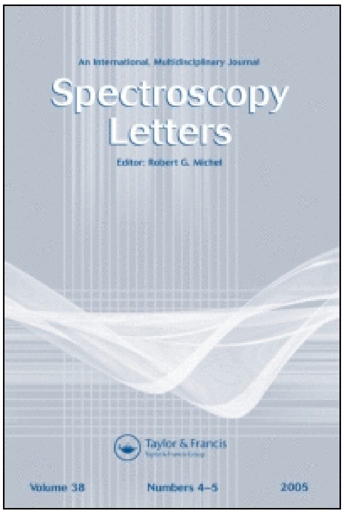

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Machado, Vanderlei Gageiro , Nascimento, Maria da Graça and Rezende, Marcos Caroli(1998) 'The Halochromism of the 1-Methyl-8-Oxyquinolinium Dye', Spectroscopy Letters, 31: 2, 359 — 367
To link to this Article: DOI: 10.1080/00387019808003260
URL: http://dx.doi.org/10.1080/00387019808003260

SPECTROSCOPY LETTERS, 31(2), 359–367 (1998)

THE HALOCHROMISM OF THE 1-METHYL-8-OXYQUINOLINIUM DYE

keywords: Halochromism, 1-methyl-8-oxyquinolinium dye, solvatochromism.

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ABSTRACT: The halochromic behaviour of the title dye (**1**) was studied in methanol, ethanol, 2-propanol, 1-butanol, 2-butanol, dimethyl acetamide, dimethyl sulfoxide, acetone and acetonitrile, in the presence of sodium iodide, potassium perchlorate and lithium perchlorate. The observed shifts of the charge-transfer band of **1**, caused by the addition of increasing concentrations of the salts, was interpreted in terms of dye-salt and solvent-salt interactions and compared with the behaviour of other solvatochromic dyes which exhibit cationic halochromism.

The phenomenon of halochromism is related to the more thoroughly investigated solvatochromic behaviour of dyes exhibiting a medium-sensitive absorption arising from an internal charge transfer.[1-8] The position of the charge-transfer band of a halochromic dye in solution is sensitive to the nature and concentration of an added salt. We may distinguish two kinds of behaviour , a cationic and an anionic halochromism, depending on which species is mainly responsible for the spectral changes induced by the salt added to the dye solutions.[3]

The halochromic shifts may be explained in terms of dye-salt associations.[9,10] Most studies have been concerned with the halochromism of pyridinium phenoxides. For these compounds, which exhibit cationic halochromism, it is the association of the dye with the metal cation which determines the spectral shifts in solution.

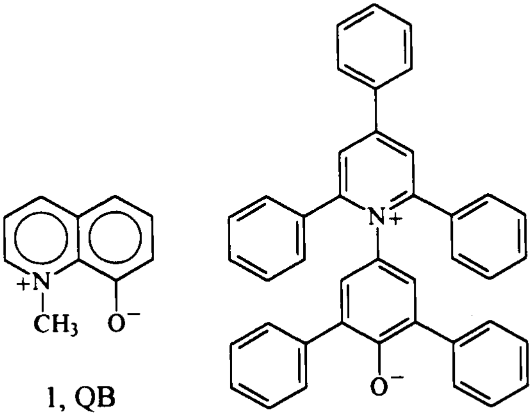
The 1-methyl-8-oxyquinolinium betaine **1** (QB) was originally described by Ueda and Schelly [11] . More recently, solvatochromic shifts of this dye in 28 solvents were recorded and compared to the solvatochromic behaviour of the widely employed $E_T(30)$ polarity probe **2** [12] . A good correlation of the transition energies of the solvatochromic band of **1** ($E_T(QB)$) was obtained with the ccorresponding $E_T(30)$ values in these media, with a correlation coefficient of 0.9935.

In the present communication we studied the spectral properties of organic solutions of dye **1** in the presence of various salts. Because of the similarity of its solvatochromic behaviour with that of the $E_T(30)$ dye, it seemed natural to compare the halochromic properties of **1** with those of other pyridiniophenolate dyes previously studied by us and others. [1,6,8]

EXPERIMENTAL:

The absorption spectra were registered in a Beckman DU-65 and HP 8452A spectrophotometers, employing a dye concentration of 7×10^{-4} mol dm^{-3} for all solutions.

All employed solvents were analytically pure and were further purified by standard procedures [13]. Potassium perchlorate was prepared by reaction of potassium carbonate with concentrated perchloric acid and recrystallized in water.



1, QB

2

Scheme 1

Potassium perchlorate, sodium iodide (Merck) and lithium perchlorate (Fluka) were dried in vacuum (0.1 mm Hg) in an Abderhalden apparatus at 100°C for 10 hours. Dye **1** was prepared following Ueda and Schelly's procedure.[11]

The $E_T(QB)$ values were calculated from the λ_{max} values of the corresponding solvatochromic bands in the visible region, by means of the relationship $E_T(QB)$ (kcal mol^{-1}) = $28590/\lambda_{max}$. For a given salt concentration c, $\Delta E_T(QB)$ is the difference between the absorption energy for the solvatochromic band in the presence and absence of electrolyte.

