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The Halochromism of Pyridinium *N*-Phenoxide Betaine Dyes in Acetonitrile Solution

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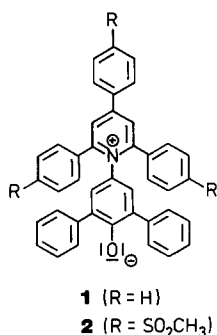
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Key Words: Acetonitrile-electrolyte solutions / $E_T(30)$ values / Halochromism / Pyridinium *N*-phenoxide betaine dyes / Solvatochromism / Solvent polarity

The halochromism of the negatively solvatochromic pyridinium *N*-phenoxide betaine dye **1** has been measured in acetonitrile solution and linearly correlated with the effective charge of the cations of the added alkaline and alkaline earth

salts. The observed negative halochromism of betaine dye **1** constitutes a new type of true halochromism, in contrast to the trivial halochromism found for the first time by Baeyer and Villiger in 1902.

Pyridinium *N*-phenoxide betaine dyes are solvatochromic, thermochromic, piezochromic, halochromic, and possibly chiro-solvatochromic. That is, the longest wavelength, intramolecular charge-transfer (CT) absorption band of their UV/Vis solution spectra depends on the polarity of the solvent, the temperature of the solution, the external pressure, the nature and concentration of added salts (electrolytes; ionophores), and possibly — in the case of homochiral betaine dyes — on diastereomeric solute/solvent interactions with pairs of enantiomeric solvent molecules^[3–5]. The exceptionally large negative solvatochromism of **1** has been used to define an empirical parameter of solvent polarity, the $E_T(30)$ values, which are known for numerous organic solvents and many binary solvent mixtures^[3–5]. The better water-soluble tris(methanesulfonyl)-substituted betaine dye **2** recently enabled us to determine $E_T(30)$ values of aqueous electrolyte solutions^[6]. The chance to determine empirically the polarity of aqueous and nonaqueous electrolyte solutions by means of the solvatochromic standard betaine dyes **1** and **2** has recently led to increased investigations by us^[6–8] and others^[9–17] of the halochromism of **1** and **2**, caused by the addition of ionophores^[18] to solutions of **1** and **2** at room temperature.



The study of the ionophore-induced halochromism of solvatochromic dyes other than **1** and **2** has also been intensified in recent years^[19–24].

In this paper we report on the ionophore-induced halochromism of **1** in acetonitrile solution at 25°C. Acetonitrile

was chosen because of its good solvency for salts, its rather high relative permittivity ($\epsilon_r \approx 36$), thus promoting the dissociation of ion pairs, and its non-hydrogen bond donor (non-HBD) character, thus avoiding specific solute/solvent interactions such as intermolecular hydrogen bonding.

The addition of alkaline and alkaline earth iodides as well as magnesium perchlorate — up to a tenfold excess or up to a saturated salt solution — to a 10^{-4} M solution of **1** in acetonitrile leads in all cases to a hypsochromic shift of its long-wavelength CT band by ca. 31–213 nm (depending on the nature of the added ionophore; cf. Figure 1 and Table 1), without substantially changing its shape. Only with tetra-

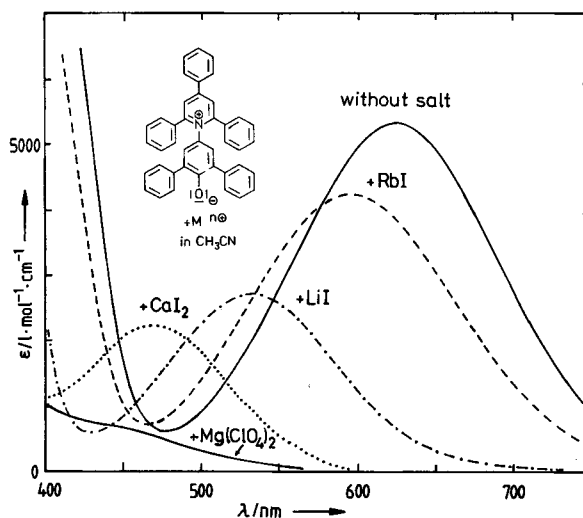


Figure 1. Long-wavelength UV/Vis absorption CT band of betaine dye **1**, measured in acetonitrile at 25°C, without and with addition of an excess of alkaline and alkaline earth salts [$c(\text{betaine}) \approx 1 \cdot 10^{-4}$ mol/l; $c(\text{salt}) \approx 1 \cdot 10^{-3}$ mol/l]; the intensity of absorption, ϵ_{max} , decreases slowly after the addition of salt; therefore, the extinction coefficients ϵ of the salt-containing betaine solutions are only approximate, measured relative to the absorption intensity of the salt-free betaine solution (cf. Table 1)

