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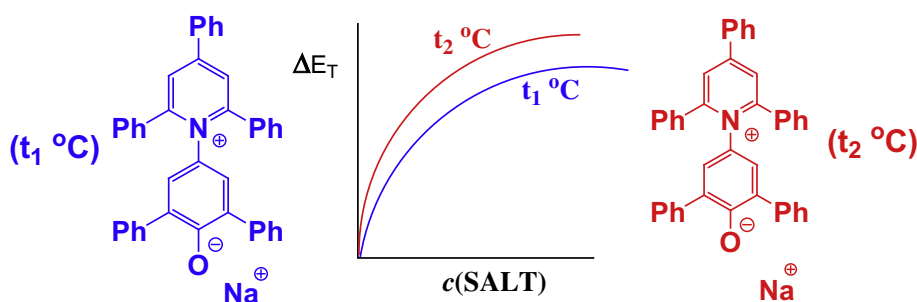
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HIGHLIGHTS

- The halochromism of the $E_T(30)$ dye is affected by temperature in what is termed thermohalochromism.
- The phenomenon was studied for the first time in NaI solutions of the $E_T(30)$ dye in HBD- and non-HBD-solvents.
- A rise in temperature may increase or decrease halochromic shifts, leading to a positive or negative thermohalochromism.
- The effect depends on the solvent, reflecting salt–dye, solvent–salt and dye–solvent interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

The thermohalochromic behavior of Reichardt's $E_T(30)$ betaine – the temperature-dependent variation of its halochromic band in the presence of a cation – was investigated for the first time in NaI solutions of HBD- (methanol, ethanol, 1-propanol, 1-butanol) and non-HBD-solvents (acetonitrile, dimethylformamide) at 15 and 55 °C. The solvent-dependent thermohalochromism of the pyridinium-*N*-phenolate betaine dye was interpreted in terms of the effect of the temperature on the dye–cation association in solution.

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Introduction

Pyridinium-*N*-phenolate betaine dyes constitute an interesting family of compounds, whose UV–Vis spectra are rather sensitive to its environment. The ability of these compounds to sense changes in the solvent nature or composition (solvatochromism), in the solvent temperature (thermochromism), in the nature or concentration of added electrolytes (halochromism) and in the medium

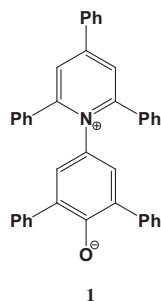
pressure (piezochromism) has led to the proposal of a general term – perichromism – to describe their multifarious behavior [1].

Since their perichromism reflects their interactions with the medium, it should not be a surprise that different types of behavior, e.g. solvato- and halochromism, should be rationalized by analogous models and treatments. Thus, by analogy with the general distinction between a negative and a positive solvatochromism, a negative and a positive halochromic behavior of these dyes in solution, in the presence of inorganic or organic salts, has been described [2–6].

Quantitative treatments for the halochromism of these dyes in the presence of various inorganic cations have been derived from

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Scheme 1. Molecular structure of the $E_T(30)$ pyridinium-*N*-phenolate betaine dye **1**.

models that treat the added salt as a “co-solvent” in binary solvent mixtures [7,8].

This parallelism may be extended even further, by regarding the hydrogen-bond interactions of these pyridinium-*N*-phenolate betaine dyes with hydrogen-bond-donor (HBD)-solvents as a particular case of a more general phenomenon, in which hydroxylic solvents and organic or inorganic salts act as electrophile-bond donors (EBD) to these dyes [5].

By an analogous reasoning, a well-known behavior of these compounds in a particular environment, the thermochromism in pure solvents or solvent mixtures [9–13], may be sought in a different environment – electrolyte solutions. The question that we have tried to answer in the present communication arises from such an analogous reasoning: do salt solutions of solvatochromic phenolate dyes exhibit, at variable temperatures, a thermochromic behavior that unequivocally reflects their interactions with the salt? We termed this effect thermohalochromism, to distinguish it from the known thermochromism elicited by interactions of the dye with the solvent at variable temperatures.