RESULTS AND DISCUSSION:

The absorption spectra of salt solutions containing dye **1** were obtained at 25°C for different concentrations of lithium perchlorate, sodium iodide and potassium perchlorate. We employed solutions of electrolytes in alcohols (methanol, ethanol, 2-propanol , 1-butanol and 2-butanol) and aprotic solvents (dimethyl acetamide, dimethyl sulfoxide, acetone and acetonitrile).

Dye **1** exhibited a negative halochromic behaviour in all solvents (shifts to shorter λ_{max} values with the addition of salt) irrespective of the nature of the added electrolyte. The relative trends may be compared by plotting the band energy shifts, $\Delta E_T(QB)$, for each system against salt concentrations. The variations of the $E_T(QB)$ values of the various salt solutions with the concentration of the added $LiClO_4$ are shown in Fig. 1 and 2 for protic and aprotic solvents, respectively.
The halochromic behaviour of **1** in various aprotic solvents in the presence of increasing amounts of NaI is shown in Fig. 3.

For protic solvents, the halochromic shift induced by lithium perchlorate increased in the following order: MeOH < EtOH < 1-BuOH < 2-PrOH < 2-BuOH. (See Figure 1). This order was the same as that observed for other pyridiniophenoxides[1] and can be explained in terms of the relative ease of association of the dye with the lithium cation in each solvent. This association should be strongest in the alcohol (2-BuOH) which forms the weakest hydrogen bonds with the dye, diminishing with the increasing hydrogen-bond-donor (HBD) character of the solvent.

The halochromic behaviour of dye **1** in polar aprotic solvents also parallels that of Reichardt's pyridiniophenolates [1] and Brooker's merocyanine [3] both for the lithium (Figure 2) as for the sodium cation (Figure 3). These trends had been interpreted in terms of competing interactions or associations with the cation in solution, on the part of the phenoxide dye or the solvent. Halochromic shifts were thus rather small in DMSO because this solvent was very effective in solvating the metal cation, with the result of decreasing the association constant between the dye and M^+ in solution. However, dye **1** differed from the other phenoxide dyes studied previously as regards its relative halochromic behaviour in acetone and acetonitrile. Contrary to the $E_T(30)$ dye [1] and to Brooker's cyanine [3], the halochromic shifts of dye QB (**1**) in the presence of Li^+ or Na^+ were more pronounced in acetonitrile than in acetone. Clearly, in the case of **1** , the greater cation-solvating ability of acetone (donor number DN = 17 $kcal.mol^{-1}$), when compared with acetonitrile (donor number DN = 14.1 $kcal.mol^{-1}$), determines the

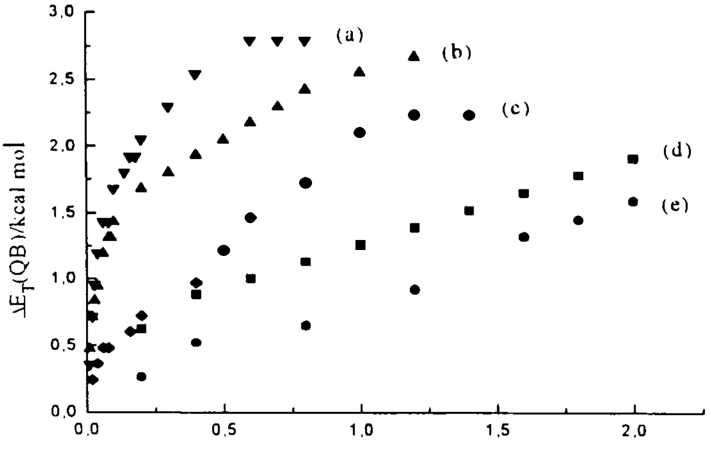


FIG. 1 - Variations of the E_T(QB) value of alcoholic lithium perchlorate solutions with the electrolyte concentration. The concentration of the dye QB in all cases was 7 × 10^{-4} mol dm^{-3}. Curves refer to lithium perchlorate solutions in (a) 2-butanol, (b) 2-propanol, (c) n-butanol, (d) ethanol and (e) methanol

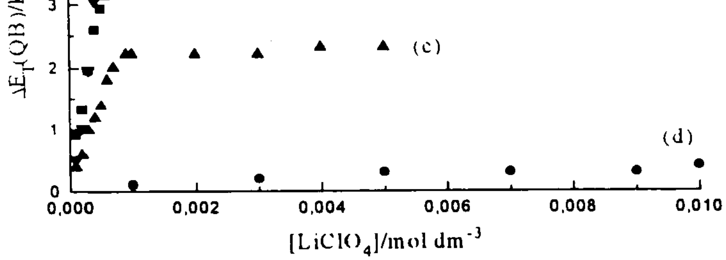


FIG. 2 - Variations of the E_T(QB) value of lithium perchlorate solutions with the electrolyte concentration. The concentration of dye QB in all cases was 7 × 10^{-4} mol dm^{-3}. Curves refer to $LiClO_4$ solutions in (a) acetonitrile, (b) acetone, (c) dimethyl acetamide, (d) dimethyl sulfoxide

