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CATIONIC AND ANIONIC HALOCHROMISM

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The spectral changes of organic solutions of *N,N,N′,N′*-tetramethylenediaminoacetylacetonatocopper(II) perchlorate and a merocyanine dye in the presence of NaI or LiClO$_4$ provide examples of anionic and cationic halochromism, respectively. The observed changes are interpreted as arising from all possible interactions in the three-component system of the dye, the salt and the solvent.

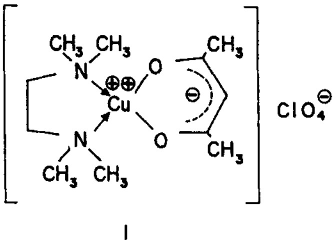
INTRODUCTION

The introduction of solvatochromic dyes as solvent polarity indicators more than 30 years ago represented a breakthrough in the study of solvent effects. The ease and sensitivity of the method prompted the use of a variety of dyes for the measurement of medium polarities. Following reports of their utilization in the determination of the polarity of pure solvents or solvent mixtures, we had the idea of measuring in this way the polarity of electrolyte solution.[1] Our idea ultimately proved naive because it overlooked the specific interactions between the dye and the electrolyte that are responsible for the solvatochromic shifts observed in these systems. Ignoring these interactions may lead to completely misleading interpretations and values of the 'polarity' of salt solutions. In fact, as we show in this paper, depending on these interactions, contradictory 'polarity' values may be derived from the same salt solution.

In the systematic study of these salt–dye interactions in solution, responsible for the halochromic properties of the dye,[2] we have drawn a parallel between solvatochromism and halochromism, basing our analysis on the interplay of three components, the dye, the salt and the solvent.[3] We now compare two extreme behaviours of these dyes, which we define as cationic and anionic halochromism, according to the ionic fragment which determines the spectral shifts in electrolyte solutions. A sharp distinction may be drawn between dyes which exhibit cationic and anionic halochromism. In order to illustrate this, we have chosen two well known solvatochromic dyes, compounds **1** and **2**, which typify these distinct behaviours.

Dye **1**, *N, N, N′, N′*-tetramethylethylenediaminoacetylacetonatocopper(II) perchlorate, was introduced by Fukuda and Sone[4] nearly 20 years ago. It exhibits positive solvatochromism and the energies of its longest wavelength band in various solvents correlate well with the corresponding donor numbers DN. Migron and Marcus[5] have recently emphasized its potential as an exclusive β-sensitive probe, β values being defined from Taft and Kamlet's multiparameter equation[6] as a measure of the donicity of the solvent. In addition, the position of its longest wavelength band in a given solvent is also sensitive to the nature of the counter anion present.[4,7]

The merocyanine dye **2** is a classic example of a compound which exhibits reverse solvatochromism: it changes from a positive solvatochromic behaviour in



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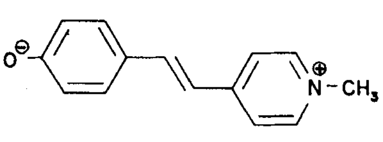

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solvents of low polarity to negative solvatochromism in more polar media. This property is shared with other azo merocyanines[8] and has been rationalized in terms of semi-empirical MO calculations.[9] Compound **2** may be classed among a large group of solvatochromic dyes which include Reichardt's widely used pyridiniophenoxide betaines,[2a] all of which possess a phenoxide group as the donor moiety in the molecule. The charge-transfer band energies of these compounds tend to correlate with the acceptor properties of the medium. The halochromic behaviour of dye **2** in aqueous salt solutions was studied by Davidson and Jencks,[10] who rationalized the observed spectral shifts in terms of equilibria between the free dye and 1 : 1 dye–salt complexes.

This paper reports a comparison of the halochromic properties of these compounds in organic solutions of two different electrolytes and presents an interpretation of the trends observed for each system.

RESULTS AND DISCUSSION

The visible spectra of salt solutions containing dye **1** or **2** were recorded at 25 °C for different electrolyte concentrations. We employed solutions of sodium iodide or lithium perchlorate in acetone, acetonitrile, benzonitrile and dimethylformamide (DMF). For such solvents, dye **1** exhibits a positive halochromic behaviour (shift of the longest wavelength band to longer λ values with the addition of a salt), whereas dye **2** behaves as a negative halochromic indicator. The relative trends may be compared by plotting the band energy shifts, ΔE, for each system against the salt concentration. These plots are shown in Figures 1 and 2 for the copper dye **1** and in Figures 3 and 4 for the merocyanine dye **2**.