In order to search for this effect, we recorded the spectra of Reichardt's pyridinium phenolate betaine $E_T(30)$ **1** (Scheme 1) in HBD- and non-HBD solvents, in the presence of increasing concentrations of a sodium salt and at different temperatures.

Experimental part

All employed solvents were analytically pure and were used without any further purification. Sodium iodide was dried by heating under vacuum prior to use. The $E_T(30)$ betaine was prepared by a reported procedure [5].

UV–Vis spectra were recorded on a Scinco S-4100 spectrometer, equipped with thermostated cells. Halochromic shifts (in kcal mol^{−1}) were measured as variations of the $E_T(30)$ values of the electrolyte solutions, from the recorded λ_{\max} values (in nm) (obtained as averages of two measurements), employing Eq. (1) and [1].

$$E_T(30) = 28590/\lambda_{\max} \quad (1)$$

Conversion to the SI unit kJ mol^{−1} is achieved through 1 kcal mol^{−1} = 4.18 kJ mol^{−1}.

Results and discussion

Variations of the position of the charge-transfer band of dye **1** were recorded in methanol, ethanol, 1-propanol, 1-butanol, acetonitrile and *N,N*-dimethylformamide solutions, in the presence of increasing concentrations of NaI, at 15 and 55 °C. In all cases, hypsochromic shifts of the CT band were observed, as the cation concentration was increased.

The halochromism of the pyridinium-*N*-phenolate betaine dye **1** has been rationalized in terms of a 1:1 association between the dye

D and the cation M^+ , to give a dye-cation complex DM^+ [14,15]. The equilibrium constant K for this process is given by

$$K = c(DM^+)/c(D) \cdot c(M^+) \quad (2)$$

The concentrations c of the free (D) and cation-bound dye (DM^+) may be expressed in terms of the total dye concentration D_T and the fraction α of associated dye as $c(DM^+) = \alpha \cdot c(D_T)$ and $c(D) = (1 - \alpha) \cdot c(D_T)$. This allows K to be expressed as

$$K = \alpha/(1 - \alpha) \cdot c(M^+) \quad (3)$$

where $c(M^+)$ is the molar concentration of cation M^+ . At a given cation concentration, the transition energy of the dye in the salt solution may be expressed as a linear combination of the transition energies of the free ($E_T(30)_0$, with zero salt concentration) and the cation-bound dye ($E_T(30)_\infty$, at a hypothetically infinite salt concentration), affected by their relative concentrations.

$$E_T(30) = (1 - \alpha) \cdot E_T(30)_0 + \alpha \cdot E_T(30)_\infty \quad (4)$$

Substitution of α from Eq. (3) into Eq. (4) leads to Eq. (5)

$$E_T(30) = E_T(30)_0 + (E_T(30)_\infty - E_T(30)_0) \cdot K \cdot c(M^+)/[1 + K \cdot c(M^+)] \quad (5)$$

By defining the halochromic shift at a given cation concentration $c(M^+)$ as $\Delta E_T(30) = E_T(30) - E_T(30)_0$, and the total halochromic shift of the system as $\Delta E_T(30)_\infty = E_T(30)_\infty - E_T(30)_0$, where the subscripts 0 and ∞ refer to values in the absence of salt, and at a salt concentration where a plateau value is attained, Eq. (5) reduces to Eq. (6)

$$\Delta E_T(30) = \Delta E_T(30)_\infty \cdot K \cdot c(M^+)/[1 + K \cdot c(M^+)] \quad (6)$$

The total halochromic shift $\Delta E_T(30)_\infty$ of electrolyte solutions of the betaine **1** depends on the solvent and the salt, and reflects, like K , the degree of dye-cation association in solution. Both K and $\Delta E_T(30)_\infty$ are large in solvents where strong, and intimate dye-cation pairs are formed in dilute salt concentrations.

