

Properties of Cationic Polyelectrolytes of the Ionene Type

Aldina B. Ayres, Jucélia B. Dário, Alfredo T. N. Pires

and Valdir Soldi*

*Departamento de Química, Universidade Federal de Santa Catarina
88040-970 Florianópolis, SC, Brasil*

Received: June 9, 1993.

As propriedades de quatro polieletrólitos catiônicos do tipo $[n, 22]$ -ioneno ($n=3, 4, 5$ e 6) e três do tipo $[R, 22]$ -ioneno com $R=2$ -hidróxi-1,3-propileno, $[2HP, 22]$ -, com contraíon brometo e $R=1,4$ -dimetilenobenzeno, $[1,4-DMB, 22]$ -, com contraíons brometo e cloreto, foram investigadas utilizando-se pireno como sonda fluorescente. As razões entre as bandas vibracionais III/I do espectro de fluorescência do pireno situam-se na faixa de 0.66-0.81 (valores típicos de um microambiente mais hidrofóbico que água pura (0.55)). A ausência de supressão pelo cátion hidrofílico N-etilpiridínio (NEP), um supressor seletivo da fluorescência residual do pireno na fase aquosa, indica a incorporação total desta sonda nos ionenos. A adição de NaCl a soluções dos ionenos com contraíon brometo aumenta significativamente a intensidade de fluorescência do pireno devido a troca cloreto/brometo na superfície do ioneno. Medidas condutimétricas foram usadas para avaliar o grau de dissociação iônica do contraíon. As anisotropias de fluorescência (r) da fluoresceína ou bis(carboxietil)fluoresceína (BCF) adsorvidas no ioneno dão informações quanto à densidade de carga e conformação do ioneno. Os resultados mostram que, em solução aquosa, todos os ionenos anfífilicos estudados aqui preferem uma conformação mais compacta (globular) com alta densidade de carga na superfície.

The properties of four cationic polyelectrolytes of the $[n, 22]$ -ionene type ($n=3, 4, 5$ and 6) and three of the $[R, 22]$ -ionene type with $R=2$ -hydroxy-1,3-propylene, $[2-HP, 22]$, with counterion bromide and $R=1,4$ -dimethylenebenzene, $[1,4-DMB, 22]$, with counterions bromide and chloride, were studied using pyrene as fluorescent probe. The ratios of the vibrational bands III/I in the pyrene fluorescence spectrum were in the range of 0.66-0.81 (typical values for a microenvironment more hydrophobic than pure water (0.55)). The absence of quenching by the hydrophilic, ionene-excluded N-ethylpyridinium (NEP) cation, a selective quencher of the fluorescence of residual pyrene in the aqueous phase, indicates total incorporation of this probe into the ionenes. Addition of chloride ion results in a significant increase in the intensity of pyrene fluorescence due to chloride/bromide exchange at the ionene surface. Conductimetric measurements were used to evaluate the degree of counterion dissociation. Fluorescence anisotropies (r) ionene-adsorbed fluorescein or bis(carboxyethyl)fluorescein (BCF) gave additional information on the ionene charge density and conformation. The results show that, in aqueous solution, all of the ionenes studied here prefer more compact conformations (globular) with high surface charge densities.

Key words: polyelectrolytes; properties: conformation.

Introduction

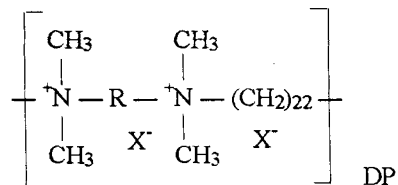
Amphiphilic polyelectrolytes of the $[n, m]$ -ionene type are cationic polymers with dimethylammonium charge centers interconnected by alternating chain segments with n and m methylene groups¹⁻⁶,

The catalytic effect of ionenes on the alkaline hydrolysis of *p*-nitro-phenyl octanoate (NPO) was studied by Nieves *et*

*al.*⁷ It was found that the $[3, 10]$ - and $[6, 10]$ -ionenes had no effect on the rate of this reaction. On the other hand, the $[3, 22]$ - and $[3, 16]$ -ionenes accelerated the reaction rate. Detailed studies by Soldi *et al.*^{8,9} of the physical and catalytic properties of homologous $[3, m]$ -ionenes (with $m = 6, 10, 13, 14, 16, 18$ and 22) confirmed that the catalytic properties of the ionenes were dependent on the preferred conformation. It was also confirmed that the catalytic properties of the ionenes were dependent on the


preferred conformation of the ionene in aqueous solution, the transition from an extended (non-catalytic) to a globular (catalytic conformation occurring when $m \geq 14$).