n-butylammonium iodide is the hypsochromic shift negligible ($\Delta\lambda = -2$ nm). All hypsochromic shifts are accompanied by a decrease of the intensity of the halochromic CT absorption band of **1** (cf. Figure 1).

By analogy with the definition of solvatochromism^[3], we have suggested^[7] the term "negative (positive) halochromism" for such a hypsochromic (bathochromic) shift of the

Table 1. Maximally measurable alkaline and alkaline earth salt-induced hypsochromic shifts ("negative halochromism") of the longest wavelength intramolecular CT absorption band of the standard pyridinium *N*-phenoxide betaine dye **1**, measured in acetonitrile at 25 °C, after addition of $(n\text{Bu})_4\text{N}^+\text{I}^-$, LiI, NaI, KI, RbI, and CsI, as well as $\text{Mg}(\text{ClO}_4)_2$, CaI_2 , SrI_2 , and BaI_2 ; including the effective ion radii and effective ion charges of the corresponding cations M^{n+} ; betaine dye concentration: ca. $1 \cdot 10^{-4}$ mol/l; salt concentration: in each case ca. $1 \cdot 10^{-3}$ mol/l, except NaI, KI, RbI, and CsI (saturated solutions)

Salt	$\lambda_{\text{max}}/\text{nm}$	$E_{\text{T}}(\mathbf{30})$ kcal/mol	Effective cation radii ^[a] $r_{\text{M}^{n+}}/\text{pm}$	Effective cation charges ^[b] $(n^+/r_{\text{M}^{n+}}) \cdot 10^3/\text{pm}^{-1}$
Without salt	626.3	45.6	—	—
$(n\text{-Bu})_4\text{N}^+\text{I}^-$ [c,d]	625.8	45.7	—	—
LiI ^[e]	533.0	53.6	76	13.2
NaI ^[e]	546.8	52.3	102	9.8
KI ^[e]	584.7	48.9	138	7.2
RbI ^[e]	594.8	48.1	152	6.6
CsI ^[e]	608.9	47.0	167	6.0
$\text{Mg}(\text{ClO}_4)_2$ [f]	(413.3)	(69.2)	72	27.8
CaI_2 [e]	468.2	61.1	100	20.0
SrI_2 [e]	490.0	58.3	118	16.9
BaI_2 [e]	496.0	57.6	135	14.8