The thermohalochromism of betaine **1** in the presence of a salt becomes evident when comparing curves of $\Delta E_T(30)$ vs c (salt) recorded at different temperatures. Two limit situations may be anticipated, as depicted in Fig. 1. If both the total halochromic shift and the association constant increase with the temperature ($t_1 < t_2$ in Fig. 1), a positive thermohalochromism is observed. On the contrary, a decrease of the association constant with the temperature ($t_1 > t_2$ in Fig. 1) implies a negative thermohalochromism.

Thus, in order to investigate the existence of a thermohalochromic effect in NaI solutions of dye **1** in different solvents, we recorded the $E_T(30)$ values of dilute salt solutions at two temperatures (15 and 55 °C), and compared the obtained plots of $\Delta E_T(30)$ vs $c(\text{NaI})$. Such plots are shown in Fig. 2 for methanol (a), ethanol (b), 1-propanol (c), 1-butanol (d), acetonitrile (e) and DMF (f). All the experimental data were fitted to curves drawn from Eq. (6).

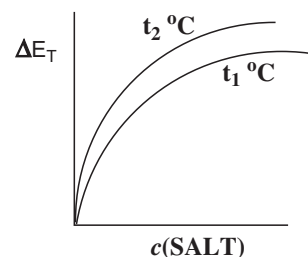


Fig. 1. Schematic representation of variations of the halochromic shift ΔE_T with the salt concentration $c(\text{salt})$ at temperatures t_1 and t_2 . A thermohalochromic behavior is defined as positive if $t_1 < t_2$ and negative if $t_1 > t_2$.

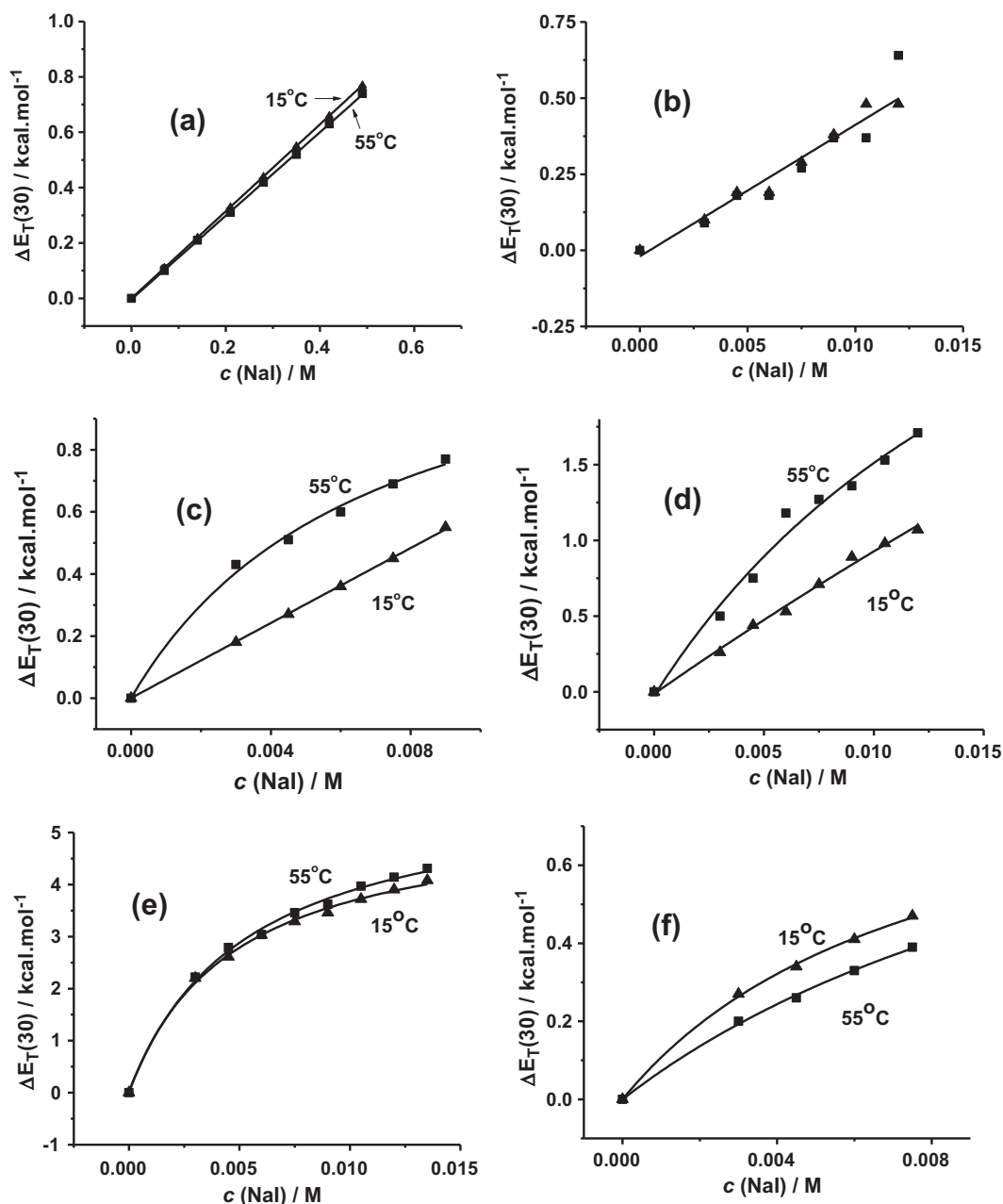
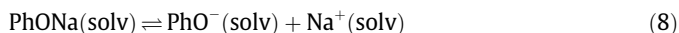
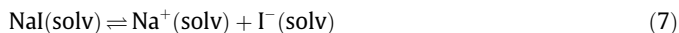