In this work, we report a comparison of seven amphiphilic ionenes with respect to conformation in aqueous solution, effects of packing on charge density, counterion exchange and adsorption of anionic fluorescent probes in the ionene surface.



[*n*,22]-Ionene; R = —(CH₂)*n*— with *n* = 3,4,5 and 6;
(X⁻ = Br⁻)

[2-HP, 22]-Ionene; R = —CH₂—CH—CH₂—
(X⁻ = Br⁻)

[1,4-DMB,22]Ionene; R = —CH₂——CH₂—
(X⁻ = Br⁻ and Cl⁻)

Experimental Section

Pyrene (Aldrich, 99%) was purified by the method of Geiger and Turro¹⁰. Hexadecyl-trimethylammonium bromide (CTAB, Merck) was recrystallized from acetone-methanol (85:15). NaBr (BDH, 99+%), NaCl (Merck) and [3,6]-ionene (Polybrene, Aldrich) were used as received. N-Ethylpyridinium bromide was prepared as described in the literature.⁹ The fluorescent probes bis (carboxyethyl)-fluorescein (BCF)⁹ and fluorescein were a gift from Dr. F. H. Quina (USP-São Paulo, Brazil).

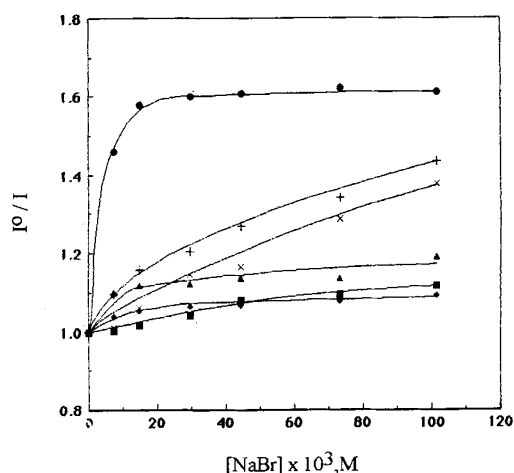


Figure 1. Stern-Volmer plots of the effect of added NaBr on pyrene (1×10^{-7} M) fluorescence in water (+) and in aqueous solutions of: [3,6]- (x, 1.0×10^{-2} M); [3,22]- (■, 1.02×10^{-2} M); [2-HP,22]- (◆, 1.0×10^{-2} M); [1,4-DMB,22]-ionene bromides (Δ, 9.9×10^{-3} M) and [1,4-DMB,22]-ionene chloride (●, 1.0×10^{-2} M).

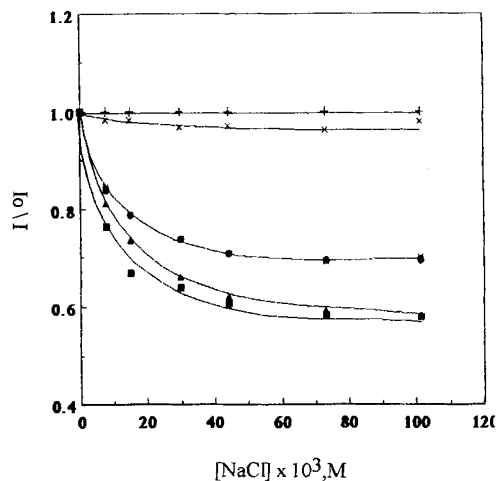


Figure 2. Stern-Volmer plots of the effect of added NaCl on pyrene (1×10^{-7} M) fluorescence in water (+) and in aqueous solutions of: [3,6]- (x, 1.5×10^{-2} M); [3,22]- (■, 1.03×10^{-2} M); [4,22]- (Δ, 8.5×10^{-3} M); [5,22]- (●, 1.4×10^{-2} M) and [6,22]-ionene bromides (*, 9.6×10^{-3} M).