[a] R. D. Shannon, *Acta Crystallogr. Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1976**, 32, 751–767; see also N. N. Greenwood, A. Earnshaw, *Chemie der Elemente*, VCH Verlagsgesellschaft, Weinheim **1988**, Appendix 5, p. 1652 (effective Pauling cation radii of ions with coordination number 6). — [b] Effective cation charge = ion charge/Pauling cation radius. — [c] $c(\text{salt}) = \text{ca. } 1 \cdot 10^{-3}$ mol/l, corresponding to a tenfold excess of salt relative to the betaine dye concentration; at this salt concentration, the maximally measurable λ_{max} shift has been already achieved. — [d] Even at a 100-fold excess of $(n\text{Bu})_4\text{N}^+\text{I}^-$ [$c(\text{salt}) = \text{ca. } 1 \cdot 10^{-2}$ mol/l; $\lambda_{\text{max}} = 624.2$ nm], only a rather small hypsochromic band shift of $\Delta\lambda = 2$ nm (relative to the absorption of the salt-free betaine dye solution) has been found. — [e] $c(\text{salt}) = \text{saturated solution}$, corresponding to 1.26 mol/l (NaI)^[g], $4.44 \cdot 10^{-3}$ mol/l (KI)^[h], $4.35 \cdot 10^{-3}$ mol/l (RbI)^[h], and $4.25 \cdot 10^{-3}$ mol/l (CsI)^[h]; at lower salt concentrations of ca. $1 \cdot 10^{-3}$ mol/l, the λ_{max} shifts are of the order of only 0–11 nm; with these four salts, the maximally measurable hypsochromic band shifts have been observed in salt-saturated acetonitrile solutions only. — [f] The λ_{max} and $E_{\text{T}}(\mathbf{30})$ values given in parentheses have been calculated from the correlation equation given in Figure 2; in this case, the λ_{max} value cannot be measured directly because the Mg^{2+} -induced hypsochromic band shift is at $c[\text{Mg}(\text{ClO}_4)_2] = 1 \cdot 10^{-3}$ mol/l already so large, that the less intensive long-wavelength CT absorption band of **1** is largely hidden by the more intensive UV absorption bands at $\lambda = 375$ ($\epsilon \approx 9200$) and 302 nm ($\epsilon \approx 40000$) (cf. the complete UV/Vis spectrum of **1**, measured in acetonitrile, in the *DMS-UV Atlas organischer Verbindungen*, Butterworths, London, and Verlag Chemie, Weinheim, **1968**, Vol. IV, spectrum no. G12/1); the added $\text{Mg}(\text{ClO}_4)_2$ contained traces of acid which, by protonation of the betaine dye **1**, led to a complete disappearance of its long-wavelength CT absorption band; therefore, before addition of the magnesium salt to the betaine solution, one drop of ethyldiisopropylamine as base has been added; the addition of this nonpolar solvent does not alter the $E_{\text{T}}(\mathbf{30})$ value of acetonitrile. — [g] T. Pavlopoulos, H. Strehlow, *Z. Phys. Chem.* **1954**, 202, 474–479. — [h] D. V. S. Jain, B. S. Lark, P. K. Nayyar, *Indian J. Chem.* **1970**, 8, 73–75.

UV/Vis absorption band of a dissolved compound with increasing ionophore concentration. Since the CT absorption band of **1** lies within the visible region of the electromagnetic spectrum (cf. Figure 1), its halochromism can be easily followed by eye: the addition of salts to the turquoise-coloured solution of **1** in acetonitrile changes the colour to blue, red, orange or yellow, depending on the nature and concentration of the added ionophore.

For the solvent given, the ionophore-induced hypsochromic band shifts of **1** increase in the order $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$ and $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$, i.e. obviously proportional to the charge-to-size ratio of the cations (cf. also ref. [9,10,13,14]). The effective cation charges (ion charge/ion radius) have been calculated by using Pauling's cation radii and included in Table 1. Surprisingly, there exists an excellent linear correlation between the salt-modified molar transition energy $E_{\text{T}}(\mathbf{30})$ of **1**^[5] and the effective charge of the respective alkaline and alkaline earth cations, as shown in Figure 2 (cf. also ref. [14]). This linear correlation has been used to calculate the λ_{max} value of **1** in the $\text{CH}_3\text{CN}/\text{Mg}(\text{ClO}_4)_2$ solution, which is not available directly because of the extreme Mg^{2+} -induced halochromic band shift (cf. Figure 1 and footnote [f] of Table 1).

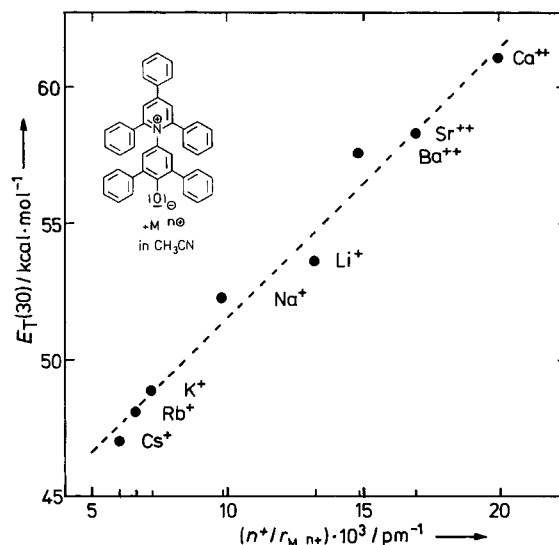


Figure 2. Correlation between the molar electronic excitation energy $E_{\text{T}}(\mathbf{30})$ of betaine dye **1**, measured in acetonitrile at 25 °C after addition of an excess of salt, and the effective charge of the respective alkaline and alkaline earth cation M^{n+} ; the correlation equation is

$$E_{\text{T}}(\mathbf{30}) = 0.992 \cdot [(n^+/r_{\text{M}^{n+}}) \cdot 10^3] + 41.6$$

with pairs of values $n = 8$; correlation coefficient $r = 0.989$; standard deviation of the estimate $s = 0.85$

