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SOLVATOCHROMISM AND PREFERENTIAL SOLVATION OF ARYLIMINOMETHYLPYRIDINIUM IODIDES IN BINARY MIXTURES

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Studies on the solvatochromic behaviour of *N*-methyl-4- and *N*-methyl-2-[(4-dimethylaminophenyl)iminomethyl]pyridinium iodide dyes in a variety of solvents and the preferential solvation of the former dye in binary mixtures of protic and non-protic solvents are presented and interpreted in terms of solute–solvent and solvent–solvent interactions. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

The spectral properties of (aminostyryl)pyridinium salt dyes have recently attracted the interest of different research groups.[1–3] Their solvent-dependent fluorescence in the red region of the spectrum makes them attractive probe molecules in biological systems.[1,2] The symmetrical solvatochromism observed in their absorption/emission spectra constitutes an intriguing feature in the study of cyanine dyes.[3] Such interesting behaviour justifies new efforts at investigating related systems.

We had previously studied a family of solvatochromic pyridinium iminophenolate dyes closely related to Brooker *et al*'s styrylpyridinium betaine **1**,[4] where a CH was replaced by a nitrogen atom, as in dye **2**.[5] The resulting dyes behaved very much like their styryl analogue, absorbing in general, in a given solvent, at longer wavelengths than betaine.

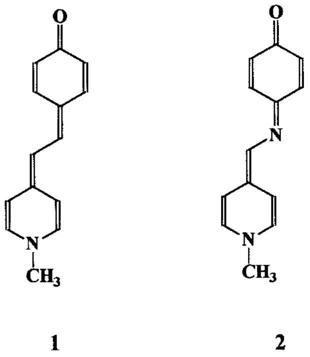
Following the same approach, we report here on the solvatochromic properties of dyes **3** and **4**, which constitute imino analogues of the (aminostyryl)pyridinium dyes investigated recently.[1–3]

In addition to comparing them with those related systems, we describe their spectral behaviour in several binary mixtures, interpreting the observed preferential solvation in mixtures of protic and aprotic solvents in terms of solvent–solvent and dye–solvent interactions.

EXPERIMENTAL

All spectra were recorded using a Beckman DU-65 or an HP 8452A spectrophotometer. Melting points were obtained with a Koffler hot-stage apparatus.

The substrates employed in this work were prepared following a reported procedure,[6] giving **3** in 35% yield, m.p. 164–165°C (lit. m.p. 163–164°C[6]) and **4** in 42% yield, m.p. 200–202°C, (lit. m.p. 197–199°C[6]).



Scheme 1.

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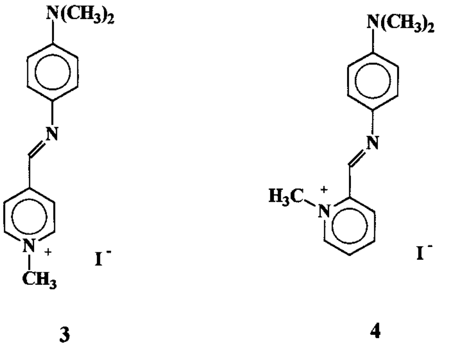
Deionized water was used to prepare all aqueous solutions. The analytically pure non-aqueous solvents were further purified by standard procedures[7] and kept dry over molecular sieves. Spectral measurements employed dye solutions with a constant concentration of $4{\cdot}8\times10^{-5}$ mol dm^{-3}.

RESULTS AND DISCUSSION

Solvatochromic studies

The longest wavelength charge-transfer band of dyes **3** and **4** was recorded in several protic and non-protic solvents. In order to investigate the possible formation of dye aggregates, spectroscopic measurements in the different solvents were made using different dye concentrations in the range 10^{-5}–10^{-3} mol dm^{-3}. No change in the profile and absorption wavelength were observed for the solvatochromic band. The stability of the iminoaniline dyes in water was also verified. A dye solution of spectrophotometric concentration was prepared in water, the absorbance was recorded at regular intervals for 2 h and no changes were observed during the course of the experiment. The values of the molar absorptivity (ε) of the solvatochromic bands were measured in ethanol to be 20 400 l mol^{-1} cm^{-1} **3** and 24 920 l mol^{-1} cm^{-1} for **4**.