The ionenes were prepared by heating (70°C, 30h, N₂ atmosphere) equimolar quantities of 1,22-bis(N,N-dimethylamino)docosane⁹ and the corresponding dibromoalkanes or dichloroalkane (Aldrich in spectrograde acetonitrile (Aldrich) and purified according to literature procedures^{2,3,9,11}).

The ¹H NMR spectra (200 MHz, D₂O) of the [*n*,22]-ionenes were in agreement with the proposed structure. For the [3,22]-ionene: δ 1.38 (36 H, internal methylenes of long segment), 1.80 (4H, β CH₂s of long segment), 2.34 (2H, central CH₂ of trimethylene segment), 3.30 (12H, CH₃), 3.58 (8H, CH₂-N). For the [4,22]-ionene: δ 1.35 (36 H, -(CH₂)₁₈-), 1.92 (8 H, β CH₂s), 3.19 (12 H, CH₃), 3.48 (8H, CH₂N). For the [5,22]-ionene: δ 1.36 - 1.84 (46 H, -(CH₂)₁₈; β CH₂s of long segment and (CH₂)₃ of -NCH₂(CH₂)₃CH₂N-), 3.20 (12 H, CH₃), 3.44 (8 H, -CH₂-N). For the [6,22]-ionene: δ 1.37-1.80 (48H, -(CH₂)₁₈ - β CH₂s of long segment and (CH₂)₄ of NCH₂(CH₂)₄CH₂N-), 3.19 (12 H, CH₃), 3.41 (8 H, CH₂N). For the [2-HP, 22]ionene: δ 1.39 (36 H, -(CH₂)₁₈), 1.90 (4H β CH₂), 2.36 (1 H, CH group), 3.35 (12 H, CH₃), 3.67 (8H, CH₂-N). For the [1,4-DMB, 22]-ionene: δ 1.34-1.37 (36 H, -(CH₂)₁₈), 1.95 (4 H, β CH₂), 3.24 (12 H, CH₃); 8H, CH₂N), 7.76 (4 H, 1,4-DMB). All ionenes exhibited satisfactory elemental analysis assuming one residual water of hydration per quaternary ammonium group¹².

Fluorescence measurements were performed at 30.0 ± 0.5 °C in 1 cm path length quartz fluorescence cell (Hellma). Relative vibronic intensities were determined from pyrene fluorescence spectra recorded at small band pass (10 and 2 nm for excitation and emission, respectively) on an Aminco Mod. SL fluorescence spectrometer. All other fluorescence measurements were performed on a Perkin Elmer LS-5B spectrometer. Fluorescence quenching and counterion-exchange experiments were performed by adding successive aliquots of quencher or salt stock solution to 2.00 ml of aqueous ionene solution containing pyrene ($(2-5) \times 10^{-7}$ M

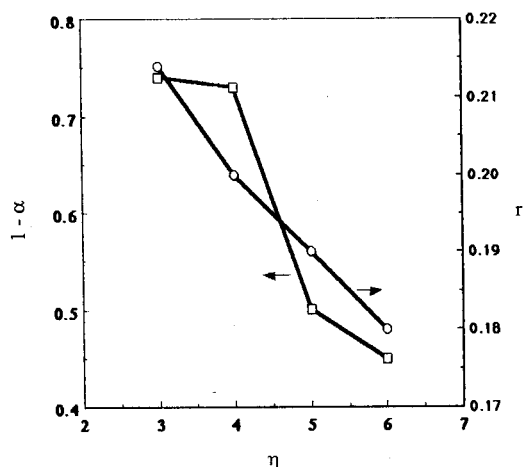


Figure 3. Experimental degrees of counterion association ($1-\alpha$, Table) and fluorescence anisotropy of BCF (r , Table) as function of the number n of the $[n,22]$ -ionenes.

final, excitation at 310 nm, emission spectrum at 360-460 nm). Fluorescence anisotropies (r) of BCF and fluorescein (1×10^{-7} M) in alkaline aqueous ionene solutions (pH=9-10) were determined on the Perkin Elmer LS-5B equipped with polarization accessory, employing excitation and emission wavelengths of 490 and 520 nm, respectively. Conductivity measurements were performed at 25 ± 1 °C with a Digimed Mod. CD 20 conductimeter using a cell with a constant of 1.0 cm^{-1} .

