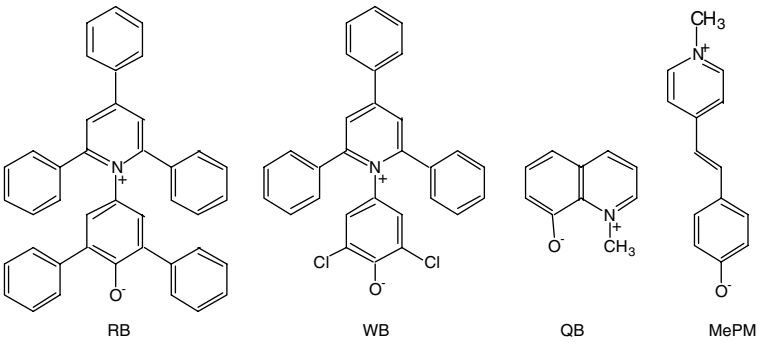


Figure 1. Structures of some previously employed solvatochromic probes; their pK_a values are 8.32, 4.78, 6.80 and 8.37, respectively

This scale converts the electronic transition within the probe into the corresponding intramolecular transition energy in kcal mol^{-1}; this allows quantification of the above-mentioned solvent effects. The solvent polarity scales of the probes depicted in Fig. 1 are referred to as $E_T(30)$, $E_T(33)$, E_T(QB) and E_T(MePM), respectively.

The use of solvatochromic indicators as models underlines the need for studying probes with widely different structures and hence physicochemical properties. The acid–base character of the indicator is of prime importance, because of solute–solvent hydrogen bonding. Use of a zwitterionic probe whose pK_a is relatively high is somewhat limited by the ease of reversible protonation of its phenolate oxygen (zwitterion + $H_3O^+ \leftrightarrows$ cation + H_2O) because the zwitterion is the solvatochromic form. Examples where this problem may arise include the study of relatively acidic solvents,[5] buffer solutions that are employed in the acid region of the pH scale and solutions of organized assemblies (aqueous micelles, micro-emulsions, etc.). In the latter case, the charged micelle interface shifts the indicator equilibrium so that the zwitterionic form may be observed only if acid or base is added.[6,7] This procedure (addition of acid or base to the micellar solution) may be problematic because the added electrolyte may change the properties (e.g. the morphology) of the micellar aggregate or lead to the formation of mixed micelles, e.g. alkyltrimethylammonium halide and hydroxide.[7] Use of solvatochromic probes of low pK_a is therefore advantageous for the study of both bulk and micellar solutions.

In addition to its relatively high pK_a value of 8.37 in water,[8a] MePM is not soluble in several important classes of organic solvents, including haloalkanes (e.g. chloroform and dichloromethane), aromatic solvents (e.g. benzene and toluene) and ethers (e.g. 1,4-dioxane and diethyl ether), therefore E_T(MePM) values for eight solvents have been calculated by extrapolation of polarity versus composition plots of binary solvent mixtures.[8b] Use of this procedure is debatable, however, because the dependence of E_T on solvent composition can be quite complex,[4] i.e. extrapolation may be an unreliable procedure.

In order to address the above-mentioned problems, and because merocyanines of different structures have applications in several fields,[9] we have synthesized the following probes: 4-[(*E*)2-(1-*n*-butylpyridinium-4-yl)ethenyl] phenolate (BuPM), 2-nitro-4-[(*E*)2-(1-*n*-butylpyridinium-4-yl)ethenyl] phenolate ($BuPMNO_2$) and 2,6-dibromo-4-[(*E*)-2-(1-butylquinolinium-4-yl)vinyl] phenolate ($BuQMBr_2$), where M, P and Q refer to the basic merocyanine structure, pyridine and quinoline rings, respectively (see Fig. 2). Of these probes, the last one was found to be the most convenient and its properties were examined in detail.

For $BuQMBr_2$, the properties investigated included its pK_a, solubility in organic solvents (where MePM is insoluble) and thermo-solvatochromism in pure solvents and binary solvent mixtures. Compared with MePM, this novel probe has a much lower pK_a and is soluble in a wider range of organic solvents. The solvatochromic response of $BuQMBr_2$ has been measured in water and in 39 organic solvents at 25 °C; $E_T(BuQMBr_2)$ correlates with the $E_T(30)$ scale. The solvatochromism of $BuQMBr_2$ in a binary mixture of *n*-butanol, *n*-BuOH and cyclohexane (Cyhex) has been studied and the contributions of dielectric enrichment and specific probe–solvent interactions were calculated. Thermo-solvatochromism has been studied in mixtures of water with methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH) and 2-methyl-2-propanol (2-Me-2-PrOH). Non-ideal behavior has been observed for all binary mixtures due to preferential solvation of the probe by the appropriate alcohol. Finally, It is shown that the

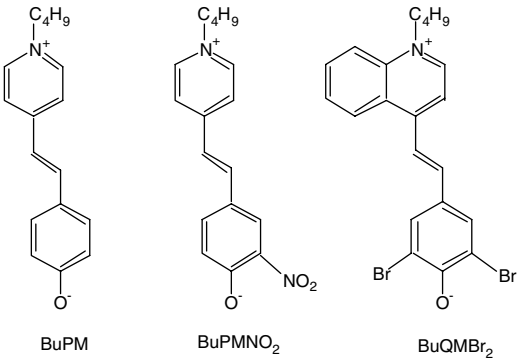


Figure 2. Solvatochromic probes BuPM, $BuPMNO_2$ and $BuQMBr_2$

microscopic polarity of water in the interfacial region of sodium dodecyl sulfate (SDS) can be determined by employing this probe without resorting to the addition of alkali to generate the zwitterionic form.

EXPERIMENTAL

Materials

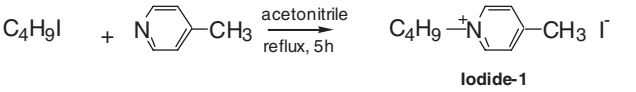
All chemicals were purchased from Acros or Merck. The solvents were purified by the recommended procedures,[10] followed by storing over activated 4 Å molecular sieves. Their purity was established from their densities (using a DMA 40 resonating-tube densimeter, Anton Paar, Graz, Austria) and from agreement between their experimental $E_T(30)$ and published data.[2b] The aromatic aldehydes employed were purified by recrystallization from aqueous ethanol and dried to give: white needles, m.p. = 115.5–117 °C (4-hydroxybenzaldehyde); and dark yellow needles, m.p. = 140–142 °C (4-hydroxy-3-nitro-benzaldehyde).[11] Sodium dodecyl sulfate was crystallized from methanol and dried before use.

Apparatus

Melting points were determined with IA 6304 apparatus (Electrothermal, London, UK). Elemental analyses were carried out on a Perkin-Elmer 2400 CHN-analyzer (Perkin-Elmer, Wellesley, USA) in the analytical center of this Institute. The IR and NMR spectra were recorded on a Bruker Victor-22 FTIR spectrometer (Bruker Optics, Ettlingen, Germany) and a Varian Innova-300 NMR spectrometer (Varian, Palo Alto, USA). Analysis of the ^{1}H NMR data was based on simulation of the one-dimensional spectra and the DQF-COSY experiment.[12] A tube rotator (Lab Industries, Berkeley, USA) was employed for probe dissolution; solubilization in water required the use of a sonication bath (Inpec Eletronica, São Paulo, Brazil).