Fig. 2. Plots of $\Delta E_T(30)$ vs $c(\text{NaI})$ for salt solutions of **1** at 15 °C (▲) and 55 °C (■), in (a) methanol, (b) ethanol, (c) 1-propanol, (d) 1-butanol, (e) acetonitrile, (f) *N,N*-dimethylformamide. Experimental data were fitted with curves drawn from Eq. (6).

Inspection of Fig. 2 reveals that a positive thermohalochromism is observed with salt solutions of **1** in 1-propanol (c), 1-butanol (d) and acetonitrile (e). A negative behavior is observed in methanol (a) and DMF (f). In ethanol there was practically no difference between the curves at 15 and 55 °C. Thus, as the polarity and the hydrogen-bond strength of the alcoholic solvent decrease, a transition from a negative (methanol), to zero (ethanol), and to an increasingly positive (1-propanol, 1-butanol) thermohalochromism is observed. Acetonitrile and DMF are examples of non-HBD solvents with opposite thermohalochromic responses, positive in acetonitrile, and negative in DMF.

The thermohalochromism of the pyridinium-*N*-phenolate betaine dye **1** is the result of the interplay of three interactions in solution, a dye-cation, a dye-solvent and a cation-solvent interaction, and of how temperature affects these interactions. The analysis of this three-component system is rather complex. A simplified

picture may be invoked to rationalize the observed trends, based on the two dissociation processes below, both of which involve the solvated Na^+ cation, and where $\text{PhO}^-(\text{sol})$ stands for the solvated pyridinium-*N*-phenolate betaine dye **1**.



Any factor that favors the NaI dissociation will increase the concentration of free $\text{Na}^+(\text{sol})$ and shift the equilibrium with phenolate **1** to the left, thereby increasing the dye-cation association.