The relative trends observed for the two salts in a given solvent, in the presence of dyes **1** and **2**, may be compared in Figures 1 and 3. For the copper dye **1**, addition of sodium iodide to all solvents always caused greater halochromic shifts than lithium perchlorate. This situation was reversed when the probe was the merocyanine dye **2**. If one retains the notion that the position of the charge-transfer maximum of these dyes is a measure of the polarity of the medium, one is led to a contradictory conclusion, namely that for the same salt concentration in a given solvent, a sodium iodide solution is more 'polar' than a lithium perchlorate solution when dye **1** is the probe and is less 'polar' when dye **2** is used as the polarity indicator. In fact, this apparent contradiction disappears if one regards **1** as an example of a dye which exhibits anionic halochromism, complementary to the cationic halochromic behaviour of dye **2**.

The halochromism of the copper complex **1** stems from a transition from a square-planar structure to an octahedral form where the solvated anion acts as a more or less bound axial ligand.[4,7] As more salt is added to the medium, a competition is established between the solvent molecules loosely bound to the planar copper complex and the solvated anions. The greater 'polarity' of the sodium iodide solutions reflects the greater ligand strength of the iodide anions compared with ClO_4^-.

In contrast, the halochromic behaviour of the merocyanine dye **2** is governed by the nature of the added cation. We have carried out detailed studies of this behaviour for the related pyridiniophenoxide dyes[3] and have shown that it is the association between the solvated cation and the phenoxide moiety of the molecule which determines the halochromic shifts in solution. The charge density of the cation is of paramount importance here, smaller, harder species being more tightly bound to the negatively charged oxygen atom.[3,11] It follows that, according to the cation-governed halochromic dye **2**, lithium perchlorate solutions are more 'polar' than sodium iodide solutions.

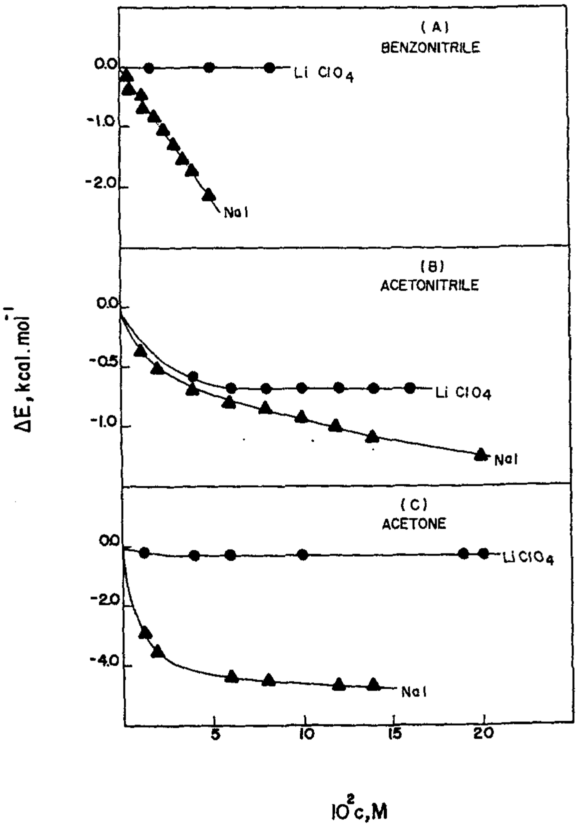

Figure 1. Differences ΔE in the absorption energy of the longest wavelength band from the spectra of dye **1** in various solvents, in the presence of NaI or $LiClO_4$, as a function of the molar salt concentration, c

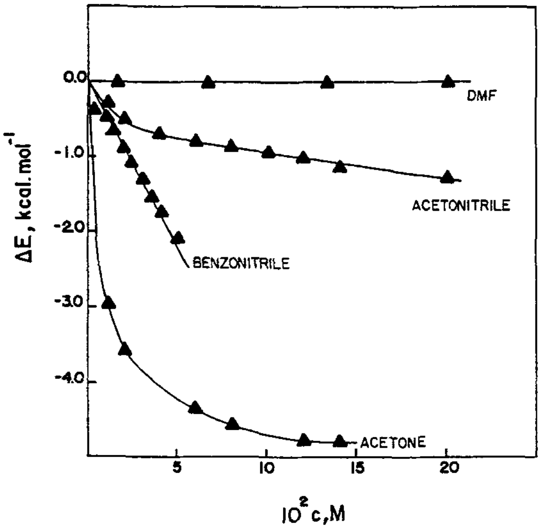

Figure 2. Halochromic shifts of dye **1** in various solvents, in the presence of NaI