Probes

A commercial sample of RB was employed and MePM was available from previous studies,[4d,e] BuPM was synthesized according to the following equations:[8a,c,d]



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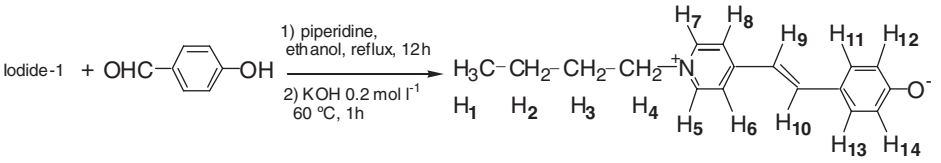
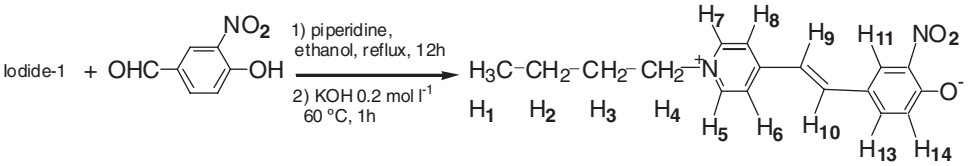


(3)

Yield 83%, purple crystals that shrink at 175 °C and melt at 210 °C, literature m.p. = 215 °C;[8d] IR (KBr, cm^{-1}): 3023, 2957 ($\nu_{C—H}$), 1592 ($\nu_{C=C}$); 1146 ($\nu_{C—N}$), The ^{1}H NMR results are given in Table 1.

The BuPMNO$_2$ probe was synthesized similar to BuPM, except that 1-*n*-butyl-4-methylpyridinium iodide was condensed with 4-hydroxy-3-nitro-benzaldehyde instead of 4-hydroxy-benzaldehyde (Eqn (4)). Yield 85%, orange crystals, m.p. 203–205 °C; IR (KBr, cm^{-1}): 3049, 2957 ($\nu_{C—H}$), 1573 ($\nu_{C=C}$); 1531, 1348 (ν_{NO_2}); 1177 ($\nu_{C—N}$). For ^{1}H NMR, see Table 1.



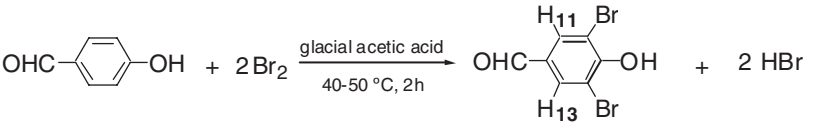
(4)

Table 1. The ^{1}H NMR data for probes BuPM, $BuPMNO_2$ and $BuQMBr_2$[a]

	BuPM		$BuPMNO_2$		$BuQMBr_2$	
	δ(ppm)	J(Hz)	δ(ppm)	J(Hz)	δ(ppm)	J(Hz)
H1	0.908 (t)	$J_{1-2}=7.4$	0.914 (t)	$J_{1-2}=7.4$	0.926 (t)	$J_{1-2}=7.4$
H2	1.279 (sx)	$J_{2-3}=7.4$	1.282 (sx)	$J_{2-3}=7.4$	1.379 (sx)	$J_{2-3}=7.4$
H3	1.821 (q)	$J_{3-4}=7.4$	1.837 (q)	$J_{3-4}=7.4$	1.845 (q)	$J_{3-4}=7.4$
H4	4.311 (t)	—	4.339 (t)	—	4.659 (t)	—
H5	8.566 (d)	$J_{5-6}=6.7$	8.634 (d)	$J_{5-6}=6.8$	8.710 (d)	$J_{5-6}=6.9$
H6	7.857 (d)	—	7.918 (d)	—	7.935 (d)	—
H7	[b]	—	[b]	—	—	—
H8	[b]	—	[b]	—	—	—
H9	7.820 (d)	$J_{9-10}=15.4$	7.893 (d)	$J_{9-10}=15.7$	8.060 (d)	$J_{9-10}=15.1$
H10	6.907 (d)	—	6.874 (d)	—	7.600 (d)	—
H11	7.455 (d)	—	8.062 (dd)	$J_{11-13}=2.4$	8.071 (s)	—
H12	6.518 (d)	—	—	—	—	—
H13	[b]	—	7.553 (dd)	$J_{13-14}=9.3$	[b]	—
H14	[b]	—	6.400 (d)		—	—
H15	—	—	—	—	8.964 (d)	$J_{15-16}=8.5$
H16	—	—	—	—	7.776 (t)	—
H17	—	—	—	—	[c]	—
H18	—	—	—	—	8.202 (d)	$J_{18-17}=9.2$

[a] The discrete hydrogen atoms of the compounds synthesized are numbered according to the structures shown in Eqn (3) (BuPM), Eqn (4) ($BuPMNO_2$) and Eqn (7) ($BuQMBr_2$), respectively. At 300 MHz and 25 °C, all compounds were dissolved in DMSO-*d6*. The reference used was tetramethylsilane. The abbreviations used for peak splitting (d, dd, q, s, sx and t) stand for doublet, doublet of doublets, quintet; singlet, sextet and triplet, respectively.
[b] No chemical shifts are listed for these protons because of their chemical and magnetic equivalence to other protons in the molecule, namely $\delta_{H5}=\delta_{H7}$, $\delta_{H6}=\delta_{H8}$, $\delta_{H11}=H_{13}$ and $\delta_{H12}=\delta_{H14}$, respectively.
[c] The chemical shift is not listed because the corresponding peak is 'buried' under those of H11 and H13.

The $BuQMBr_2$ probe was synthesized according to the following equations:



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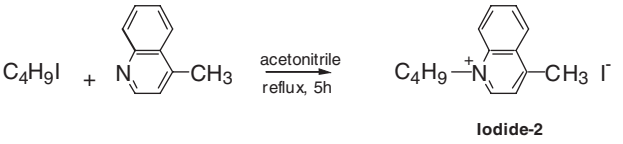

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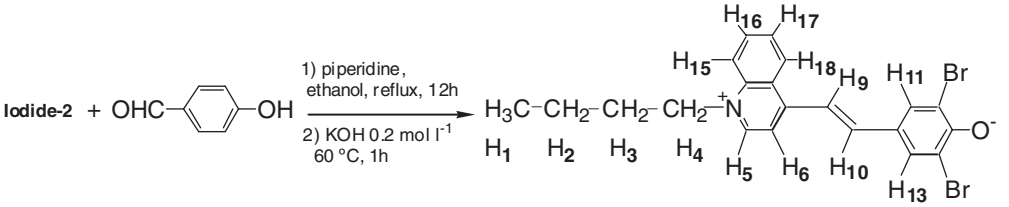

(7)

The reaction of bromine with 4-hydroxybenzaldehyde (Eqn (4)) was carried out as described elsewhere.[13] The reaction product was washed with water, recrystallized from aqueous ethanol (1:1) and dried under reduced pressure. Yield 85%, white needles, m.p. = 177.5–179.5 °C; literature m.p. 177–179 °C.[13] Calculated for $C_7H_4O_2Br_2$ (%): C, 30.04; H, 1.44. Analyzed (%): C, 30.30; H 1.53. IR (KBr, cm^{-1}): 3189 ($\nu_{O—H}$), 1679 ($\nu_{C=O}$), 1580 ($\nu_{C—H}$), 1036 ($\nu_{C—Br}$); ^{1}H NMR (DMSO-d_6): δ (ppm) = 8.08 (s, 2H, H11, H13), 9.79 (s, ArC*H*=O).

