

Pyridiniophenolate Dyes as Probes for Selective Cation Solvation in Binary Solvent Mixtures

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Received: January 7, 1991; Mars 15, 1991

Um novo método é descrito para o estudo de solvatação seletiva de cátions em misturas binárias de solventes. O método utiliza piridiniófenolatos halocromicos (1) como sensores de solvatação catiônica, e é ilustrado com exemplos de soluções binárias orgânicas de iodeto de sódio.

A new method is described for the study of selective cation solvation in binary solvent mixtures. The method exploits halochromic pyridiniophenolates (1) as probes for cation solvation in solution, and is illustrated with examples of sodium iodide solutions of binary mixtures.

Key words: selective cation solvation, pyridiniophenolate dyes.

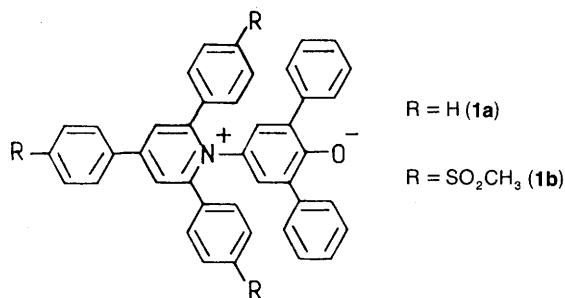
Introduction

Ions in binary solvent mixtures have solvation shells with different composition from that of the bulk solution. The solute surrounds itself by the component which leads to the more negative solvation energy. As a result, a selective or preferential solvation of the solute is often observed in solvent mixtures^{1,2}

Different methods, including electrochemical³, nuclear magnetic resonance⁴ and optical⁵ (IR and UV) measurements, have been developed for the study of selective solvation.

It has been known for some time that the spectra of solvatochromic dyes in solution is affected by the addition of inorganic salts⁶⁻⁹. The halochromic properties of these compounds have been rationalized as reflecting salt-dye interactions^{6,8,9} or changes in the bulk solvent structure^{7a}, caused by the added electrolyte.

We have shown in a systematic study¹⁰ that the halochromic behaviour of Reichardt's pyridiniophenolate dye E_T (30) (1a)¹¹ in alcoholic solutions is mainly caused by interactions between the solvated cation and the phenoxide moiety of the dye.



According to our view, compound (1a) and the related dye (1b) behave like probes of the solvated cation in solution. We have now exploited this property in the development of an alternative method for the study of selective cation solvation in binary solvent mixtures. The rationale of

this method, followed by its application to examples of selective solvation of Na⁺ in binary mixtures, is the subject of the present report.

Experimental

Spectral measurements were carried out on a Hewlett Packard 8450A UV-visible spectrometer.

Commercial solvents (p.a. grade) were further purified following standard procedures¹². Sodium iodide (Merck) was thoroughly dried prior to use. Compound (1b)¹³ was a gift from Professor C. Reichardt.

The E_T values of dye (1b) in solution (average concentration 5×10^{-4} M) were obtained by the simple relationship $E_T = 28590/\lambda_{\max}^{13,14}$ where λ_{\max} corresponded to the maximum of the longest wavelength absorption band in the visible region.¹⁵

The values of (dE_T/dc) were determined as the slopes of the straight lines obtained when E_T values of dilute salt solutions were plotted against the corresponding salt concentrations (Figure 1). The range of salt concentrations employed varied with the solvent. An optimum range was normally chosen so as to yield an unequivocal halochromic shift with the maximum amount of added salt, without showing any appreciable deviation from the expected linear dependence of E_T on c . Each straight line was drawn with a minimum of five data points.

Discussion

The pyridiniophenolate dyes (1) show a unique sensitivity to environmental changes in solution¹⁶. Their E_T polarity values, derived from the position of a charge-transfer band of these dyes visible region, yield information about the solvent region around the dyes.