In solvents where the ions Na^+ and I^- are poorly solvated, the endothermal separation of these charged species is facilitated by higher temperatures, which also favor the dye-cation association. By contrast, in solvents where both ions are strongly solvated,

higher temperatures favor their desolvation, reducing their dissociation. This has also the effect of reducing dye–cation association.

The relative solvating power of the studied solvents may be compared with the aid of the free-energies of transfer of Na^+ and I^- from water to a non-aqueous solvent [16].

The positive sum of the free-energies of these two ions, in kJ mol^{-1} , increases in the order DMF (10.8) < MeOH (15.5) < EtOH (26.9) < MeCN (31.9) < 1-PrOH (36) < 1-BuOH (41). This order reflects the transition from the negative thermohalochromism observed in DMF and MeOH to the indifferent situation in EtOH and the positive behavior in MeCN, 1-PrOH and 1-BuOH.

A highly polar solvent, like methanol, solvates the iodide and the sodium ions rather strongly. A temperature increase desolvates these ions, destabilizing them in solution and shifting the equilibrium Eq. (7) to the left, thereby decreasing the dye–cation association. The same argument applies to DMF. Iodide solvation in this solvent is rather poor, the free-energy of transfer of I^- from water to DMF is 20.4 kJ mol^{-1} , almost the same of 1-BuOH (22 kJ mol^{-1}) and much larger than that of methanol (7.3 kJ mol^{-1}) [16]. However, this poor solvating power of I^- by DMF is compensated by the largest cation solvating power of this set of solvents, with a negative (-9.6 kJ mol^{-1}) free-energy of transfer of Na^+ from water.

As the solvating power of the Na^+ and I^- ions decreases in less polar solvents, the NaI molecules require higher temperatures to dissociate. In such media, increasing the temperature has the effect of shifting the equilibrium Eq. (7) to the right, and therefore of increasing the dye–cation association, leading to a positive thermohalochromism.

The above interpretation finds support in a previous calorimetric study of alcoholic solutions of the pyridinium-*N*-phenolate betaine dye **1** in the presence of increasing concentrations of NaI [17]. Addition of the salt to these solutions was found to be endothermic in the case of ethanol, and exothermic in the case of 1-butanol. There was practically no enthalpic variation when the solvent was 1-propanol. Though carried out at a constant temperature, these calorimetric measurements shed light on the interplay of solvation and association of **1** and NaI in HBD-solvents. The gradual dilution of NaI in a strong hydrogen-bonding medium, like an ethanolic solution of **1**, disrupts solvent–solvent and dye–solvent bonds, which are endothermal processes. The exothermal contribution that originates from the dye–cation interaction is not sufficient to counterbalance these endothermal processes. As the hydrogen-bond strength of the solvent decreases, the exothermal dye–cation interaction takes precedence over the endothermal hydrogen-bond breaking processes. Thus, although originating from calorimetric measurements at a constant temperature, the comparison of different alcoholic solutions of dye **1** and NaI leads to conclusions that parallel those derived from thermohalochromic measurements at variable temperatures. In both cases, two situations are observed: in strongly hydrogen-bonding solvents, dye–cation association is governed by solvent bonds with the added electrolyte and the dye. As the hydrogen-bonding strength of the alcoholic solvent decreases, dye–cation association becomes increasingly important, taking precedence over other solute–solvent interactions.

The above analysis was based on systems where solvent and salt are different chemical species. An area of interest that has received increasing attention recently is the study of the thermochromism of dyes in ionic liquids (IL) [18]. Ionic liquids act both as solvents and electrolytes, so that such studies are ultimately descriptions of the thermohalochromic behavior of a dye in these media. Accordingly, the observed thermohalochromic responses should be explained within the same framework employed in the present paper. For example, for solutions of the $E_T(30)$ dye in pyridinium- and pyrrolidinium-based ionic liquids, the E_T^N values (normalized $E_T(30)$ values) decreased with temperature, implying a decreased