The synthesis of 1-*n*-butyl-4-methylquinolinium iodide from 4-methylquinoline and *n*-butyl iodide

(Eqn (6)) was carried as given elsewhere.[8e] The solvent and excess *n*-butyl iodide were removed and the product (light amber liquid, free of 4-methylquinoline) was used without further purification. Condensation of this iodide with 3,5-dibromo-4-hydroxybenzaldehyde in the presence of piperidine (Eqn (7)), followed by treatment with KOH[8c] and recrystallization from ethanol–acetone (1:1), gave $BuQMBr_2$ as green–violet crystals, yield 80%, m.p. = 235–237 °C. Calculated for $C_{21}H_{19}Br_2NO$ (%): C, 54.29; H, 4.15; N, 3.04. Analyzed (%): C, 54.29; H, 4.22; N, 3.01. IR (KBr, cm^{-1}): 3069, 2958 ($\nu_{C—H}$); 1594 ($\nu_{C=C}$); 1201 ($\nu_{C—N}$), 1041 ($\nu_{C—Br}$). For ^1H NMR, see Table 1.

Sample preparation and spectrometric determination of E_T

Binary mixtures (16 per set) were prepared by weight at 25 °C. Probe solution in acetone was pipetted into 1-ml volumetric tubes, followed by solvent evaporation under reduced pressure over P_4O_{10}. Pure solvents and/or binary solvent mixtures were added, and the probe (final concentration 2–5 $\times 10^{-4}$ mol l^{-1}, was dissolved. The 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 10^{-4}–10^{-3} mol l^{-1}. This was taken to indicate that no intermolecular probe interactions occur under our experimental conditions. A Beckman DU-70 UV–Vis spectrophotometer was used. The temperature *inside* the thermostatted cell-holder was controlled to within ± 0.05 °C with a digital thermometer (model 4000A, Yellow Springs Instrument, Ohio, USA). Each spectrum was recorded twice at a rate of 120 nm min^{-1}; the values of λ_{max} were determined from the first derivative of the absorption spectra. The uncertainties in E_T(BuPM), E_T($BuPMNO_2$) and E_T($BuQMBr_2$) are 0.1 kcal mol^{-1}. The temperature range investigated was dictated either by the b.p. of the solvent (MeOH, 64.5 °C) or its m.p. (2-Me-2-PrOH, 25.5 °C). Stable absorbance readings were observed for probe solutions in the latter alcohol at 25 °C, probably because its m.p. is depressed by the solute and by the low atmospheric pressure in the city of São Paulo.

Spectrometric determination of log *P*, the partition coefficient of the probe between water and *n*-octanol

The definition of this coefficient is: $\log P = [probe]_{n\text{-octanol}}/[probe]_{water}$.[14] The aqueous phase was a phosphate buffer solution (0.05 mol l^{-1}, pH 7.50). Equal volumes of this buffer and *n*-octanol were agitated for 1 h (tube rotator) and the phases were separated. A probe solution (5×10^{-4} mol l^{-1}) in buffer-saturated *n*-octanol was prepared and its absorbance ($A_{initial}$) was measured. A 0.7 ml aliquot of this solution was agitated with 4 ml of *n*-octanol-saturated buffer at room temperature for 2 h. After phase separation at 25 °C, the absorbance ($A_{equilibrium}$) of the *n*-octanol phase was measured and the partition coefficient was calculated from: $\log P = \log (A_{equilibrium} \times 4/(A_{initial} - A_{equilibrium}) \times 0.7)$; $\log P_{BuQMBr_2}$ was found to be 2.51 ± 0.05.

Spectrometric determination of pK_a of $BuQMBr_2$

The pK_a was calculated from the Henderson–Hasselbach equation. Solutions of the probe (final concentration = 5×10^{-4} mol l^{-1}) were prepared in a potassium hydrogen phthalate buffer (0.05 mol l^{-1}) and the concentrations of the zwitterionic form were measured at 490 nm at 25 °C. The pK_a of $BuQMBr_2$ at this ionic strength was found to be 4.89 ± 0.02.

Determination of the polarity of interfacial water of SDS micelles

The probe solution in acetone (0.1 ml, 5×10^{-3} mol l^{-1}) was pipetted into 1-ml volumetric tubes, followed by solvent evaporation under reduced pressure. The volumes then were made up to the mark with aqueous SDS solutions. Values of λ_{max} were found to be practically constant at 542.5 ± 0.5 nm as a function of [SDS] in the concentration range of 0.016–0.204 mol l^{-1}. The zwitterionic form of $BuQMBr_2$ was present in SDS solutions without the addition of base, whereas the corresponding form of MePM appeared at a (bulk) solution pH of 12.8. The polarity of interfacial water was found to be 52.7 kcal mol^{-1}.

RESULTS AND DISCUSSION

Comment on the structure of the probe

The BuPM probe was synthesized to evaluate the effect of increasing the hydrophobic character of the merocyanine structure on its solubility in organic solvents. Indeed, this probe was found to be soluble in THF, 1,4-dioxane and chloroform, i.e. in solvents where MePM is not soluble. In order to decrease the probe pK_a, a strong electron-attracting group (NO_2) was introduced into the phenolate moiety. The expected pK_a of $BuPMNO_2$ is 5.6, based on the pK_a of MePM (8.37) and those of 4-hydroxybenzaldehyde (7.66) and 3-nitro-4-hydroxybenzaldehyde (4.9). The new probe was found to be soluble in the same solvents as BuPM, although its solvatochromism was much less, as shown by values of $\lambda_{max,\ pyridine} - \lambda_{max,\ ethanol} = 31$ and 93 nm for $BuPMNO_2$ and BuPM, respectively. This decreased solvatochromism is due to the competition of the nitro group and

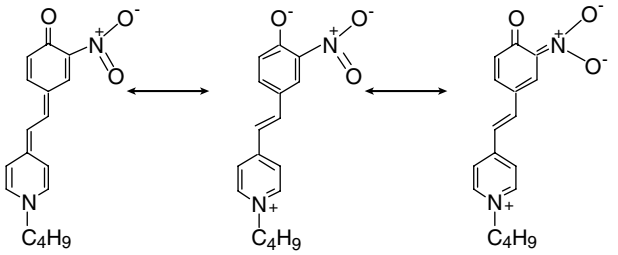

Figure 3. Resonance structures of $BuPMNO_2$

the positively charged heterocyclic ring for the electron pair of the phenolate oxygen, as discussed elsewhere[15] (Fig. 3).

The probe pK_a also may be decreased by the introduction of halogen atoms, where the contribution of the above-mentioned competition is expected to be less important. Our calculations have indicated that the introduction of one or two bromine atoms in 4-hydroxybenzaldehyde should reduce the pK_a of MePM to ca. 6.9 and 4.9, respectively. We decided to use 3,5-dibromo-4-hydroxybenzaldehyde because the pK_a of the resulting probe should be comparable to that of WB (4.78). Log *P* is a measure of the hydrophobic character of compounds and the values are 1.22 and 2.61 for (the precursor) 4-methylpyridine and 4-methylquinoline, respectively. Because the contribution of the rest of the molecule (namely, the hydroxybenzaldehyde moiety) to log *P* is constant, a quinoline-based merocyanine probe is expected to be ca. 25 times ($10^{(1.39)}$) more hydrophobic, i.e. more soluble in organic solvents than its pyridine-based counterpart. Therefore, we decided to synthesize $BuQMBr_2$ and test its solubility and solvatochromism in organic solvents. The results obtained agreed with our calculations; pK_a and log *P* for this probe were found to be 4.89 and 2.51, respectively. Additionally, the probe was found to be soluble in (at least) eight important organic solvents where MePM is not soluble, namely, benzene, toluene, xylenes, chloroform, chlorobenzene, ethyl acetate, 1,4-dioxane and THF.