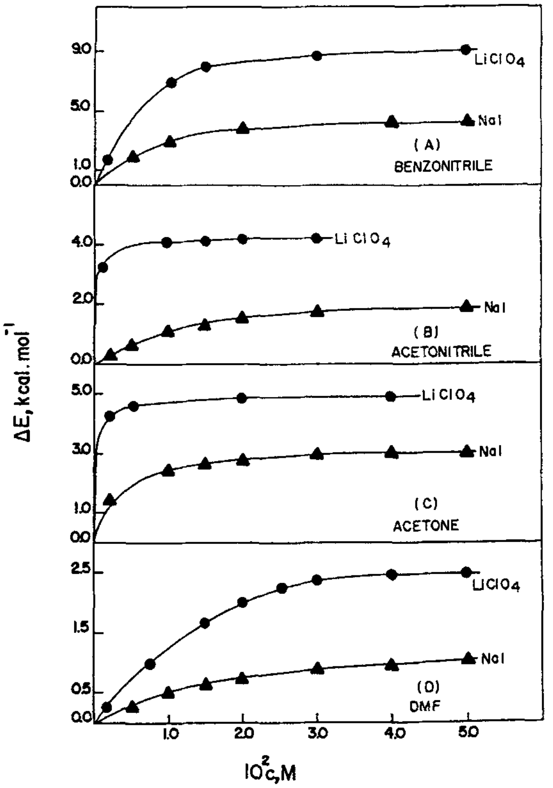

Figure 3. Differences ΔE in the absorption energy of the longest wavelength band from the spectra of dye **2** in various solvents, in the presence of NaI or $LiClO_4$, as a function of the molar salt concentration, *c*

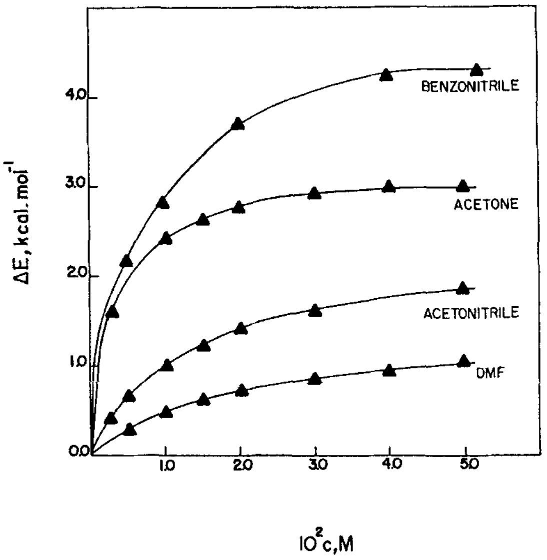

Figure 4. Halochromic shifts of dye **2** in various solvents, in the presence of NaI

The same salt–dye pair may show different halochromic behaviour depending on the solvent employed. This is seen in Figures 2 and 4, where trends are compared for sodium iodide solutions of dyes **1** and **2** respectively, in different solvents. These trends may be understood by an analysis based on all possible interactions which arise in the three-component system of the dye, the dominant ionic species and the solvent.

In the case of dye **1**, a competition is established between the solvated anion, which acts as a ‘co-solvent’, and the solvent molecules, for axial associations with the copper(II) complex. This situation is analogous to the solvatochromic shifts observed for the same dye in binary solvent mixtures, when the proportion of the more ‘polar’ co-solvent is increased. For the variations of the position of the longest wavelength band of the copper complex **1** in nitromethane–DMF mixtures,[12] a plot (not shown) of ΔE against the molar DMF concentration can be drawn which resembles closely the plots depicted in Figures 1 and 2. We observed a similar behaviour in acetone–methanol and acetonitrile–ethanol mixtures: addition of an alcohol to solutions of **1** in either acetone or acetonitrile was accompanied by positive solvatochromic shifts. These shifts were initially large, for dilute solutions of the more ‘polar’ co-solvent, attaining plateau values when the concentration of the alcohol was high enough to displace completely the weaker donor component from the axial positions.