Scheme 2.

Table 1 presents the λ_{max} values obtained for **3** and **4** in various hydroxylic and non-protic solvents. For the sake of comparison, absorption maxima for the related ASPT dye **5**[2] in some of the solvents employed are also given. Comparison between dye **5** and dyes **3** and **4** is limited by the fact that their counteranions are different. We assume that the effect of the iodide anion on the solvatochromic behaviour of **3** and **4** is negligible. This assumption is supported by the observed insensitivity of the charge-transfer (CT) absorption bands of those dyes to their concentration and eventual aggregation. Hence, the solvatochromic bands do not seem

Table 1. Variation of the λ_{max} values for the charge-transfer absorption of dyes **3** and **4** in different solvents

			λ_{max} (nm)		
Solvent	μ (10^{-30} C m)[a]	$E_T(30)$ values[b] (kcal mol^{-1})	Dye **5**[c]	Dye **3**	Dye **4**
Chloroform	3·8	39·1	483	538	532
Dichloromethane	5·2	40·7	–	541	534
Acetophenone	9·8	40·6	–	516	516
Acetone	9·0	42·2	482	494	490
Acetonitrile	11·8	45·6	478	492	489
N,N-Dimethylacetamide	12·4	43·7	–	494	485
N,N-Dimethylformamide	10·8	43·8	484	492	488
Dimethyl sulphoxide	13·5	45·1	484	493	487
Butan-2-ol	5·5	47·1	–	518	507
Propan-2-ol	5·5	48·4	–	515	505
Hexan-1-ol	–	48·8	–	514	504
Pentan-1-ol	5·7	49·1	–	513	503
Butan-1-ol	5·8	50·2	–	512	502
Ethanol	5·8	51·9	486	507	501
Butane-1,2-diol	–	52·6	–	506	499
Diethylene glycol	7·7	53·8	–	503	495
Methanol	5·7	55·4	479	500	494
Ethane-1,2-diol	7·7	56·3	–	499	492
Water	5·9	63·1	457	484	471

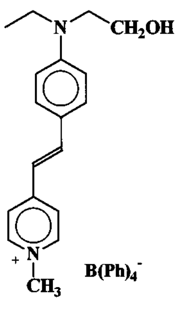
[a] Dipole moments taken from Ref. 8.

[b] Values from Ref. 8, pp. 365–371.

[c] Data from Ref. 2.

to reflect any association between the iodide donor and the pyridinium ring acceptor.

As observed for the iminomerocyanines reported previously,[5] replacement of a CH group of the unsaturated link by a nitrogen atom leads to dyes which absorb in general at longer wavelengths than their styryl analogue. All dyes exhibit similar solvatochromic behaviour, characterized by a general decrease in wavelength with increase in the polarity of the medium (negative solvatochromism). This general trend, however, is not continuous, as can be seen from Figure 1. In non-protic solvents, wavenumber values $\bar{\nu}$ of dyes **3** and **4** correlate only roughly with the $E_T(30)$ solvent values. This correlation is much better in protic solvents, where a steady linear increase with the $E_T(30)$ values of the solvent is observed for both dyes ($r>0{\cdot}98$ for both compounds). This is a strong suggestion that different kinds of solute–solvent interactions are responsible for the solvatochromic behaviour of these dyes in the two groups of solvents.



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Scheme 3.

In non-protic media, dipole–dipole interactions should play a dominant role in dye solvation. Polar solvents provide an increasingly stronger solvation and stabilization of the ground state of these dyes, thereby increasing their charge-transfer transition energies in solution. This is shown by the variation of the λ_{max} values in non-protic media with the solvent dipole moments given in Table 1. Such values are smaller in polar solvents with moments in the range $(9{\cdot}0–13{\cdot}5)\times10^{-30}$ C m (acetone, acetonitrile, DMA, DMF, DMSO) than in less polar solvents such as chloroform or dichloromethane [$\mu=(3{\cdot}8–5{\cdot}2)\times10^{-30}$ C m].