Results

The aromatic hydrocarbon pyrene was chosen as a probe for the solubilization capacity of the ionenes. In aqueous homogeneous solution the N-ethylpyridinium (NEP) cation is a diffusion-controlled quencher of the excited single state of pyrene ($k_q = 1,4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). In the presence of the ionenes, no fluorescence quenching of pyrene by NEP was detected. This observation indicates total incorporation of the pyrene in these ionenes, where it is protected from NEP quenching by the positive surface charge of the ionene.

In water and in aqueous solutions of [3,6]-ionene (0.01 M), a polyelectrolyte with an extended conformation, pyrene fluorescence is quenched by the addition of NaBr (Figure 1). Very little quenching upon addition of NaBr is observed for pyrene in solutions of the ionene bromides. The strong quenching observed for the [1,4-DMB,22]-ionene chloride is due to bromide/chloride ion exchange at the surface of the ionene (vide infra). Conversely, the addition of NaCl (0-0.1 M) to aqueous solutions of the $[n,22]$ -ionene bromides results in significant increase of pyrene fluorescence intensity, also due to counterion exchange at the surface of the ionene (figure 2). This effect decreases in the presence of NaBr and is inversely dependent on the ionene concentration. The data for the effect of added NaCl on the fluorescence of pyrene at one fixed ionene concentration and four fixed NaBr concentrations (0.005, 0.010, 0.015 and 0.020 M) were treated according to the method of Abuin *et al.*¹³, using experimentally determined degrees of counterion dissociation (Table 1), to obtain values of the selectivity coefficients for chloride/bromide counterion exchange ($K_{Cl/B}$) at the surface of the ionenes (Table 1).

Finally, fluorescence anisotropies (r) for the probes bis(carboxyethyl) fluorescein (BCF) and fluorescein adsorbed onto the ionenes are approximately tenfold higher than the values in water (Table 1).

Table 1. Vibronic intensity Ratios of Pyrene Fluorescence, Apparent Degrees of Bromide Counterion Dissociation (α), Selectivity Coefficients ($K_{Cl/B}$) for Counterion Exchange, and Fluorescence Anisotropies (r) of BCF and Fluorescein.

Ionene	Conc ^a M $\times 10^3$	III/I ^b	α	$K_{Cl/Br}$	r	
					BCF	Fluorescein
	water	0.55	-	-	0.022	0.011
[3,6]-	10	0.57	0.71	-	0.059	0.047
[3,12]-(c)	13	0.55	0.81	-	0.055	-
[3,22]-	8.4	0.65	0.26	0.23(c)	0.214	0.170
[4,22]	9.2	0.70	0.27	0.56	0.200	0.161
[5,22]-	9.5	0.73	0.50	0.30	0.190	0.158
[6,22]-	8.5	0.69	0.55	0.54	0.180	0.144
[1,4-DMB,22]	9.9	0.68	0.32	0.22	0.207	0.180
[2-HP,22]	10	0.81	0.23	0.43	0.227	0.205
CTAB	20	0.74	0.25	-	0.123	0.084
	Metanol	0.72	-	-	-	-

^a As equivalent ionic bromide. ^b Vibronic bands designated as in ref. 14. ^c Values from ref. 9.

Discussion

As shown by Soldi *et al.*⁹, the catalytic properties of ionene polyelectrolytes are directly related to their ability to solubilize hydrophobic substrates and to bind and exchange counterions at the ionene surface.