Addition of an electrolyte to a solution of (1) changes this region, and consequently, the CT band energy of the dye. This halochromic shift arises mainly because of association between the phenoxide group of (1) and the solvated cation¹⁰. Because of ionic attraction, solvent molecules are replaced by solvated cationic species in the microenvironment around the ArO⁻ group of the dye. For a given amount of added salt, the larger the observed halo-

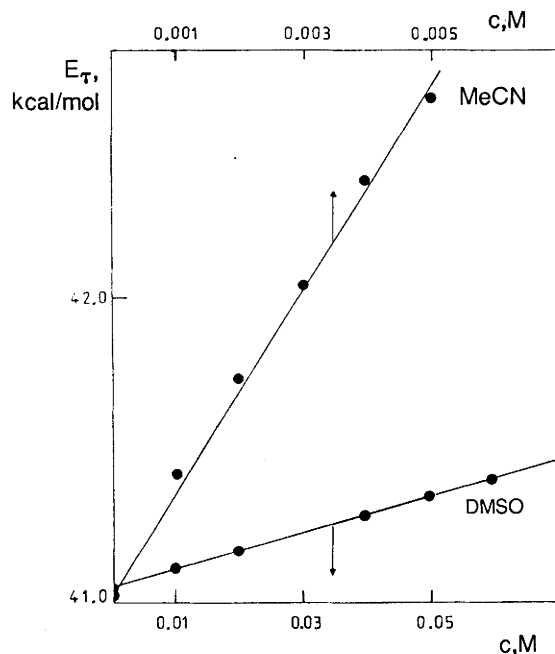


Figure 1. *NaI* solutions of dye (1b) ($c = 5 \times 10^{-4} M$) in dimethylsulfoxide and acetonitrile. Variation of the E_T value of the system with the molar concentration of added *NaI*.

chromic shift, the greater is the association or interaction between the dye and the solvated cation.

In order to compare different systems, we must quantify the susceptibility of the dye in a given solvent to the addition of a salt. The E_T polarity value of (1) does not vary monotonously with the concentration c of added salt^{10,17}. However, for very dilute solutions, the E_T value tends to increase linearly with the concentration c ¹⁰ (see Figure 1). The derivative (dE_T/dc) is therefore constant in this region, and may be taken as a measure of the susceptibility of the solution to polarity changes caused by the added electrolyte.

Let us now consider two of these halochromic susceptibilities, $(dE_T/dc)_A$ and $(dE_T/dc)_B$, measured for the same salt in two pure solvents A and B. A small value of (dE_T/dc) is an indication of little association between the solvated cation and the dye in that solvent. For a given mixture A/B of the two solvents, the value of $(dE_T/dc)_{A/B}$ is not only a measure of this association. It also tells us how much the bulk solvent mixture A/B differs from the solvating shell around the cations. The phenoxide probe associates with the solvated cation and therefore "sees" a microenvironment – the cybotactic region around the cation – which is different from that of the bulk solution. A susceptibility value in the mixture A/B closer to that of pure solvent B, for example, indicates that molecules of B predominate in the solvation shell of the added cation. Thus, the variation of $(dE_T/dc)_{A/B}$ with the composition of the binary mixture may yield information regarding the selective solvation of the cation by solvent A or B.

We now illustrate this method with a few examples.

A study of selective cationic solvation of sodium iodide in DMF/MeCN yielded the plot shown in Figure 2. In spite of the fact that acetonitrile is a more polar solvent than DMF ($E_T(30) = 45.6$ for MeCN and 43.8 kcal/mol for DMF¹⁶), the sodium cation is preferentially solvated by the latter. From the graphic we estimate that the "equisol-

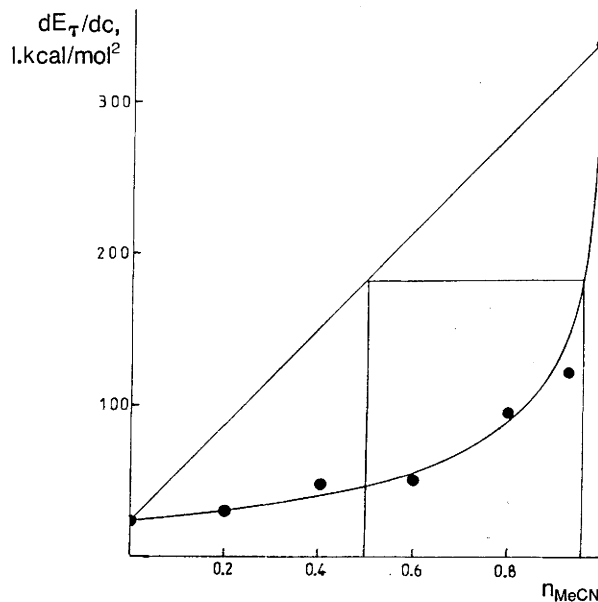


Figure 2. Variation of the susceptibility parameter (dE_T/dc) with the molar fraction of acetonitrile n_{MeCN} for *NaI* solutions of DMF/MeCN

vation point"¹⁸, the proportion of the bulk mixture that corresponds to a 1:1 ratio of the two solvents in the solvating shell, is attained for $n_{MeCN} \approx 0.95$.