The dipole moments of the protic solvents in Table 1 do not vary much, falling in the narrow range of $(5{\cdot}5–7{\cdot}7)\times10^{-30}$ C m. However, the charge-transfer wavenumber $\bar{\nu}$ of both dyes in these solvents increases linearly with the corresponding $E_T(30)$ values. This observation points to hydrogen-bond interactions between the dye and the hydroxylic solvent, responsible for the observed negative solvatochromism. This is in disagreement with studies on similar hemicyanine dyes, where such specific solute–solvent interactions were apparently absent.[3] In the case of **5**, where this effect was reported, a hydrogen bond was postulated between the protic solvent and the hydroxy group of the dye.[2] Since this group is not available in dyes **3** and **4**, we postulate a hydrogen-bonding interaction between the

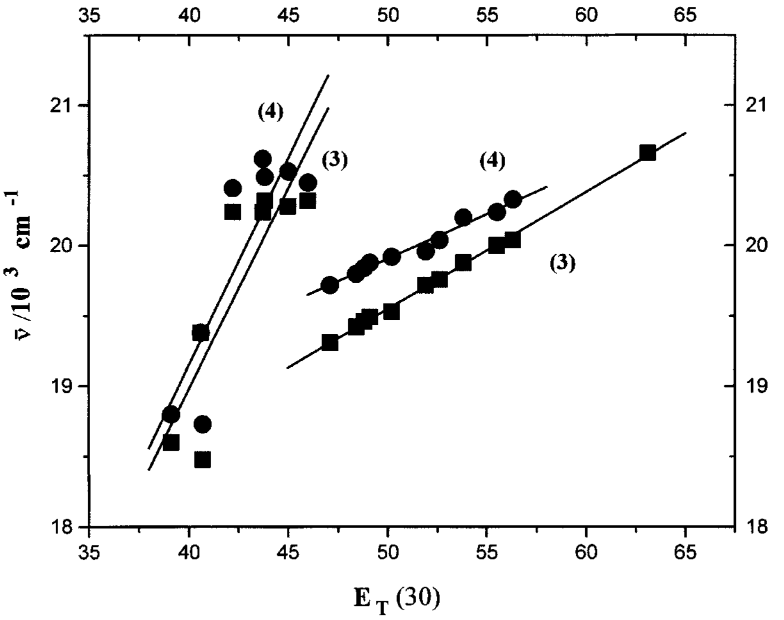

Figure 1. Variation of the wavenumber values $\bar{\nu}$ of the charge-transfer band of dyes **3** and **4** as a function of the $E_T(30)$ polarity values of the solvent. Squares refer to **3**, circles to **4**, with protic solvents spanning the more polar [$E_T(30)>47$ kcal mol^{-1}] region of the graph

solvent and the dimethylamino group. Such an interaction was apparently absent in the hemicyanines reported by Fromherz,[3] presumably because of the much greater hydrophobicity of the *N,N*-dibutylamino group present in his series of compounds. The length of the alkyl substituents on the latter group would prevent a strong interaction between the dialkylamino group and a hydroxylic solvent.

Fromherz[3] stressed the symmetry of the charge-transfer process in analysing the solvatochromism of these hemicyanine dyes. In the case of the less hydrophobic compounds **3** and **4**, hydrogen bonding with HBD solvent reduces the symmetry of this process, because the ground and excited states do not interact equally well with the solvent. Protic solvents might interact with the three nitrogen atoms of **3** and **4**. This interaction should, however, be much stronger with the more basic tertiary amine nitrogen of the dimethylamino group in the ground state than with either the imino N or the pyridinium ring N in the quinonoid excited state. This has the effect of providing additional stabilization of the dye ground-state by protic solvents, reducing at the same time the degree of charge donation to the pyridinium ring of **3** and **4**, with a consequent hypsochromic shift of the CT band with the increased HBD strength of the medium.

