Binding of Electrolytes to Poly(ethylene oxide) in Methanol

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ABSTRACT: The binding of potassium and sodium salts (thiocyanate and iodide as anions) to poly(ethylene oxide) in methanol solutions has been studied. The study was performed by the use of fluorescence techniques and ultrafiltration experiments coupled with conductivity measurements. The results obtained conform to an adsorption model of fixed adsorption sites where the cations are the primary species adsorbed, thus creating a charged polymer able to concentrate the anions in the surroundings of the coil. For a given cation, the local concentration of the anions depends on the ionic strength of the media in a manner not accounted for by considering only electrostatic interaction, thus indicating that specific interactions such as ion-pair formation (or other factors such as differences in the activity coefficients of the counterions) must be considered in the adsorption process. The ultrafiltraton experiments are compatible with a simple model of "bound" and "free" counterions by showing that at least some of the anions are able to move freely in the solution, but the experiments also indicate that specific interactions of the counterions with the charged polymer are operative.

Introduction

The binding of electrolytes to poly(ethylene oxide) is a well-known phenomenon. The process, which is closely related to cation complexation by crown ethers,[1] has been investigated by conductivity,[2-6] solvent extraction,[7] and viscosimetry.[8] The most comprehensive set of studies have been carried out by Ono et al.,[2-6] who developed a method for the analysis of the ion binding based on a one-dimensional lattice model. On the basis of this model, they defined an equilibrium constant (the "binding constant") in terms of the normalized activity of the bound solute.[3] They consider that there exist a fixed number of adsorption sites and that the main factor determining the change in θ (the fraction of occupied sites) with salt concentration is the interaction between the ions (the cations) bound to the lattice points. This interaction has been approximated by the Debye–Hückel pair by pair potential, and its evaluation allows one to obtain the "activity coefficients" that relate the normalized activity to θ. This interpretation considers that only the cations are "bound" to the poly(ethylene oxide) chains. For several salts in methanol (I^- and SCN^- as anions and Na^+, K^+, and Rb^+ as cations) it is concluded that since the charge density on the polymer chain is small, the binding of the anion to the polymer–cation complex can be disregarded.[4] This conclusion, which is contrary to previous conclusions drawn from conductance measurements,[2] is not of general validity since in other systems the contribution of the anion associated with the chain must be introduced in order to quantitatively describe the conductivity data.[6] In the present work we have employed a fluorescence technique and conductivity measurements coupled to ultrafiltration experiments with the aim of evaluating the local concentration of anions (the "counterions") in the vicinity of the PEO chain and to what extent these "counterions" are able to freely move in the solution.

Experimental Section

Commercial poly(ethylene oxides) (PEO) of nominal molecular weights 2×10^4 and 7×10^3 (Unilever, Research Lab, the Frythe Welwyn Hertz) were used. 1-Naphthylacetic acid (NAA) was employed to obtain the fluorescent-labeled polymers and the model compound 1-naphthylacetic acid, methyl ester (NAAM). All inorganic salts were reagent grade and dried under vacuum before use; the actual salt contents in the working solutions were-determined by titration. Methanol used was Merck (pa).

Naphthalene end-labeled poly(ethylene oxides) (PEON) were obtained by esterification of the polymers with (NAA), following the procedure previously described.[9]

Ultrafiltration experiments[10] were carried out in a 50-cm^3 Amicon stirred ultrafiltration cell Model 52 fitted with a PM-10 membrane. This cell is designed for the pressure and stirring speed that produce optimum performance with DIAFLO PM membranes. KSCN and NaSCN solutions in methanol were prepared in the presence of different concentrations of PEO, and the solutions were ultrafiltered. The conductivities of both the ultrafiltrate (solution collected in the compartment below the membrane) and the filtrand (solution remaining in the compartment where the PEO is retained) were measured with a radiometer conductimeter CDM 83. For this purpose samples of no more than 2 cm^3 were taken from the cell and returned again into it after the measurements. This procedure was repeated eight or nine times in order to attain equilibrium. The concentrations of free salts in the filtrand and filtered solutions were obtained from conductimetric calibration curves.

Fluorescence measurements were carried out on a Perkin-Elmer LS5 luminescence spectrometer at room temperature (20 ± 2 °C). The measurements were carried out at 38 mM concentration (monomolar units) by employing, in most experiments, the polymer of high molecular weight. Excitation and emission wavelengths were 290 and 340 nm, respectively.