These results clearly demonstrate that not only the polarity of pure solvents and binary solvent mixtures can be empirically determined by means of halochromic dyes such as **1**, but also the polarity of ionophore solutions (cf. for example ref. [6,10–13,16,17]). For a more systematic study, there are some limiting factors: the often poor solubility of salts in organic solvents, sometimes a salting-out of the betaine dye by the added salt^[6], the decrease in absorption intensity

of **1** with increasing salt concentration, and occasionally salt-induced aggregation of the halochromic dyes with concomitant changes in the UV/Vis absorption.

According to Langhals^[25], the $E_T(30)$ values of binary solvent mixtures can be empirically described by the two-parameter Eq. (1),

$$E_T(30) = E_D \cdot \ln(c/c^* + 1) + E_T(30)^\circ \quad (1)$$

in which $E_T(30)^\circ$ is the value of the less polar solvent, c , the molar concentration of the more polar solvent, and E_D and c^* are adjustable parameters specific for the solvent mixture under investigation. It has been recently shown by Rezende^[16] that, at least for alcoholic solutions, Eq. (1) can be equally applied to the binary system "solvent + salt" to give Eq. (2),

$$E_T(30) = A \cdot \ln(c/c^* + 1) + E_T(30)^\circ \quad (2)$$

in which $E_T(30)$ and $E_T(30)^\circ$ represent the polarity values for the ionophore solution and the pure solvent, respectively, c is the molar concentration of the added salt, and A and c^* are again adjustable parameters.

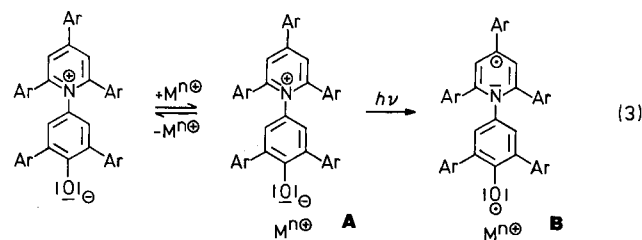
Obviously, the addition of ionophores to solutions of **1** leads to similar hypsochromic band shifts as the addition of more polar solvents to the betaine solution. How can this be explained with respect to the structure of **1** and the type of its long-wavelength solvatochromic and halochromic absorption?

The long-wavelength absorption of dyes such as **1** and **2** results from an *intramolecular* charge transfer from the electron-donating phenoxide part to the electron-accepting pyridinium ring of the nonplanar betaine molecule (interplanar angle between pyridinium and phenoxide moiety: 65° ^[26]). This follows from the dramatic decrease of the permanent ground-state dipole moment on excitation ($\mu_g = 49 \cdot 10^{-30}$ Cm^[27a] $\xrightarrow{h\nu}$ $\mu_e = 20 \cdot 10^{-30}$ Cm^[27b]; $\Delta\mu = 29 \cdot 10^{-30}$ Cm = 8.7 D) and from recent quantum-chemical HMO calculations^[28]. The position of such CT absorption bands depends on the ionization energy of the electron donor and on the electron affinity of the electron acceptor^[29]. Thus, the introduction of electron-withdrawing substituents into the 4-phenylpyridinium ring of **1** increases its electron affinity and causes a bathochromic shift of the CT band of **1**^[30], whereas hydrogen bond donor (HBD) solvents increase, by hydrogen bonding to the oxygen atom, the ionization energy of the phenoxide part of **1**, with an enhanced hypsochromic band shift as consequence^[30].

In the light of these facts, the negative halochromism of **1** can be best explained by loose ion-pair formation between the negatively charged phenoxide part and the cation of the added ionophore, according to Eq. (3). The electrostatic Coulomb interaction between the electron donor part of **1** and the cation increases the ionization energy of the phenoxide part, resulting in the experimentally observed hypsochromic CT band shift. Eventually, protonation of the phenoxide oxygen atom leads to a complete disappearance of the CT band of **1**.