Preferential solvation in binary mixtures

Studies of preferential solvation of dye **3** in binary solvent mixtures were carried out in aqueous alcohols and in mixtures of acetone and a protic solvent. Figure 2 depicts the variation of the wavenumber values $\bar{\nu}$ of the longest wavelength band of dye **3** in aqueous alcohols as a function of the water molar fraction. In Figure 3, plots of $\bar{\nu}$ values in mixtures of acetone and a protic solvent are shown as a function of the molar fraction of the hydroxylic component. The experimental data for each binary mixture were fitted by a non-linear least-squares procedure to a fourth-order polynomial of the form $\bar{\nu}=A+BX+CX^2+DX^3+EX^4$, where X is the molar fraction of water or the hydroxylic component. Values for the coefficients *A, B, C, D* and *E*, corresponding to the curves drawn for each binary mixture in Figures 2 and 3, are given in Table 2.

In agreement with the above interpretation of the dye solvatochromism, we expect that solvation of **3** by strong HBD solvents would mainly result from hydrogen-bond interactions between the dimethylamino group of the dye and the hydroxylic solvent. This positive contribution to solvation should, however, be counterbalanced by a negative hydrophobic effect, arising from the non-polar aromatic fragments in the molecule. As the hydroxylic solvent becomes less polar, both hydrogen-bond interactions and hydrophobic repulsion by the solute should decrease. Finally, in a non-protic solvent such as acetone, solvation would take place by dipole–dipole interactions, in the absence of solute–solvent hydrogen–bond interactions and hydrophobic repulsion.

The trends observed in Figures 2 and 3 may be rationalized by consideration of these effects. In water–alcohol mixtures (Figure 2), **3** is preferentially solvated by methanol throughout the entire range of water molar fractions X [Figure 2(a)]. As the co-solvent shifts to less polar ethanol and propan-2-ol [Figure 2(b) and (c), respectively], this situation changes: in solutions with a relatively small content of water ($X<0{\cdot}2$ in ethanol, $X<0{\cdot}5$ in propan-2-ol), H_2O preferentially solvates dye **3**. In mixtures with a larger proportion of water, however, it is again the alcoholic co-solvent which preferentially solvates **3**. This change in behaviour reflects an interplay of the two opposing effects mentioned above. In dilute aqueous solutions, H_2O molecules are relatively free to interact through hydrogen bonding with the dimethylamino group of the dye. This positive contribution to solvation by water is, however, increasingly opposed by a negative hydrophobic

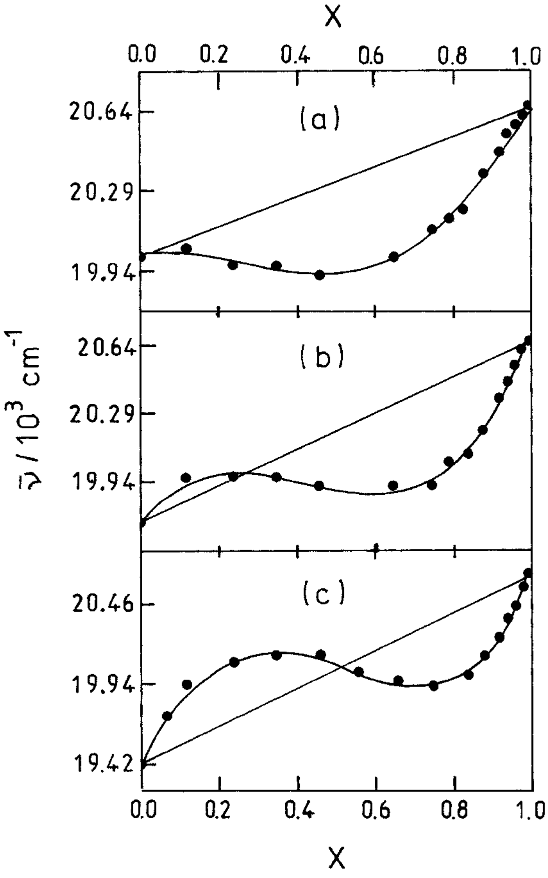

Figure 2. Variation of the wavenumber values $\bar{\nu}$ of the charge-transfer band of dye **3** in binary mixtures as a function of the water molar fraction X: (a) water–methanol; (b) water–ethanol and (c) water–propan-2-ol. Experimental data were fitted to fourth-order polynomials of the form $\bar{\nu}=A+BX+CX^2+DX^3+EX^4$, with the coefficients given in the text