Solvatochromism in pure solvents

Table 2 shows the $E_T(BuQMBr_2)$ measured; its correlation with the $E_T(30)$ scale is described by Eqn (8):

$$E_T(BuQMBr_2) = 55.473 - 0.9497\ (E_T(30)) + 0.01562\ (E_T(30))^2 \quad (8)$$
$$r_{mult} = 0.9619;\ SD = 0.6982$$

where r_{mult} and SD refer to the multiple-regression coefficient and the standard deviation of the data, respectively. This correlation is not linear (see Fig. 4), unlike those between other polarity scales, e.g. E_T(WB) and E_T(QB) and E_T(30).[4a,b] The reason is that the dipolarity of the ground state of $E_T(BuQMBr_2)$ is most certainly solvent-dependent, i.e. the probe is moderately dipolar in relatively non-polar solvents and highly dipolar in polar media, as argued elsewhere for the parent MePM.[9a,c] The preceding conclusion is corroborated by the fact that the correlation is reasonably linear if the data of four solvents (water, methanol, ethanol and ethylene glycol) were

Table 2. Solvent polarity (E_T in kcal mol^{-1})[a] based on the solvatochromic probe $BuQMBr_2$: $E_T(BuQMBr_2)$[b]

Number	Solvent	$E_T(BuQMBr_2)$
1	Water	58.25
Normal-chain alcohols		
2	Methanol	50.67
3	Ethanol	48.01
4	1-Propanol	47.08
5	1-Butanol	46.53
6	1-Hexanol	45.76
7	1-Octanol	45.11
Branched-chain alcohols, other alcohols, 2-alkoxyethanols		
8	2-Propanol	46.04
9	2-Butanol	45.22
10	2-Methyl-2-propanol	43.52
11	3-Methyl-1-butanol	45.97
12	Ethylene glycol	52.58
13	Benzyl alcohol	47.12
14	Cyclohexanol	45.20
15	2-Methoxyethanol	48.28
16	2-Ethoxyethanol	46.84
17	2-Propoxyethanol	46.26
18	2-Butoxyethanol	45.87
19	2-(2-Methoxy-ethoxy)ethanol	46.75
Chlorinated and aromatic solvents		
20	Chloroform	41.63
21	Dichloromethane	42.68
22	1,2-Dichloroethane	42.71
23	Chlorobenzene	41.20
24	Benzene	40.85
25	Toluene	40.86
26	Xylenes	40.93
Polar aprotic solvents		
27	Acetone	44.07
28	Acetonitrile	46.00
29	*N*,*N*-Dimethylacetamide	44.54
30	*N*,*N*-Dimethylformamide	45.03
31	1,3-Dimethyl-2-imidazolidinone	44.41
32	DMSO	45.61
33	1,4-Dioxane	41.38
34	Ethyl acetate	42.22
35	Diethyl Ether	41.22
36	Ethylene glycol dimethylether	42.5
37	Methyl carbonate	42.11
38	Nitromethane	46.00
39	Pyridine	43.04
40	THF	42.07

[a] Values of $E_T(30)$ determined in this work for 2-propoxyethanol, 2-(2-methoxy-ethoxy)ethanol and 1,3-dimethyl-2-imidazolidinone are 50.64, 50.59 and 42.80 kcal mol^{-1}, respectively.
[b] MePM is not soluble in apolar solvents such as benzene, toluene, xylenes, chloroform, chlorobenzene, dioxane, THF, ethyl acetate and diethyl ether. All values were determined at 25 °C and the uncertainty in $E_T(BuQMBr_2)$ is 0.1 kcal mol^{-1}.

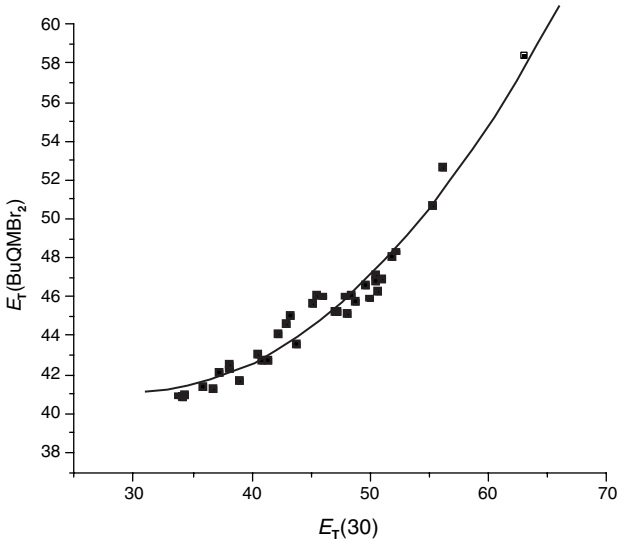

Figure 4. Correlation between the E_T(BuQMBr$_2$) and E_T(30) polarity scales, data at 25 °C

eliminated ($E_T(\text{BuQMBr}_2) = 27.746 - 0.377\ (E_T(30))$, correlation coefficient = 0.9674). These are the most polar solvents among those tested; their relative permittivities are high and they form strong hydrogen bonds to the probe phenolate oxygen. These solvent properties stabilize the probe zwitterionic form, i.e. increase its contribution to the corresponding resonance hybrid (see the first two structures of Fig. 3). This leads to the observed positive deviation in the E_T(BuQMBr$_2$) versus E_T(30), because λ_{max} quinonoid structure > λ_{max} zwitterionic structure (Fig. 4).[9c] Additional evidence may be deduced from our calculations of the dipole moment of BuQMBr$_2$ solvated in Cyhex–BuOH mixtures, whose value increases as a function of increasing [BuOH] (Amsol program package, version 3, University of Minnesota, USA; see Eqn 17 in the Calculations section).

The Taft–Kamlet–Abboud equation is widely employed to quantify probe–solvent interactions. For a single solute in a series of solvents, this equation takes the form:[16]

$$\text{SDP} = \text{Constant} + s(\pi^*_{\text{solv}} + \text{d}\delta) + a\ \alpha_{\text{solv}} + b\ \beta_{\text{solv}} + h\left(\delta^2_{\text{H}}\right) \quad (9)$$

where the solvent-dependent property (SDP), such as a solvatochromic shift, is modeled as a linear combination of a dipolarity/polarizability term s ($\pi^*_{\text{solv}} + \text{d}\delta$), 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 (δ^2_{H}). The latter 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 use the subscript (solv) so that they are not confused with other known quantities, e.g. α and β of the Brønsted equation.

Equation (9) has been applied to the data of BuQMBr$_2$, taking into account the conditions required to obtain meaningful statistical correlations.[4a,b,16] Table 3 shows the regression coefficients calculated from data at 25 °C; the corresponding data for MePM, RB and WB are those published elsewhere.[2,4a,b]

The number of solvents employed in Eqn (9) is smaller than that used in Eqn (8) because of the unavailability of solvatochromic parameters for some solvents, namely ethylene glycol dimethylether, methyl carbonate and 1,3-dimethyl-2-imidazolidinone. The regression coefficients indicate that *all probes* are much more sensitive to the dipolarity/polarizability and acidity of the solvent than to its basicity, most certainly because the probes do not carry groups that can act as a hydrogen-bond donor, e.g. OH. As expected, the susceptibility of BuQMBr$_2$ to hydrogen bonding with the solvent (through its phenolate oxygen) is much lower than that of the structurally similar but more basic MePM. Values of the regression coefficient (a) for BuQMBr$_2$ and WB merit comment because their pK_a values are similar (4.89 and 4.78, respectively). We have discussed previously the reasons for the enhanced susceptibility of WB as a hydrogen-bond acceptor, e.g. relative to RB, whose pK_a is 8.65.[4b] Briefly, this results from two structural features:

(i) *Steric*. The two *ortho*-chlorine atoms of WB lie in the plane of the phenol ring, whereas the two *ortho*-phenyl rings of RB are twisted in opposite directions with respect to the plane of the phenol ring. Therefore, the *free* solid angle around the oxygen atom of the phenolate ion of RB (a measure of its accessibility to hydrogen bonding) should be smaller than the corresponding one for WB.[17]

Table 3. Results of the application of Eqn (9): E_T (probe) = Constant + s ($\pi^*_{\text{solv}} + \text{d}\delta$) + $a\alpha_{\text{solv}} + b\beta_{\text{solv}}$

Probe	Constant	$s(\pi^*_{\text{solv}})$	d	a	b	r_{mult}	$F_{4,95}$	Number of solvents
BuQMBr$_2$[a]	38.10 (±0.99)	9.13 (±0.99)	−2.69 (±0.76)	7.78 (±0.60)	−2.59 (±1.06)	0.9145	86	37
MePM[a]	40.37 (±1.08)	11.45 (±1.01)	−3.84 (±0.86)	11.78 (±0.54)	−2.46 (±0.93)	0.9605	133	28
RB[b]	30.9 (±1.32)	14.35 (±1.32)	−4.40 (±1.01)	15.39 (±0.79)	−0.72 (±1.40)	0.9617	200	37
WB[b]	38.6 (±1.8)	14.7 (±2)	−4.0 (±1.2)	15.30 (±0.97)	0.2 (±1.6)	0.9490	94	28

[a] Present work: solvent polarities measured at 25 °C.
[b] Values calculated from published data at 25 °C.[2,4a,b]

(ii) *Electronic*. The C—Cl bond of chlorophenols is polarized appreciably so that the chlorine atom forms hydrogen bonds with suitable donors, e.g. the solvent.[18] The effects of the above-mentioned structural features are expected to be operative for $BuQMBr_2$. Their contribution is probably less than in the case of WB because the presence of a 'spacer' (the double bond) between the heterocycle and the phenoxide ring of merocyanines is expected to decrease its susceptibility to solvent properties. This conclusion is corroborated by the fact that $s(\pi^*_{solvent})$ and a for the two merocyanine dyes are smaller than their counterparts of RB and WB, respectively (Table 3). Additionally, the bromine atoms are less electronegative and more voluminous than the chlorine atoms (Pauling electronegativity scale: atomic radii are 3.0 and 3.2 and 1.96 and 1.81 Å, respectively). Both factors should result in a decreased susceptibility of $BuQMBr_2$ as a hydrogen-bond acceptor relative to WB.

Solvatochromism in binary solvent mixtures

If probe solvation in binary solvent mixtures was ideal, E_T(probe) should be a linear function of the mole fraction (χ) of the more polar component. It is possible to test this hypothesis by examining solvatochromism in certain binary mixtures, e.g. cyclohexane–THF and cyclohexane–1-butanol (Cyhex–BuOH). The reason is that these are ideal mixtures; their relative permittivities are linear functions in χ_{THF} and χ_{BuOH}, respectively.[19] This expectation is in variance with the upper curve of Fig. 5, where the relationship between the reduced polarity $E_T^r = [E_T(\text{binary mixture}) - E_T\ (\text{Cyhex})/E_T\ (\text{BuOH}) - E_T\ (\text{Cyhex})]$ and χ_{BuOH} is clearly non-linear.

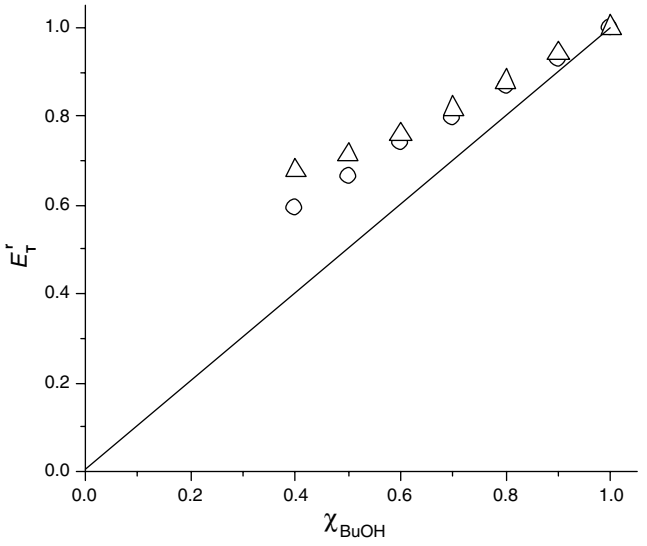

Figure 5. Dependence of E_T^r ($BuQMBr_2$) on χ_{BuOH}. The diagonal line represents the expected behavior if solvatochromism were ideal, i.e. if there were no preferential solvation of the probe: (△) experimental results; (○) calculated contribution to E_T^r of dielectric enrichment (see Eqn (16) of the Calculations section)

The observed deviation from linearity results in part from 'preferential solvation' of the probe by a component of the binary mixture. In principle, this phenomenon includes contributions from: 'Dielectric enrichment', which denotes enrichment of the solvation shell of the probe in the solvent of higher relative permittivity (BuOH) due to probe-dipole–solvent-dipole interactions; and specific probe–solvent interactions, e.g. hydrogen bonding.[19] Non-linear behavior also results from solvent microheterogeneity, i.e. when one component of the binary mixture prefers a molecule of the same type.[2,4,19,20] The contribution of non-specific (dielectric enrichment) and specific interactions (hydrogen bonding) has been calculated and the results are shown in Fig. 5 (details of these and all subsequent calculations are given in the Calculations section). Note that: 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; the energy difference between the diagonal line and the curve defined by the symbol ○ represents the contribution to preferential solvation by dielectric enrichment; and the energy difference between the curves defined by the symbols ○ and △ represents the contribution to preferential solvation by specific solute–solvent interactions, e.g. hydrogen bonding. It is clear from Fig. 5 that both solvation mechanisms contribute to the deviation of E_T^r from ideality. The results of these calculations show that the contribution of hydrogen bonding is more important at lower χ_{BuOH}, i.e. where the auto-association of the alcohol is not extensive. Compared with the results of RB in the same binary mixture, the contribution of hydrogen bonding to the preferential solvation of $BuQMBr_2$ is less, in agreement with the difference between the basicities of both probes.

Thermo-solvatochromism in binary solvent mixtures

Thermo-solvatochromism of $BuQMBr_2$ has been studied in mixtures of water with five alcohols: MeOH, EtOH, 1-PrOH, 2-PrOH and 2-Me-2-PrOH, respectively. In all cases, the compositions investigated covered the whole range, from pure water to pure solvent; the temperature range, where possible, was 10–60 °C. Considering our results, the following factors are relevant.

As discussed above, the dependence of E_T on solvent composition, e.g. on the mole fraction of water (χ_W), is not linear because of specific and non-specific probe–solvent interactions and the microheterogeneity of the binary mixture. The first two mechanisms are probe-induced whereas solvent microheterogeneity is not.[22]

Our solvatochromic data have been treated according to the following recently introduced model:[4c]

$$\mathrm{ROH} + \mathrm{W} \rightleftharpoons \mathrm{ROH\text{–}W} \tag{10}$$

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

$$\mathrm{Probe(W)}_m + m\ (\mathrm{ROH\text{–}W}) \rightleftharpoons \mathrm{Probe(ROH\text{–}W)}_m + m\ \mathrm{W} \tag{12}$$

where m represents the number of solvent molecules whose exchange in the probe solvation microsphere affects E_T; usually $m \leqslant 2$. The relevant point about this model is that it *explicitly* considers the formation of the complex solvent species ROH–W, whose formation constant is K_{assoc}. Consequently, the mole fractions employed in all calculations are 'effective' and not analytical. The equilibrium constants of Eqns (10)–(12) are termed solvent 'fractionation factors', defined as:

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

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

$$\varphi_{ROH-W/W} = \frac{\chi_{ROH-W}^{Probe} / \chi_{W}^{Probe}}{\left(\chi_{ROH-W}^{Bk;\,Effective} / \chi_{W}^{Bk;\,Effective}\right)^m} \tag{15}$$

where Bk refers to bulk solvent. In Eqn (13) $\varphi_{W/ROH}$ describes the composition of the probe solvation microsphere relative to that of bulk solvent. For $\varphi_{W/ROH} > 1$, the solvation microsphere is richer in W than bulk solvent; the converse is true for $\varphi_{W/ROH} < 1$, i.e. the probe is solvated preferentially by ROH. Finally, a solvent fractionation factor of unity indicates an ideal behavior, i.e. the solvation microsphere and bulk solvent have the same composition. The same line of reasoning applies to $\varphi_{ROH-W/ROH}$ and $\varphi_{ROH-W/W}$, depicted in Eqns (14) and (15).