This line of reasoning is supported by the following findings:

(a) As a function of salt concentration, the halochromic effect of **1** and **2** is to induce a hypsochromic band shift in the sample UV/Vis spectrum, without substantially changing its shape. This resem-



1: $\lambda_{\max} = 626$ nm (CH₃CN)

2: $\lambda_{\max} = 509$ nm (H₂O)^[6]

$\lambda_{\max} = 413$ nm [CH₃CN + Mg(ClO₄)₂]

$\lambda_{\max} = 480$ nm [H₂O + Mg(ClO₄)₂]^[6]

bles analogous shifts observed with the same sample in pure organic solvents by adding a more polar solvent (cf. Figure 1 and ref.^[9]).

(b) With given solvent and salt, the salt-induced hypsochromic band shift of **1** and **2** increases with increasing salt concentration, finally leading to a maximally measurable shift which corresponds to a kind of saturation, i.e. complete ion-pair formation (cf. Table 1 and ref.^[6,10,16,17]).

(c) With a given solvent and different salts, the salt-induced hypsochromic band shift is directly proportional to the effective charge of the cation, i.e. its charge-to-size ratio (cf. Figure 2 and ref.^[14]). With LiClO₄ in nonpolar solvents such as diethyl ether and tetrahydrofuran, 1:1 complex formation between **1** and lithium ions according to Eq. (3) with very high association constants of up to 10^6 has been found^[13]. The cation-complexing capability of **1** can be increased even further by means of crown ether rings surrounding its phenoxide part^[8].

(d) With tetraalkylammonium salts, i.e. salts containing large cations of low effective charge, prone to poor ion-pair formation with anions because of steric hindrance, the salt-induced hypsochromic band shifts are negligibly small (cf. Table 1 and ref.^[10,16]). There is obviously no ion-pair formation between **1** and the tetra-*n*-butylammonium cation according to Eq. (3), which explains the only small halochromic band shift observed.

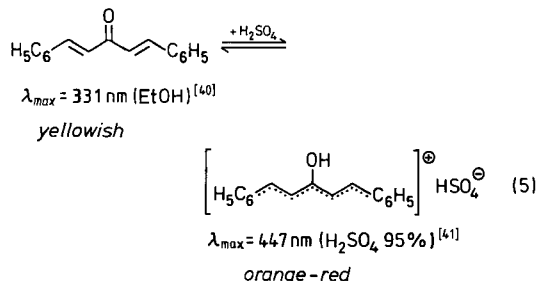
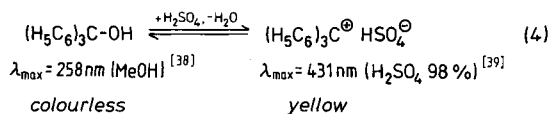
(e) In comparison with the strong cation influence on the salt-induced band shifts of **1** and **2**, the nature of the corresponding anion seems to be of minor importance for the halochromic shifts observed (cf. ref.^[6,10,16]). However, further systematic measurements are necessary to clarify this point.

In conclusion, the negative halochromism of **1** in acetonitrile stems mainly from the specific dye/cation interaction according to Eq. (3), thus reflecting salt-induced perturbations in the molecular-microscopic environment of the phenoxide part of the betaine dye, in accordance with the findings of Rezende et al.^[17]. However, additional nonspecific halochromic effects due to salt-induced changes in the structure of the bulk solvent (i.e. interruption or reinforcement of the intermolecular solvent/solvent interactions with concomitant consequences for the betaine dye solvation) cannot be entirely excluded. Such nonspecific, indirect halochromic effects should be preferably found in highly structured solvents such as water^[10a,15]. In less structured solvents such as acetonitrile (its Trouton constant is with 94 close to the normal value of $88 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ^[31]), this nonspecific halochromic effect can be neglected.

The halochromism of betaine dyes such as **1** and **2** constitutes a fundamentally new type of halochromism, in contrast to the trivial halochromism first described by Baeyer and Villiger in 1902^[31]. According to Baeyer^[31] and authors of recent text books^[32–36], halochromism means the colour

change of a dissolved compound on addition of acid (or base) during which a chemical reaction (e.g. ion formation) transforms a colourless compound into a coloured one with different UV/Vis absorption.