Results and Discussion

Fluorescence quenching experiments have been extensively employed to evaluate local concentrations in microheterogeneous systems.[11] Data for the quenching of 1-naphthylacetic acid methyl ester (NAAM) and the PEON labeled at the ends with the same chromophore by several salts in water are presented in Figures 1 and 2. These figures show that the quenching of both the polymer (PEON) and the model compound (NAAM) in water is determined by the anion (the quencher) and is independent of the cation. The bimolecular quenching rate constants k_Q obtained from the Stern–Volmer plots are given in Table I. The quenching of the model compound in methanol (see Figures 1 and 2) shows a similar behavior. The values of k_Q are also given in Table I. In this table are also included k_Q values obtained for PEON in methanol by employing LiSCN and LiI as quencher. For these salts the Stern–Volmer plots are also linear over the entire concentration range employed (see Figures 3 and 4).

The results in Table I conform to a simple pattern. The values of k_Q are larger in water and almost a factor of 2

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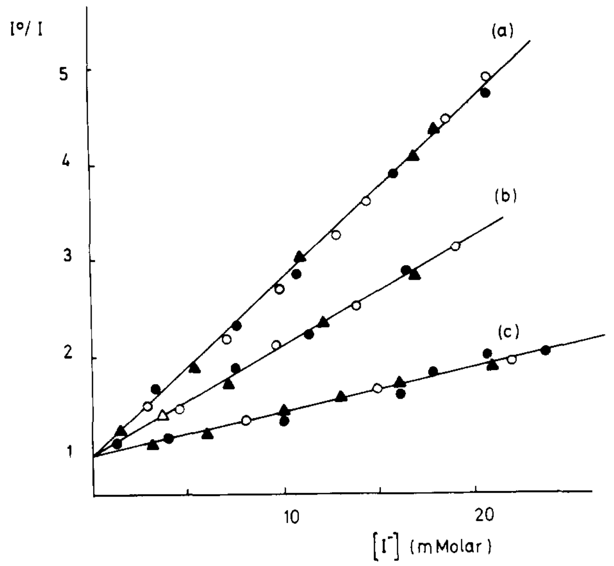

Figure 1. Stern–Volmer plots for the quenching of NAAM and PEON by I⁻: (a) NAAM in water (10 mM); (b) PEON in water (38 mM, MW = 2 × 10^4); (c) NAAM in methanol (10 mM); (▲) KI; (●) NaI; (○) LiI.

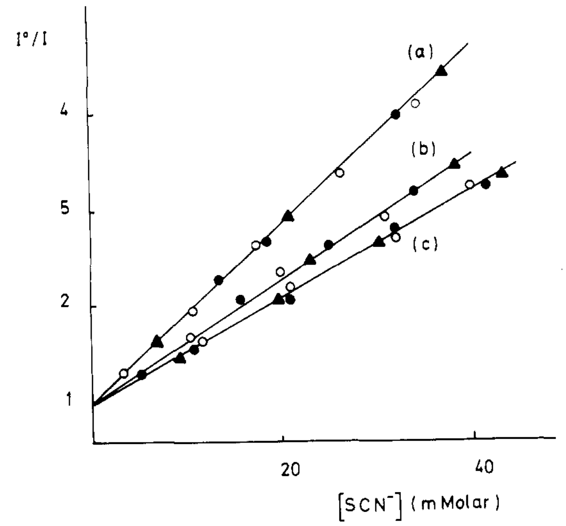

Figure 2. Stern–Volmer plots for the quenching of NAAM and PEON by SCN⁻: (a) NAAM in water (10 mM); (b) PEON in water (38 mM, MW = 2 × 10^4); (c) NAAM in methanol (10 mM) (salt concentrations have been multiplied by 10^{-1}); (▲) KSCN; (●) NaSCN; (○) LiSCN.

Table I
Bimolecular Quenching Rate Constants[a]

quencher	compd	solvent	k_Q, M^{-1} s^{-1}
I⁻	NAAM	methanol	3.6 × 10^9
		water	7.4 × 10^9
	PEON	methanol[b]	2.1 × 10^9
		water	4.7 × 10^9
SCN⁻	NAAM	methanol	4.5 × 10^8
		water	3.7 × 10^9
	PEON	methanol[c]	2.7 × 10^8
		water	1.7 × 10^9

[a] Obtained from the slope of Stern–Volmer plots and lifetimes estimated from quantum yield measurements by taking naphthalene as reference.[14] [b] Data obtained by employing LiI as quencher. [c] Data obtained by employing LiSCN as quencher.