Rather than reporting extensive lists of $E_T(BuQMBr_2)$ and solvent compositions, we have calculated the (polynomial) dependence of polarity on $\chi_W^{Analytical}$ and present the regression coefficients in Table *ESI* 1 (see Supplementary material). 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^2). The quality of our data is evidenced by these statistical criteria and by the excellent agreement between calculated and experimental $E_T(BuQMBr_2)_{ROH}$, and $E_T(BuQMBr_2)_W$ *at all temperatures* (see Table 4). Preferential solvation by the organic component of the binary solvent mixture leads to $E_T(BuQMBr_2)$ values that lie *below* the line that connects the polarities of the two pure components, as shown in Figs 6 and 7.

As discussed above, all probes employed act as hydrogen-bond acceptors through their phenolate oxygens.[21] There are also hydrophobic interactions between the probe and the alkyl chain of the alcohol (either as pure species or as ROH–W), therefore preferential solvation is expected to depend on the pK_a and hydrophilic/hydrophobic character of both the probe and the alcohol. The importance of $BuQMBr_2$–ROH hydrophobic interactions can be deduced from the fact that $\varphi_{W/ROH}(MeOH) > \varphi_{W/ROH}(EtOH) > \varphi_{W/ROH}$ (1-PrOH) *at each temperature* (Table 4), i.e. more hydrophobic, linear alcohols solvate $BuQMBr_2$ more efficiently, although they are weaker acids. Apparently, the decrease in hydrogen bonding to the probe is more than compensated for by probe–ROH hydrophobic interactions. This conclusion appears to be a general one, as shown in the third column of Table 5 ($\varphi_{W/ROH}$), for MePM, $BuQMBr_2$ and WB, respectively.

All $\varphi_{ROH-W/ROH}$ and $\varphi_{ROH-W/W}$ values are >1, indicating that $BuQMBr_2$ is preferentially solvated by ROH–W. Additionally, all $\varphi_{ROH-W/W}$ values are larger than the corresponding $\varphi_{ROH-W/ROH}$ values, indicating that ROH–W displaces water more efficiently than alcohol (from the solvation microsphere of the probe). Because all alcohols employed are more basic than water, the structure of the complex species may be depicted as: H_w—O—H . . . O(R)H_{ROH}, i.e. water is the hydrogen bond donor to alcohol so that the two hydrogen atoms marked in italic are the sites for hydrogen bonding with the probe phenolate oxygen. As argued elsewhere, this hydrogen bonding partially deactivates H_w towards further hydrogen bonding and this deactivation is greater with a more basic alcohol.[23,24] Therefore, the order observed ($\varphi_{ROH-W/W} > \varphi_{ROH-W/ROH}$) may be due to a combination of partial deactivation of hydrogen bonding by H_w and the presence of an additional solvation mechanism that is not operative for water. Note that hydrogen bonding and hydrophobic interactions contribute to solvation by ROH and/or ROH–W, whereas hydrogen bonding is the main contributing mechanism to solvation by water. Again, these conclusions apply to all three probes shown in Table 5.

At comparable temperatures, the data of branched alcohols show that W displaces 2-Me-2-PrOH more efficiently than 2-PrOH, and that 2-PrOH–W displaces both water and the precursor alcohol more efficiently than

Table 4. Analysis of thermo-solvatochromic responses in binary water/alcohol mixtures

ROH	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]
MeOH	10	1.467	0.364	3.434	9.434	51.393 [−0.006]	58.681 [0.040]	0.064	-6.5×10^{-8}
	25	1.063	0.392	1.808	4.612	50.731 [0.030]	58.247 [0.005]	0.079	3.3×10^{-5}
	40	1.021	0.434	1.552	3.576	50.424 [−0.012]	57.785 [−0.002]	0.065	5.4×10^{-6}
EtOH	10	1.512	0.204	10.122	49.618	48.553 [0.017]	58.704 [0.017]	0.119	1.7×10^{-4}
	25	1.368	0.224	7.108	31.732	48.146 [0.014]	58.203 [0.049]	0.093	1.5×10^{-5}
	40	1.258	0.235	5.802	24.689	47.737 [−0.090]	57.786 [−0.003]	0.069	-2×10^{-6}
	60	1.140	0.247	3.965	16.053	47.200 [−0.034]	57.156 [0.003]	0.120	1.7×10^{-4}
1-PrOH	10	1.717	0.198	84.503	426.783	47.562 [−0.098]	58.722 [−0.001]	0.207	2.1×10^{-5}
	25	1.411	0.207	69.617	336.314	47.171 [−0.069]	58.285 [−0.033]	0.188	1.4×10^{-4}
	40	1.322	0.216	40.003	185.199	46.698 [−0.092]	57.783 [−0.016]	0.185	2.6×10^{-4}
	60	1.237	0.237	36.711	154.899	46.221 [−0.012]	57.169 [−0.010]	0.137	-9.5×10^{-5}
2-PrOH	10	1.582	0.329	116.760	354.894	46.569 [−0.017]	58.658 [0.063]	0.134	-1.2×10^{-4}
	25	1.413	0.336	67.585	201.145	46.006 [−0.116]	58.259 [−0.007]	0.095	2.1×10^{-5}
	40	1.287	0.362	41.666	115.099	45.684 [0.034]	57.803 [−0.020]	0.162	1.6×10^{-6}
	60	1.226	0.374	32.616	87.209	45.189 [0.014]	57.183 [−0.024]	0.155	-1.9×10^{-4}
2-Me-2-PrOH	25	1.482	0.396	32.136	81.152	43.7676 [−0.098]	58.316 [−0.064]	0.137	1.2×10^{-6}
	40	1.062	0.418	31.427	75.733	42.997 [−0.057]	57.871 [−0.088]	0.230	-5.8×10^{-6}
	60	1.035	0.420	29.288	69.733	42.543 [0.031]	57.217 [−0.028]	0.176	-2.2×10^{5}

[a] Calculated by regression of E_T of the binary mixture versus composition, in kcal mol^{-1}. The values inside the square brackets are $\Delta E_T(probe)_{Solvent}$ (ROH and/or W) = Experimental $\Delta E_T(probe)_{Solvent}$ − calculated $\Delta E_T(probe)_{Solvent}$.
[b] SD = standard deviation; ΣQ = sum of the squares of the residuals.

its 2-Me–2-PrOH–W counterpart. The subtle interplay between hydrogen bonding, hydrophobic interactions and steric factors determines the efficiency of solvation by ROH as well as by ROH–W. Compared with 2-PrOH, the solvent 2-Me–2-PrOH is less acidic, more hydrophobic and its OH group is less accessible to hydrogen bonding (see the discussion above about the adverse effect of steric crowding on hydrogen bonding). The H_w of 2-Me–2-PrOH–W should be more deactivated towards hydrogen-bond formation than the H_w of 2-PrOH–W. This combination of effects explains the efficiency of displacement of 2-Me–2-PrOH (a weaker and sterically-crowded acid) by water. On the other hand, the less basic and less crowded 2-PrOH–W displaces W and 2-PrOH more efficiently.