Historical examples for this are the Brønsted acid/base reactions of triphenylmethanol and dibenzalacetone with concentrated sulfuric acid according to Eq. (4) and (5)^[31,37], with concomitant changes of their UV/Vis absorption^[38–41].



More recent examples of halochromic compounds the halochromism of which is also based on pH-dependent salt formation can be found in ref.^[42,43].

This type of halochromism is a trivial one because addition of acid (or base) to a base (or acid) solution always leads to a chemical reaction giving products the UV/Vis absorption of which is usually different from that of the starting compound. If the absorption band of the product accidentally lies in the visible region, then its predecessor is called halochromic according to Baeyer^[31].

In contrast to this trivial halochromism, the true or genuine halochromism of dyes like **1** and **2** refers to a colour change on addition of an ionophore^[18] to the dye solution not accompanied by a change in the chemical structure of the dissolved dye. In contrast to Eq. (4) and (5), the ion-pair formation according to Eq. (3) does not destroy the chemical identity of the betaine dye. We have suggested the term “negative (positive) true halochromism” for a hypsochromic (bathochromic) shift of the UV/Vis absorption band of a dissolved compound on increasing electrolyte concentration, when this shift is *not* caused by a chemical change of the chromophore^[7]. This definition of halochromism is not restricted to salt-induced shifts of absorption bands within the visible region only, but holds for electronic transitions in the whole UV/Vis/NIR region. Since ion-pair formation as shown in Eq. (3) is temperature-dependent, the halochromism of such dyes should be temperature-dependent too, i.e. halochromic dyes should also be thermochromic^[4,15].

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Experimental

The UV/Vis spectra were recorded with a Hitachi U-3410 spectrometer with thermostated 1-cm quartz cells. Acetonitrile (Chromasolv G from Riedel-de Haën, D-3016 Seelze; purity > 99.9%)

was used without further purification. The inorganic salts employed were of analytical reagent quality and were dried before use over P₄O₁₀ in vacuo. The betaine dye **1** was synthesized according to ref.^[5]; it is now also commercially available^[44].

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[5] The Transition Energy $E_T(30)$ is defined as: $E_T(30) [\text{kcal} \cdot \text{mol}^{-1}] = h \cdot c \cdot \tilde{\nu} \cdot N_A = 28591/\lambda_{\text{max}} [\text{nm}]$. In the first publication of this series, the standard betaine dye **1** had by chance the formula number 30. Therefore, the number 30 was added in order to avoid confusion with E_T used in photochemistry as abbreviation for triplet energy. Cf. K. Dimroth, C. Reichardt, T. Siepmann, F. Bohlmann, *Liebigs Ann. Chem.* **1963**, **661**, 1–37.

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[18] Ionophores are ionic compounds (e.g. Na⁺ Cl[−]) which — in contrast to ionogens — consist of ions in the crystal, in the melt, and in solution. Ionogens (e.g. H—Cl) are compounds with molecular crystal lattices which produce ions only when dissolved in appropriate solvents; cf. R. M. Fuoss, *J. Chem. Educ.* **1955**, **32**, 527, and ref.^[13]. Somewhat unfortunately, a new definition of ionophores has been given recently, according to which ionophores are neutral macrocyclic molecules (or parts of molecules) which form complexes with ions, and as carriers transport them through biological membranes; cf. B. C. Pressman, “Alkali Metal Chelators — the Ionophores”, *Inorg. Biochem.* **1973**, **1**, 203–226 [*Chem. Abstr.* **1975**, **83**, 23537h]. In this paper, we use the term *ionophore* according to the definition first given by Fuoss.

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CAS Registry Numbers

1: 10081-39-7 / LiI: 10377-51-2 / NaI: 7681-82-5 / KI: 7681-11-0 / RbI: 7790-29-6 / CsI: 7789-17-5 / Mg(ClO₄)₂: 10034-81-8 / CaI₂: 10102-68-8 / SrI₂: 10476-86-5 / BaI₂: 13718-50-8 / acetonitrile: 75-05-8