dye–cation interaction at higher temperatures, and a negative thermohalochromism. By contrast, in phosphonium-based ionic liquids, they increased with temperature, suggesting an increased dye–cation interaction as the temperature was raised, and a positive thermohalochromism [18]. The authors commented that “while pyridinium- and pyrrolidinium-based ionic liquids are perceived as “polar” solvents by the betaine molecule the phosphonium-based ionic liquids act as “nonpolar” solvents for the same probe molecule.” This observation fits our findings in the present paper, if solvent polarity becomes a measure of the strength for salt dissociation: in “polar” solvents like methanol or DMF, the betaine molecule exhibited a negative thermohalochromism, while in “nonpolar” solvents like 1-propanol or 1-butanol, it showed a positive thermohalochromism.

The IL anion also played an important role: in 1-butylpyridinium tetrafluoroborate ($[\text{BP}][\text{BF}_4]$), the $E_T(30)$ dye exhibited a negative thermohalochromism, whereas in 1-butylpyridinium bis(trifluoromethylsulfonyl)imide ($[\text{BP}][\text{NTf}_2]$), the E_T^N values were insensitive to the temperature. As discussed above, this illustrates the importance of the salt dissociation (Eq. (7) above) on the observed thermohalochromism. The dissociation of salts with the same cation but different anions will be affected differently by an increased temperature.

Conclusions

The $E_T(30)$ pyridinium-*N*-phenolate betaine dye varies its solvatochromic response to the medium with the temperature, in what is known as thermochromism [9]. In an analogous way, it might be expected that their halochromic response to cationic solutions should vary with temperature, in what could be termed, by analogy, thermohalochromism.

The present report investigated for the first time the possible existence of a thermohalochromic behavior of the $E_T(30)$ dye in NaI solutions of methanol, ethanol, 1-propanol, 1-butanol, acetonitrile and *N,N*-dimethylformamide at 15 and 55 °C.

Two limit situations were defined: the first, characterized as a positive thermohalochromism, in which halochromic shifts and dye–cation association increase with the temperature; the other, defined as a negative thermohalochromism, in which halochromic shifts and dye–cation association decrease with the increased temperature.

A positive thermohalochromism of **1** was identified in NaI solutions of 1-PrOH, 1-BuOH and MeCN. Solutions of **1** in MeOH and DMF presented a negative thermohalochromism. Little or no thermohalochromism was observed in NaI solutions of **1** in ethanol.

The interpretation of these different responses was based on the effect of the temperature on the NaI and on the dye–cation dissociations in solution. In solvents where the ions Na^+ and I^- are poorly solvated, higher temperatures favor the NaI dissociation and the dye–cation association. By contrast, in solvents where both ions are strongly solvated, higher temperatures favor their desolvation, reducing their dissociation and the dye–cation association.

Such interpretation finds support in the values of free-energy of transfer of Na^+ and I^- from water to the studied solvents [16] and on a calorimetric study of alcoholic solutions of **1** in the presence of increasing concentrations of NaI [17].

The present study, restricted to one solvatochromic dye and to one inorganic salt in a few HBD- and non-HBD-solvents, revealed the existence of different solvent-dependent spectral responses at variable temperature, characterizing for the first time the phenomenon of thermohalochromism. Thermohalochromism also depends on the nature of the employed salt and of the solvatochromic dye. Therefore, a more detailed investigation of this phenomenon with different dyes and inorganic cations should be

envisaged in the future. The thermohalochromism of solutions of tetraalkylammonium salts should be another area of interest, since these organic cations often exhibit a halochromic behavior that is the opposite of that of alkali and alkaline-earth cations [19]. Finally, a third, expanding area of research, is the study of the thermochromism of dyes in ionic liquids. These systems constitute a particular case of the thermohalochromism of dyes, when the salt and the solvent are one and the same chemical species. As discussed above, the observed spectral responses in these systems may be explained within the same framework employed in the present work.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2012.08.032>.

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