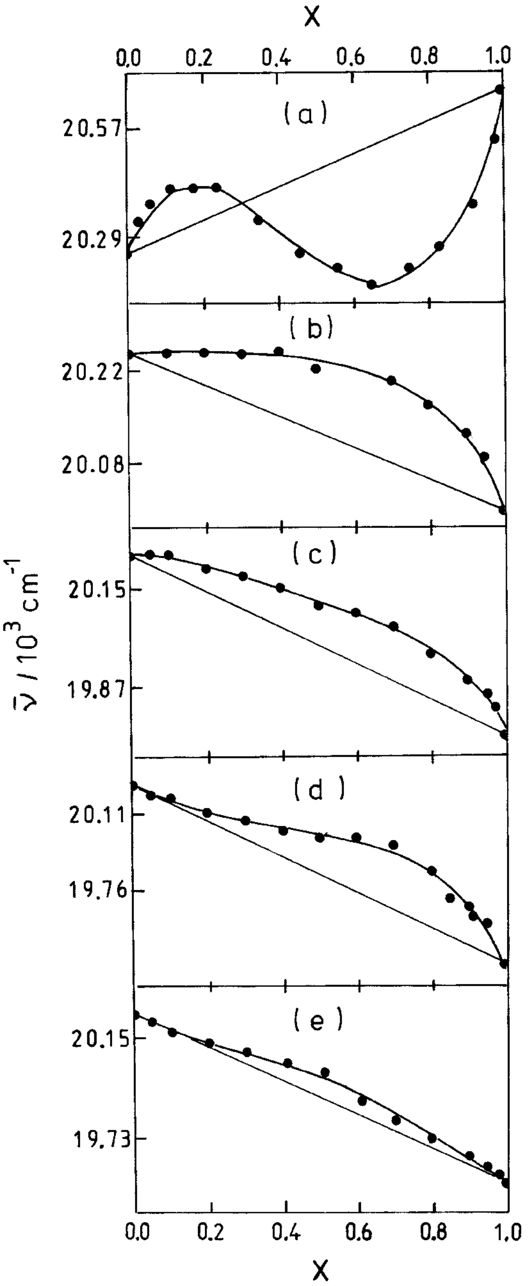

Figure 3. Variation of the wavenumber values $\bar{\nu}$ of the charge-transfer band of dye **3** in binary mixtures as a function of the molar fraction *X* of the hydroxylic component: (a) acetone–water; (b) acetone–methanol; (c) acetone–ethanol; (d) acetone–propan-2-ol; (e) acetone–butan-1-ol. Experimental data were fitted to fourth-order polynomials of the form $\bar{\nu}=A+BX+CX^2+DX^3+EX^4$, with the coefficients given in the text

interaction as the water content is increased. In solutions with a large water content, a strong net of hydrogen-bonded water molecules is formed, and the resulting hydrophobic repulsion throws the solute, so to speak, into the arms of the less polar co-solvent.

This situation is reproduced in acetone–water mixtures [Figure 3(a)], where the former acts as the less polar co-solvent. In the other acetone–alcohol mixtures [Figure 3(b)–(e)], it is always the hydroxylic solvent which preferentially solvates dye **3**. As the alcohol becomes less polar, the binary mixture approaches the ideal behaviour in acetone–butan-1-ol mixtures, the solvent compositions in the cybotactic region of **3** and in the bulk solution are nearly the same throughout the range of molar fractions *X*. Clearly, even in alcohol-rich mixtures, the hydrophobic repulsion between the solute and the hydroxylic co-solvent is never strong enough to prevent the preferential solvation of the dye by the latter.

The above analysis confirms the observations by different research groups of the complex interplay of solute–solvent and solvent–solvent interactions in the solvation of solvatochromic dyes in binary mixtures.[9–14] The opposing effects of dye–solvent hydrogen bonds and hydrophobic interactions play an important role in the solvatochromic behaviour of the $E_T(30)$ dye in binary mixtures.[10,12,13] These direct effects are however, modulated by solvent–solvent interactions, an observation which is valid also for solutions of other solvatochromic dyes.[11,14] Water as a co-solvent provides a striking example of this. Isolated water molecules, in water-poor aqueous mixtures, behave differently from H_2O in an organized associated net, in water-rich mixtures. As shown in this paper, the solvent–solvent interaction between water and a less polar co-solvent determines the ability of the former as a hydrogen bond donor species and a lipophobic medium.