The solvation of Na^+ in mixtures of DMF-DMSO is more equally distributed, the cation being preferentially solvated by DMSO (Fig. 3). The equisolvation point is attained in a bulk mixture with some excess of DMF ($n_{DMF} \approx 0.70$).

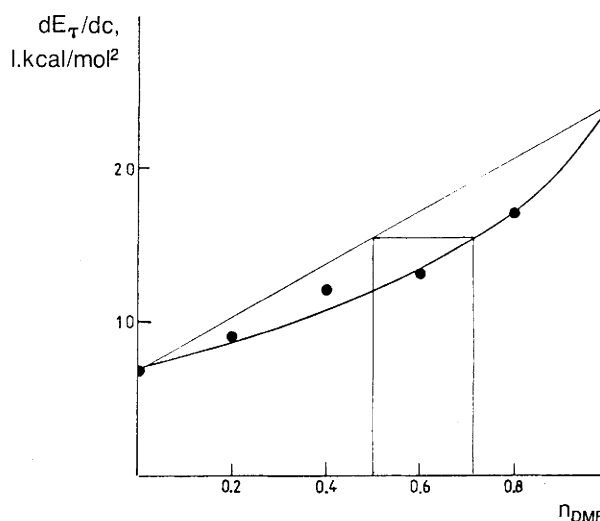


Figure 3. Variation of the susceptibility parameter (dE_T/dc) with the molar fraction of dimethylformamide n_{DMF} for *NaI* solutions of DMSO/DMF.

Figure 4 illustrates the case of a mixture of a protic and an aprotic solvent. Here again, despite its higher E_T (30) value (48.4 kcal/mol)¹⁶, 2-propanol is a much poorer solvent for the sodium cation than DMSO. The (dE_T/dc) values obtained in the range 0-0.7 of the alcoholic molar

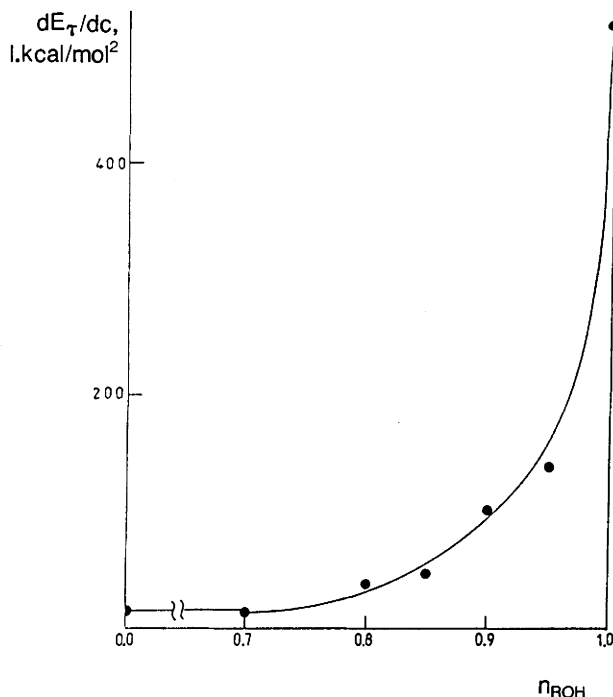


Figure 4. Variation of the susceptibility parameter (dE_{τ}/dc) with the molar fraction of 2-propanol n_{ROH} for NaI solutions of DMSO/2-PrOH.

fraction were practically constant, and equal to the susceptibility value in pure DMSO. The selective solvation of the cation by the DMSO is so overwhelming that, even in solvent mixtures containing 70% of 2-propanol, the Na^{+} solvation shell is practically composed of DMSO molecules only.