With regard to thermo-solvatochromism, Table 4 reveals the following changes as a function of increasing temperature: a *decrease* in m, $E_T(BuQMBr_2)_W$, $E_T(BuQMBr_2)_{ROH}$, $\varphi_{ROH-W/ROH}$ and $\varphi_{ROH-W/W}$; and an *increase* in $\varphi_{W/ROH}$. The decrease in polarities of pure solvents can be attributed to a decrease of solvent stabilization of the probe ground state as a result of the concomitant decrease of solvent structure and hydrogen bonding ability.[2,24,26] 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,[20,27,28] with a concomitant decrease in the ability of the mixed solvent to displace both W and ROH. This leads to a decrease of both $\varphi_{ROH-W/ROH}$ and $\varphi_{ROH-W/W}$ as a function of increasing temperature. Because W is more structured than ROH, its hydrogen bonding to the probe ground state is less susceptible to temperature increase than ROH. This leads to a measurable 'depletion' of ROH in the probe solvation microsphere, so that $\varphi_{W/ROH}$ increases as a function of increasing temperature.[4c–e]

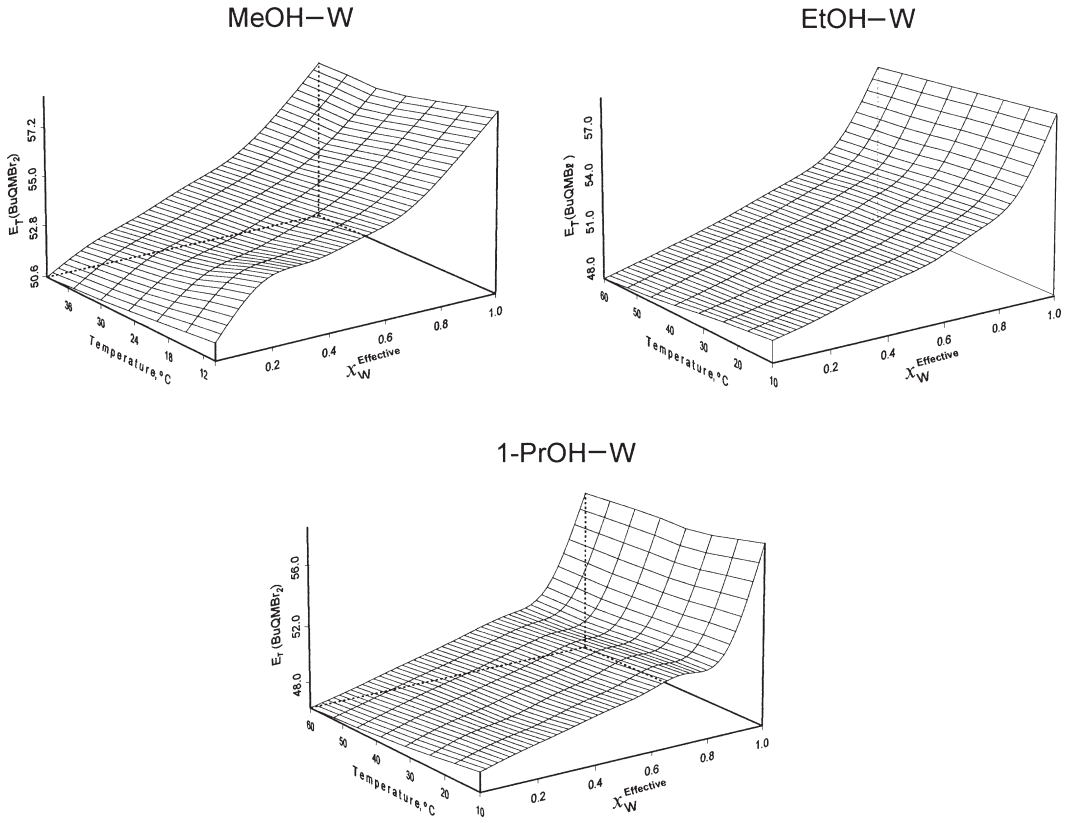

Figure 6. Solvent polarity/temperature/solvent composition contours for $BuQMBr_2$ in MeOH–W, EtOH–W and 1-PrOH–W, respectively

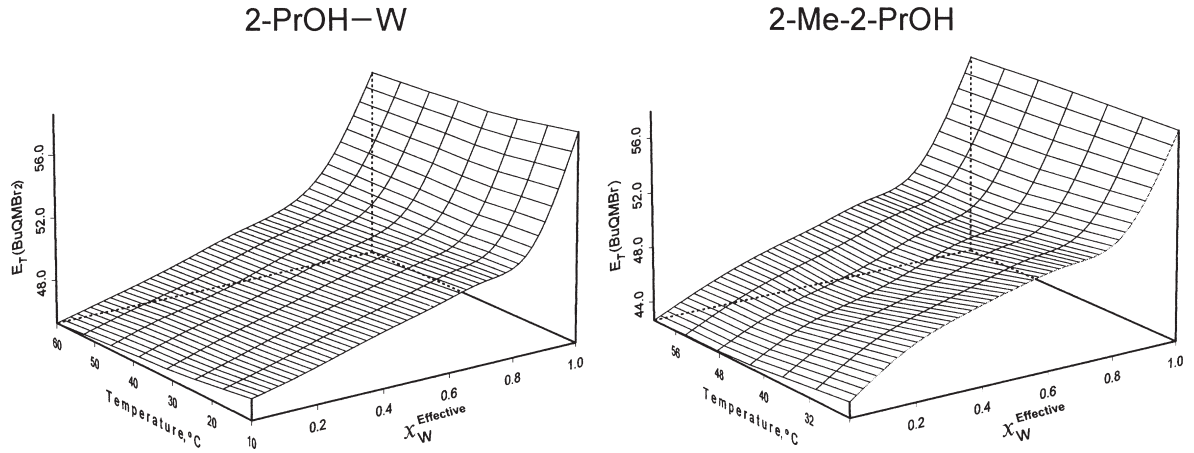

Figure 7. Solvent polarity/temperature/solvent composition contours for $BuQMBr_2$ in 2-PrOH–W and 2-Me-2-PrOH–W, respectively

Recently, it has been argued that the magnitude of preferential solvation in *aqueous alcohols* (MeOH to 2-Me-2-PrOH) may be overestimated. For example, use of the volume fraction (*VF*) instead of χ may lead to less deviation (from linearity) in the $E_T(30)$ versus solvent composition plots.[29a] Additionally, product selectivity (*S*) for the solvolysis of 4-methoxybenzoyl chloride in aqueous alcohols $S = ([\text{ester product}]/[\text{acid product}]) \times ([\text{water}]/[\text{alcohol solvent}])$ varies only slightly as a function of solvent composition, i.e. preferential solvation by the alcohol is not clearly manifested.[29b] Recently we have discussed the advantages of using the mole fraction scale over VF. Additionally, $E_T(30)$ was plotted versus χ_W and/or VF_W for aqueous 1-propanol and 2-Me–2-PrOH. Use of the former composition scale indicated preferential solvation of RB by ROH over the entire χ_W range. Use of VF_W showed, however, that the probe is solvated preferentially by water up to $VF_W = 0.5$, followed by preferential solvation by ROH.[4e] No simple rationale can be advanced for the change of the solvent that is