In conclusion, the solvatochromism of dyes **3** and **4** may be rationalized in terms of dipole–dipole interactions in non-protic media and hydrogen-bond formation between the dimethylamino group of the dye and the hydroxylic solvent in protic media. Unlike other imino dyes such as **2**, where the donor group is a phenolate,[5] the solvatochromic shifts of the analogues **3** and **4** do not correlate well with the $E_T(30)$ values of the solvent, unless only hydroxylic solvents are considered. Studies of preferential solvation of **3** in binary mixtures of protic and aprotic solvents confirm the suggestions that solute–solvent hydrogen-bond interactions play an important role in the spectral properties of these dyes. This is in disagreement with observations made previously on similar systems,[3] but this discrepancy is only apparent, because of the more lipophilic nature of the dialkylamino donor group in those molecules, as compared with the dyes reported in this paper.

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Table 2. Coefficients for the fourth-order polynomial fit to the data for the binary mixtures in Figures 2 and 3

	Coefficient[a]				
Binary solvent mixture	*A*	*B*	*C*	*D*	*E*
Methanol–water	20007	598	− 4120	6061	− 1864
Ethanol–water	19731	2372	− 6625	4932	287
Propan-2-ol–water	19433	4715	− 8479	1301	3704
Acetone–water	20266	1847	− 6670	4351	− 923
Acetone–methanol	20238	189	− 1126	2060	− 1350
Acetone–ethanol	20241	122	− 1906	3232	− 1945
Acetone–propan-2-ol	20241	− 731	350	1319	− 1749
Acetone–butan-1-ol	20238	− 853	2050	− 3617	1735

[a] General equation: $\bar{v} = A + BX + CX^2 + DX^3 + EX^4$.

REFERENCES

1. B. Wandelt, P. Turkewitsch, B. R. Stranix and G. D. Darling, *J. Chem. Soc., Faraday Trans.* **91**, 4199–4205 (1995).
2. U. Narang, C. F. Zhao, J. D. Bhawalkar, F. V. Bright and P. N. Prasad, *J. Phys. Chem.* **100**, 4521–4525 (1996).
3. P. Fromherz, *J. Phys. Chem.* **99**, 7188–7192 (1995).
4. L. G. S. Brooker, G. H. Keyes and D. W. Heseltine, *J. Am. Chem. Soc.* **73**, 5350–5356 (1951).
5. C. Machado, M. G. Nascimento and M. C. Rezende, *J. Chem. Soc., Perkin Trans. 2* 2539–2544 (1994).
6. F. Krohnke, H. Leister and I. Vogt, *Chem. Ber.* **90**, 2792–2800 (1957).
7. B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 5th ed. Longman, London (1989).
8. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed., pp. 408–410. VCH, Weinheim (1988).
9. H. Boggetti, J. D. Anunziata, R. Cattana and J. J. Silber, *Spectrochim. Acta, Part A* **40**, 719–726 (1994).
10. R. D. Skwierczynski and K. A. Connors, *J. Chem. Soc., Perkin Trans. 2* 467–472 (1994).
11. M. Scremin, S. P. Zanotto, V. G. Machado and M. C. Rezende, *J. Chem. Soc., Faraday Trans.* **90**, 865–868 (1994).
12. M. Rosés, C. Ràfols, J. Ortega and E. Bosch, *J. Chem. Soc., Perkin Trans. 2* 1607–1615 (1995).
13. J. Ortega, C. Ràfols, E. Bosch and M. Rosés, *J. Chem. Soc., Perkin Trans. 2* 1497–1503 (1996).
14. A. K. Laha, P. K. Das, D. Banerjee and S. Bagchi, *J. Chem. Soc., Faraday Trans.* **92**, 1499–1502 (1996).