For a given anion, the degree of halochromism of the system is then a function of the donicity of the solvent. In DMF [DN = 26·6 kcal mol^{-1} (1 kcal = 4·184 kJ)[13]], a strong donor solvent, no halochromic shifts are observed on the addition of sodium iodide up to a concentration of 0·2 M (Figure 2). In contrast, in acetone (DN = 17·0 kcal mol^{-1}), acetonitrile (14·1 kcal mol^{-1}) and benzonitrile (11.9 kcal mol^{-1}), the halochromic behaviour of dye **1** is much more pronounced. The above assertion does not seem to hold, however, when acetone as a solvent is compared with either of the two nitriles. The latter act as stronger donor solvents than acetone, in spite of having smaller donor numbers. This may be due to the soft nature of the copper(II) complex, which favours complexation with nitrogen ligands because of stronger π interaction with the CN group. A similar situation, again involving acetone and acetonitrile, was in fact observed for the related solvatochromic dye *N,N,N'N'*-tetramethylethylenediaminoacetylacetonatonickel(II) perchlorate.[14]

The cationic halochromism exhibited by dye **2** parallels the behaviour of pyridiniophenoxide dyes, analysed in detail previously.[3] Figure 4 illustrates the fact that here it is the acceptor strength of the solvent which determines the degree of cationic halochromism of the merocyanine–NaI system. Since solvent acceptivities correlate fairly well with $E_T(30)$ values, it is not surprising that the degree of halochromism for these systems decreases in the order benzonitrile [$E_T(30)$ = 41·5 kcal mol^{-1}] > acetone (42·2 kcal mol^{-1}) > acetonitrile (45·6 kcal mol^{-1}). The relative insensitivity of dye **2** in DMF to the addition of sodium iodide seems to contradict the above assertion, as the $E_T(30)$ value of DMF (43·8 kcal mol^{-1}) is smaller than that of acetonitrile. One should bear in mind, however, that the sodium cation is always solvated in solution. The reduced halochromism of sodium iodide solutions of **2** in DMF does not stem from a more effective association of the solvent with the phenoxide moiety of the dye, as compared with the acetonitrile molecules. It is rather caused by the more effective solvation of the sodium cation by DMF, thereby reducing the acceptivity of this solvated ionic species. In terms of the phenoxide probe, this solvation renders the Na^+ 'co-solvent' less 'polar', and consequently less capable of inducing perturbations in solution.

In the above discussions, we have emphasized the role of the dominant ionic species, ignoring all possible contributions to the halochromic behaviour of dyes **1** and **2**. This somewhat crude model is obviously open to criticism. One may wonder, for instance, about the eventual contribution of aggregation phenomena to the observed spectral changes in solution. Dye aggregation may in fact be accompanied by substantial spectral changes in the visible region.[15] It is promoted in solvents where the dye is scarcely soluble, such as water, being prevented in solvents of medium polarity.

In order to test this possibility, we recorded the spectra of dyes **1** and **2** at various concentrations in all the solvents employed in this study, and did not observe any shifts of their maxima. This was taken as an indication that either self-aggregation of the dye was negligible in these media, or that an eventual dye aggregation led to no spectral changes and, therefore, could not contribute to the observed halochromic shifts.

A second question pertains the role played by the anion in the presence of a cation-dominated halochromic dye. There are some pieces of evidence that justify our approach, which tends to regard such contributions as negligible. Davidson and Jencks's findings[10] of a 1 : 1 association between dye **2** and a salt in aqueous solutions led to the interpretation that only *one* ionic species was responsible for the observed halochromism. In our systematic study on the halochromic behaviour of Reichardt's $E_T(30)$ dye in alcoholic solutions,[1b] we also found that, in a series of salts with a common cation, the nature of the anion was only of minor importance. The small differences observed when comparing two salts MX and MY were ascribed to their different degrees of dissociation in solution. The more a salt is dissociated, the higher is the average electron density on the dominant ionic species M^+ which perturbs the dye. Thus, for the $E_T(30)$ betaine in an alcohol in the presence of different lithium salts, the induced halochromic shifts increased in the order LiCl < LiBr < LiI < $LiClO_4$.[1b] This order also shows that we may safely neglect anionic contributions arising from a direct interaction between the anion and the pyridinium acceptor moiety of pyridiniophenoxide betaines or dye **2**. In fact, had it been otherwise, the soft, charge-transferring I^- anion would be responsible for a larger halochromic shift than the hard, non-associating ClO_4^- species. Our studies in alcoholic solutions[1b] and the results in non-protic solvents presented here show that this is not observed. All minor contributions to the halochromism of dye **2** to the counter anion may be ascribed to indirect effects, such as ionic associations in solution, and not to direct interactions with the dye.