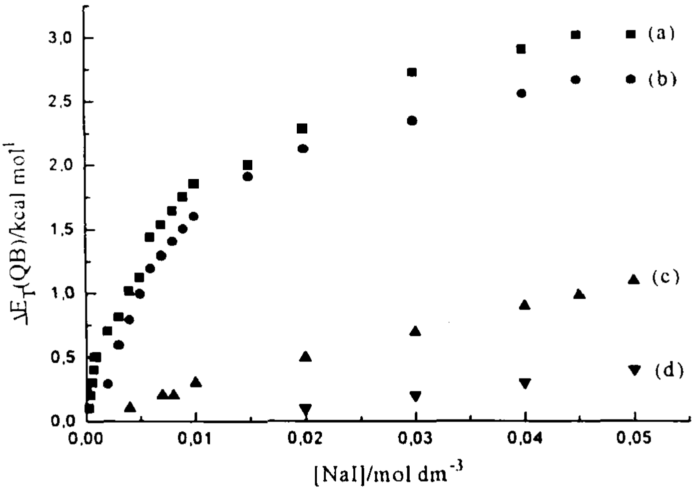


FIG. 3 - Variations of the $E_T(QB)$ value of sodium iodide solutions with the electrolyte concentration. The concentration of dye QB in all cases was 7×10^{-4} mol dm^{-3}. Curves refer to NaI solutions in (a) acetonitrile, (b) acetone, (c) dimethyl acetamide, (d) dimethyl sulfoxide

relative dye-cation association in the two solvents. In the latter medium, a greater dye-cation association is the result of the comparatively smaller cation solvation by the acetonitrile molecules, an effect which is reflected in the greater halochromic shifts observed in that solvent.

Figure 4 shows the variations of the $E_T(QB)$ values for various salt solutions in acetonitrile as function of the added electrolyte concentration.

The larger levels of halochromism were induced by $LiClO_4$, followed by NaI and $KClO_4$. This order is the same which was observed in the literature for pyridiniophenoxides,[4,14-16] and follows the effective ionic charges for the cations of the salts ($Li^+ > Na^+ > K^+$). A cation with a high effective ionic charge interacts strongly with the donor moiety of the dye, in comparison with cations that have low charge density. Thus, a harder cation like Li^+, associated more strongly with dye **1**, causing a larger halochromic shift than a relatively softer species like K^+.

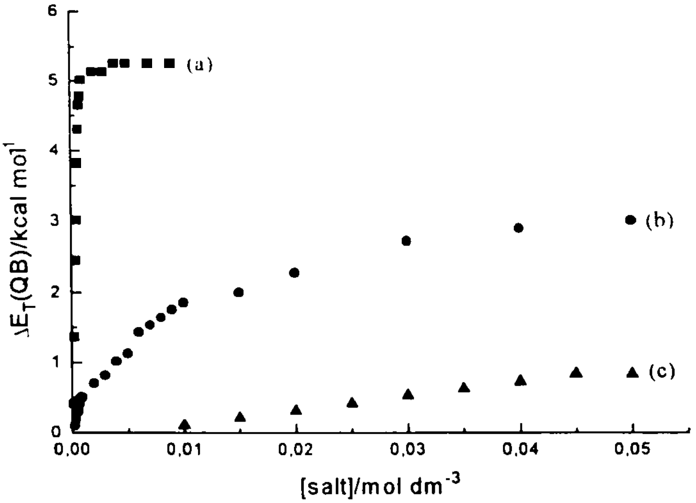


FIG. 4 - Variations of the $E_T(QB)$ value of salt solutions with the electrolyte concentration. The concentration of dye QB in all cases was 7×10^{-4} mol dm^{-3}. Curves refer to (a) $LiClO_4$, (b) NaI and (c) $KClO_4$ solutions in acetonitrile

In conclusion, the present study showed that the halochromic behaviour of dye **1**, a compound where a donor phenoxide moiety is fused with an acceptor pyridinium ring to yield a small, solvatochromic molecule, parallels the halochromism of other pyridiniophenoxide dyes like the $E_T(30)$ and Brooker's merocyanine. All such compounds exhibit a cationic halochromism, modulated by the interaction between the metal cation and the phenoxide donor moiety. The observed shifts could be rationalized in terms of the association between the dye and the cation. This association is mainly determined by the interplay of dye-cation and dye-solvent interactions, in the case of protic solvents, and by the dye-cation and cation-solvent interactions, in the case of polar aprotic solvents. For a family of metal cations in a given solvent, halochromic shifts of **1** were greater for the harder species, a result which again points to the magnitude of dye-cation association in solution as determining the halochromism of pyridiniophenoxide dyes.

ACKNOWLEDGMENTS: We are grateful to the Brazilian Conselho Nacional de Pesquisa Científica e Tecnológica, FINEP and PADCT for financing this work.

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Date Received: August 20,1997
Date Accepted: October 8, 1997