For all the ionenes studied, the fluorescence anisotropies (r) of GCF were large, indicating the predominance of globular conformations in aqueous solution. The α values and the essentially complete solubilization of a hydrophobic substrate like pyrene also points to globular conformations in which the long 22 carbon segment form a hydrophobic core surrounded by the ammonium charge centers. Indeed, the values of α for the [3,22]-, [c,22]- and [2-HP,22]-ionenes are similar to those of the spherical CTAB micelle ($\alpha = 0.25$). For the [5,22]- and [6,22]-ionenes the increase in n is accompanied by an increase in the α values. These values are very similar for the [1,4-DMB,22]-ionenes with bromide and chloride counterions, indicating that the degree of the counterion dissociation is insensitive to the nature of the counterion.

Furthermore, for the homologous [n ,22]-ionenes with $n=3,4,5$ and 6, the variation with n of r values and the apparent degree of counterion association ($1-\alpha$) occurs in a similar fashion (Figure 3). The decrease in the fluorescence anisotropy of ionene-adsorbed BCF and the degree of counterion association is consistent with a decrease in the ionene surface charge density upon increasing the length of the short segment between the charge centers.

Comparing the [1,4-DMB,22]- and the [2-HP,22]-ionenes to the [3,22]ionene, it can be verified that the presence of the intervening rigid 1,4-DMB group has only a minor effect of α and $K_{cl/BF}$, while the OH group increases both α and $K_{Cl/BF}$ somewhat.

Finally, for all the ionenes, there is clearly micelle-like selectivity in bromide/chloride counterion exchange at the ionene surface, consistent with a high surface charge density. Interestingly, there are indications of an alternation in the degree of selectivity, greater selectivity being observed when there is an odd number ($n=3$ or 5) of methylenes than when there is an even number ($n=4$ or 6) in the short segment. This alternation may reflect intrinsic odd-even differences in chain packing or folding of the type responsible, e.g., for the odd-even carbon number dependence of the helical twisting power of chiral molecules in induced cholesteric mesophases¹⁵, of alkyl chain flexibility in liquid crystal¹⁶ and of the Kerr effect for nematic mesophases¹⁷.

Acknowledgments

Financial support received from CNPq and FINEP (Brazil) is gratefully acknowledged.

References

1. A. Rembaum, *J. Macromol. Sci. Chem.* **A3**(1), 87-99 (1969).
2. A. Rembaum, W. Baumgartner, A. Einseberg, *J. Polym. Sci. Polym. Lett. Ed.* **5**, 159-171 (1968).
3. A. Rembaum, H. Noguchi, *Macromolecules* **5**, 261-269 (1972).

4. M. Schmir, A. Rembaum, *Polym. Sci. Technol.* **2**, 327-347 (1973).
5. S. P.S. Yen, D. Clason, A. Rembaum, *Polym. Sci. Technol.* **2**, 291-312 (1973).
6. S. Koda, R. Hashitani, H. Nomura, *Polymer Journal* **24**(4), 357 (1988).
7. V. E. R. Nieves, E. J. Ribaldo, R. Baroud, F. H. Quina, *J. Polym. Sci. Polym. Lett. Ed.* **20**, 433-437 (1982).
8. V. Soldi, Ph. D. Thesis, Instituto de Química, Universidade de São Paulo, 1987.
9. V. Soldi, N. M. Erismann, F. H. Quina, *J. Am. Chem. Soc.* **110**, 5137-5143 (1988).
10. M. Geiger, N.J. Turro, *Photochem. Photobiol.* **22**, 273-276 (1975).
11. H. Noguchi, A. Rembaum, *Macromolecules* **5**, 253-260 (1972).
12. T. Kunitake, A. Tsuge, K. Takarabe, *Polym. J. (Tokio)* **17**, 633-640 (1985).
13. E. Abuin, E. Lissi, N. Bianchi, L. Miola, F.H. Quina, *J. Phys. Chem.* **87**, 5166-5172 (1983).
14. K. Kalyanasundaram, J. K. Thomas, *J. Am. Chem. Soc.* **99**, 2039-2044 (1977).
15. S. Bualek, S. Patumtevapibal, J. Siripitayananon, *Chemical Physics Letters* **79**(2), 389-391 (1981).
16. E. T. Samulski, *Israel Journal of Chemistry* **23**, 329-339 (1983).
17. R. Yamamoto, S. Ishihara, S. Hayakawa, *Physics Letters* **60A**(5), 414-416 (1977).