In conclusion, the comparative study presented in this paper distinguishes two kinds of halochromic dyes. In addition to the distinction between positive and negative halochromism, which is ultimately determined by the relative polarities of ground and excited states, we bring attention here to the cation- and the anion-dominated forms of halochromism. Dyes exhibiting cationic and anionic halochromism are in a way complementary, an observation which echoes the distinction, as applied to solvents, made between α- and β-sensitive dyes.[5] This parallel classification may help to extend these studies to other dyes and confirm our suggestion put forward in this preliminary communication. To our knowledge, detailed studies of anionic halochromism have not been reported previously, the existing examples of halochromism generally applying to cation-induced processes.

EXPERIMENTAL

Spectra were recorded on a Beckman DU-65 UV–visible spectrophotometer equipped with thermostated cells.

Analytically pure sodium iodide (Merck) and lithium perchlorate (Fluka) were dried under vacuum (0·1 mmHg) in an Abderhalden apparatus at 100 °C for 1 h. Solvents were stored over molecular sieves after distillation.

The copper complex **1** was prepared following a reported procedure.[4] Compound **2** was obtained from the corresponding protonated pyridinium iodide by treatment with sodium hydroxide.[16]

The dye concentration in all investigated solutions was 2×10^{-3} M for **1** and 2×10^{-4} M for **2**. Varying these concentrations had no effect on the position of the charge-transfer bands.

The charge-transfer energies were calculated from the absorption maxima of the longest wavelength in the visible spectra by means of the relationship E (kcal mol^{-1}) = 28 590/λ_{max}.[1b] For a given salt concentration c, ΔE is the difference between the absorption energies of the longest wavelength band in the presence and absence of the salt.

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REFERENCES

1. (a) M. C. Rezende and L. I. Dal Sasso, *Rev. Roum. Chim.* **31**, 323 (1986); (b) M. C. Rezende, *Tetrahedron* **44**, 3513 (1988).
2. (a) C. Reichardt, *Chem. Soc. Rev.* **21**, 147 (1992); (b) C. Reichardt, S. Asharin-Fard and G. Schaefer, *Liebigs Ann. Chem.* **23** (1993); (c) C. Reichardt, S. Asharin-Fard and G. Schaefer, *Chem. Ber.* **126**, 143 (1993).
3. V. G. Machado, M. A. Torres and M. C. Rezende, *J. Chem. Soc., Faraday Trans.* **88**, 201 (1992).
4. Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jpn.* **45**, 465 (1972).
5. Y. Migron and Y. Marcus *J. Phys. Org. Chem.* **4**, 310 (1991).
6. M. J. Kamlet, J.-L. M. Abboud and R. W. Taft, *Prog. Phys. Org. Chem.* **13**, 485 (1981).
7. R. W. Soukup and R. Schmid, *J. Chem. Educ.* **62**, 459 (1985).
8. E. Buncel and S. Rajagopal, *Acc. Chem. Res.* **23**, 226 (1990).
9. H. G. Benson and J. N. Murrell, *J. Chem. Soc., Faraday Trans. 2* **68**, 137 (1972).
10. S. J. Davidson and W. P. Jencks, *J. Am. Chem. Soc.* **91**, 225 (1969).
11. G. Hollmann and F. Voegtle, *Chem. Ber.* **117**, 1355 (1984).
12. D. Bourdin, D. Lavabre, J. P. Beteille, G. Levy and J. C. Micheau, *Bull. Chem. Soc. Jpn.* **63**, 2985 (1990).
13. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed. VCH, Weinheim (1988).
14. A. Taha, V. Gutmann and W. Linert, *Monatsh. Chem.* **122**, 327 (1991).
15. E. Buncel, A. J. McKerrow and P. M. Kazmaier, *J. Chem. Soc., Chem. Commun.* 1242 (1992).
16. L. G. S. Brooker, G. H. Keyes and D. W. Heseltine, *J. Am. Chem. Soc.* **73**, 5350 (1951).