The NaI solutions of DMSO/2-PrOH mixtures offer an example of heteroselective solvation. The solvation of the iodide anion, like that of all halides in DMSO, is negligibly small^{19a}. It is generally smaller than the solvation in a protic solvent, like 2-propanol, where hydrogen bonds to the anion stabilize this species in solution^{19b}. The opposite is true of the sodium cation. Data for the enthalpies of transfer of Na^{+} to various solvents from propylene carbonate²⁰ indicate that DMSO solvates this cation more effectively than either water or methanol. In fact, DMSO solubilizes NaI by strongly solvating the sodium cation. Addition of protic 2-PrOH reduces the availability of solvating DMSO molecules, due to hydrogen-bonding interactions between the two solvents. This is not accompanied by any increased solvation of the iodide anion by the added alcohol, because the latter is also involved in and consumed by these interactions. As a result, sodium iodide is less soluble in the binary mixture than in either of the pure solvents.

The trends observed in the above examples are in agreement with the observation that the ability to solvate a cation increases with the donicity of the solvent. Donor numbers (DN) for DMSO, DMF and MeCN (29.8, 26.6 and 14.1 kcal/mol, respectively²¹) parallel the decreasing susceptibility values obtained in this study for the pure solvents. It is interesting to note that, according to present analysis, 2-propanol is a rather poor donor solvent. Donor numbers of hydroxylic solvents like alcohols vary widely, depending on the employed method of measurement²². Our results point to a much lower donicity of 2-PrOH,

and possibly of other alcohols, as compared with DMSO. This agrees with the known fact that the nucleophilicity of an anion is generally greater in DMSO than in an alcohol²³, an observation which is rationalized not only by the greater anion solvation by the latter, but also by the greater cation solvation by the former.

The above examples illustrate the use of halochromic dyes (1) as probes for the investigation of the solvation shells of cations in mixed solvents. One should however be aware of some critical objections to this method, which, in our view, may also be raised regarding other procedures.

In the first place, the present treatment assumes that the experimentally observed salt-induced spectral shifts of the dye are related to the composition of the solvation shell of the salt cation in a mixed solvent. Since these spectral shifts are caused by associations between the phenoxide group of the dye and the solvated cation¹⁰, what one is ultimately observing is the variation of this association or ion-pairing as the composition of the solvent mixture changes. It is perhaps reasonable to assume a relationship between these association changes and the variations of the solvent composition around the cation. However, other effects are obviously neglected here, such as the variation of the local dielectric constant, steric factors, the interaction between the solvated anion and the probe etc. Since we ignore at this stage just how important these other effects are, we must be cautious regarding any quantitative conclusions obtained from our plots.

This limitation is by no means exclusive of the present method. Any other treatment based on the measurement of a given property of the solvated cation must assume that the variations of this property depend solely on the composition of the cation solvation shell. Unfortunately, reality is not that simple. An example is the study of the preferential solvation of Na^{+} in binary solvent mixtures, by following the variations of the²⁴ Na chemical shifts in solution²⁴. After all possible contributions to these variations are taken into account, one must be content with an essentially qualitative interpretation of the results.

A second point which may be raised regarding the above method concerns the particular dye employed. The selective solvation of a given cation in a binary mixture is an absolute property of the system, independent of the halochromic dye employed to study it. However, as in any other method of observation where a perturbation is introduced into the system, ours is probably dependent to some extent on the dye employed. Pyridiniophenolate dyes differ somewhat in their sensitivity towards environmental changes. Like many other polarity indicators, they are particularly sensitive to hydrogen-bonding environments, a trend which may lead to distortions when studying cations in protic-aprotic solvent binary mixtures.

In spite of these limitations, the qualitative trends that emerge from the plots presented in this paper are in good agreement with what is known from previous studies on selective cation solvation in binary mixtures. It would be interesting to apply the above method to other systems that have been investigated by other techniques before. This will probably define the scope and limitations of this method, which may prove rather useful because of its simplicity and the ready availability of pyridiniophenolate dye (1a)²⁵.

In conclusion, readily available halochromic pyridiniophenolate dyes²⁵ may be used as probes for solvated cations in organic solutions. The above method, which exploits this property, represents a simple alternative for the qualitative study of selective solvation of cations in sol-

vent mixtures. Since the ability to solvate a cation is related with the donor number of a particular solvent, this method also affords an easy way of comparing donicities of various solvents, especially in those cases where the reported DN values vary significantly.

Acknowledgments

We are particularly grateful to Professor Christian Reichardt for the gift of a few grams of dye (1b).

Presented as a preliminary communication in the 10th IUPAC Conference on Physical Organic Chemistry, Haifa, Israel, August 1990.

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