Table 5. Calculated $\varphi_{W/ROH-W/ROH}$ and $\varphi_{ROH-W/W}$ for all aqueous mixtures studied at 25 °C for probes MePM,[a] $BuQMBr_2$ and WB[a]

ROH	Probe	m	$\varphi_{W/ROH}$	$\varphi_{ROH-W/ROH}$	$\varphi_{ROH-W/W}$
MeOH	MePM	1.092	0.375	4.416	3.776
	$BuQMBr_2$	1.063	0.392	1.808	4.612
	WB	1.106	0.601	2.212	3.681
EtOH	MePM	1.507	0.351	13.252	37.755
	$BuQMBr_2$	1.368	0.224	7.108	31.732
	WB	1.279	0.554	111.482	20.726
1-1;PrOH	MePM	1.310	0.274	23.279	84.960
	$BuQMBr_2$	1.411	0.207	69.617	336.314
	WB	1.700	0.265	149.208	563.049
2-PrOH	MePM	1.207	2.918	105.188	36.048
	$BuQMBr_2$	1.413	0.336	67.585	201.145
	WB	1.573	0.551	192.625	349.592
2-Me-2-PrOH	$BuQMBr_2$	1.482	0.418	31.427	75.733
	MePM	1.195	0.554	18.283	33.002
	WB	1.348	0.484	111.267	229.890

[a] Data for MePM and WB were taken from the literature.[4]

preferentially solvating the probe (from water to alcohol), especially in view of the negligible solubility of RB in water (2×10^{-6} mol l^{-1}).[2b] Analysis of the attenuated dependence of S on medium composition for the above-mentioned solvolytic reaction is, however, not straightforward. The reason is that the solvation microsphere of the reaction contains three solvent species, namely W, ROH and ROH–W; the latter is *always* present in excess (see Tables 4 and 5). Its presence may induce a 'leveling effect' on product distribution, leading to attenuated dependence of S on solvent composition.

Finally, the probe equilibrium (zwitterion + H_3O^+cation + H_2O) is expected to be shifted to the right-hand side by the electrostatic effect (the interface of the SDS micelle is anionic) and to the left-hand side by the 'medium' effect (the polarity of the interfacial region is less than that of bulk water).[6] Thus, addition of base is required to produce the zwitterionic form of MePM in the presence of SDS micelles. This procedure is not required for $BuQMBr_2$ because of its much lower pK_a. The concentration of water at the (average) solubilization site of the latter probe, $[W_{interfacial}] = 38.9$ mol l^{-1} is similar to that determined by other probes for the same micellar solution, e.g. RB (39.4 mol l^{-1}) and 4-[2-(1-hexadecylpyridinium-4-yl)ethenyl] phenolate (34.3 mol l^{-1}).[6b]

CONCLUSIONS

Compared with MePM, the novel merocyanine probe $BuQMBr_2$ is more convenient because of its lower pK_a and ready solubility in organic solvents. Its solvation is susceptible to the same solvent properties that affect solvatochromism of other zwitterionic probes, namely dipolarity/polarizability and acidity. Temperature effects on solvent fractionation factors are rationalized in terms of the structures of W and ROH and their mutual interactions. Temperature increase results in gradual de-solvation *in all binary mixtures*. The probe may be employed to determine the polarity of interfacial water of organized assemblies.

CALCULATIONS

Contributions of non-specific and specific solute–solvent interactions to solvatochromism

The electronic transition energy associated with dielectric enrichment at the coordinates (r, θ) of the solvent shell is given by:[19]

$$E_{enrich} = \frac{-\chi_{Cyhex}\chi_{BuOH}\Delta E_{BuOH-Cyhex}}{8} \times \int_{-1}^{1} d\rho \int_{-1}^{1} du \frac{G(u)\{1 - \exp[-G(u)Z\rho^2]\}}{\chi_{BuOH} + \chi_{Cyhex}\exp[-G(u)Z\rho^2]} \quad (16)$$

where: χ_{Cyhex} and χ_{BuOH} are the mole fractions of the two components $\Delta E_{BuOH-Cyhex}$ 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 to accommodate the probe molecule; r is a distance from the center of the probe dipole ($r \geqslant a$); $G(u) = 3(u)^2 + 1$, where $u = \cos\theta$ and Z is the 'index of preferential solvation', given by:

$$Z = \frac{3\mu_g^2 M\Delta f}{8\pi RT\delta a^6} \quad (17)$$

where μ_g is the dipole moment of the ground state of the probe, calculated at each χ_{BuOH} (the Amsol program package); δ and M refer to the mean density and the mean molecular weight of the two solvents; Δf is given by $\Delta f = f(D)_{BuOH} - f(D)_{Cyhex}$; where $f(D)$ is the Onsager dielectric function,[30] and R and T have their usual meanings.

In performing the calculations, the cavity radius (a) was taken as approximately equal to the radius of the probe molecule (4.84×10^{-10} m); this was calculated as given elsewhere.[31] Equation (16) 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 (the surface of the probe) using 100 intervals; and χ_{BuOH} from 0.4 to 1.0 using 0.1 intervals.

Determination of K_{assoc} $\chi_{Species}^{Effective}$ and solvent fractionation factors

For the alcohols studied, K_{assoc} and $\chi_{Species}^{Effective}$ were available from previous studies and the fractionation factors were calculated as detailed elsewhere.[4c–e] Briefly, knowledge of K_{assoc} (from the dependence of the density of the binary mixture on solution composition) allows calculation of the effective mole fractions of all species present. The probe solvation microsphere is composed of W, ROH and ROH–W. Observed E_T (E_T^{obs}) is the sum of the polarity of each component E_T^W, E_T^{ROH} and E_T^{ROH-W}, respectively, multiplied, by the corresponding mole fraction in the probe solvation microsphere (χ_W^{Probe}, χ_{ROH}^{Probe} and $\chi_{ROH\to W}^{Probe}$ respectively):

$$E_T^{obs} = \chi_W^{Probe} E_T^W + \chi_{ROH}^{Probe} E_T^{ROH} + \chi_{ROH-W}^{Probe} E_T^{ROH-W} \quad (18)$$

$$E_T^{obs} = \frac{\left(\chi_{ROH}^{Bk;Effective}\right)^m E_T^{ROH} + \varphi_{W/ROH}\left(\chi_W^{Bk;Effective}\right)^m E_T^W + \varphi_{ROH-W/ROH}\left(\chi_{ROH-W}^{Bk;Effective}\right)^m E_T^{ROH-W}}{\left(\chi_{ROH}^{Bk;Effective}\right)^m + \varphi_{W/ROH}\left(\chi_W^{Bk;Effective}\right)^m + \varphi_{ROH-W/ROH}\left(\chi_{ROH-W}^{Bk;Effective}\right)^m} \quad (19)$$

Equations (18) and (19) then can be solved to get E_T^{ROH-W} and the appropriate solvent fractionation factors, respectively.

Calculation of the polarity of interfacial water of SDS micelles

Aqueous 1-propanol was employed as a model for the interfacial water of SDS. The value of $[W_{interfacial}] = 38.9$ mol l^{-1} was calculated by interpolation of the polarity of interfacial water, 52.7 kcal mol^{-1}, from a plot of $E_T(BuQMBr_2)$ versus [water] (in bulk aqueous 1-propanol) at 25 °C. The data in Ref. 6b were given as relative permittivities of interfacial water ($\varepsilon_{interfacial}$) calculated by comparing λ_{max} of the probes in the micellar pseudo-phase with those in bulk water–dioxane mixtures (employed as a reference solvent for interfacial water). We have calculated [$W_{interfacial}$] from the known dependence of ε on the composition of water–dioxane mixtures.[32]

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