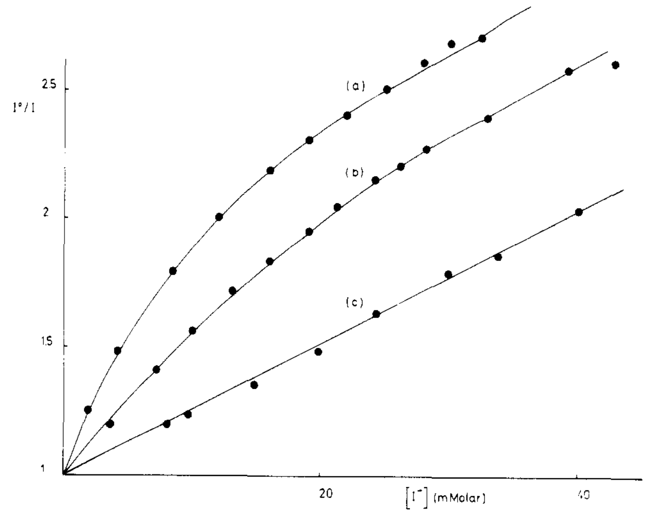

Figure 3. Stern–Volmer plots for the quenching of PEON by I⁻ in methanol solutions: (a) KI; (b) NaI; (c) LiI. PEON = 38 mM (MW = 2 × 10^4).

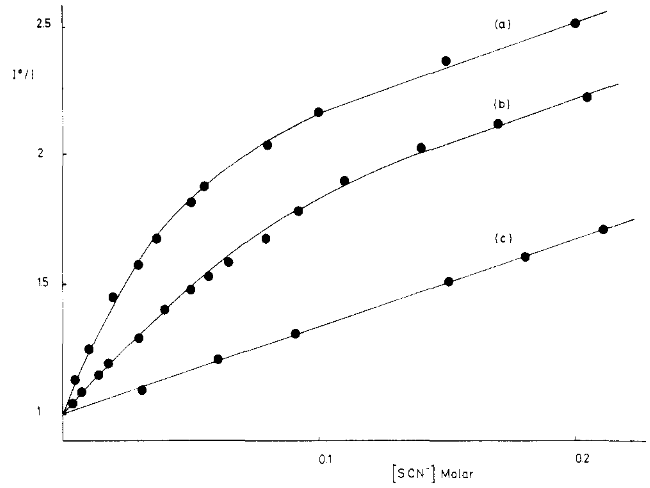

Figure 4. Stern–Volmer plots for the quenching of PEON by SCN⁻ in methanol solutions: (a) KSCN; (b) Na SCN; (c) LiSCN. PEON = 38 mM (MW = 2 × 10^4).

greater for NAAM than for PEON. The first point can be explained in terms of a quenching mechanism dominated by charge-transfer interactions.[12] The slower rate obtained when the naphthyl group is bound to the macromolecule can be attributed to the reduced mobility of the macromolecule and the nearly diffusionally controlled character of the deactivation process. Furthermore, steric effects and/or differences in the ionization potential of the naphthalene group in both compounds could also contribute to the observed difference.[13]

The deactivation of PEON in methanol by Na^+ and K^+ salts produces curved Stern–Volmer plots, and the I^0/I values are considerably larger than those obtained by employing Li^+ salts (see Figures 3 and 4). Similar results were obtained by employing PEON of lower molecular weight (7 × 10^3). These data show that the quenching efficiency of a given salt (with I⁻ or SCN⁻ as the anion) follows the order

$$Li^+ \ll Na^+ < K^+$$

over the entire range of concentrations considered. The higher quenching efficiences of Na^+ and K^+ salts relative to the Li^+ salts are not due to the presence of the cation, since neither NaCl nor KCl modifies the fluorescence of the probe, and hence must reflect an increased local concentration of the anion in the vicinity of the fluorescent chromophore. This increased local anion concentration must be promoted by the adsorption of the cation onto the PEON chain. The fact that the behavior of Li^+ is indicative of a more uniform anion concentration (equal to that in the bulk throughout the solution) and that the observed

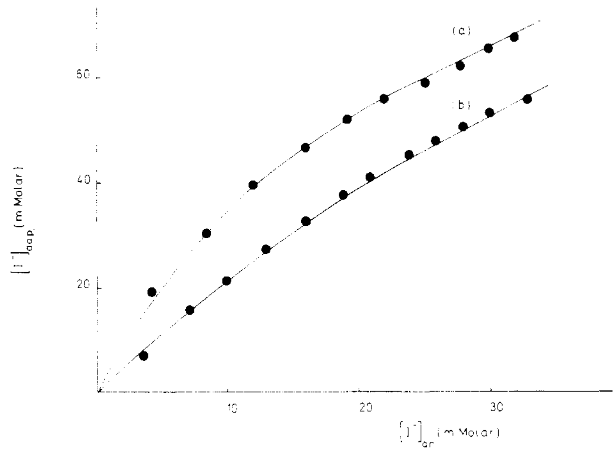

Figure 5. Plot of $[I]_{app}$ vs. $[I^-]_{an}$ (see text) obtained from the quenching of PEON by I^- salts: (a) KI; (b) NaI.

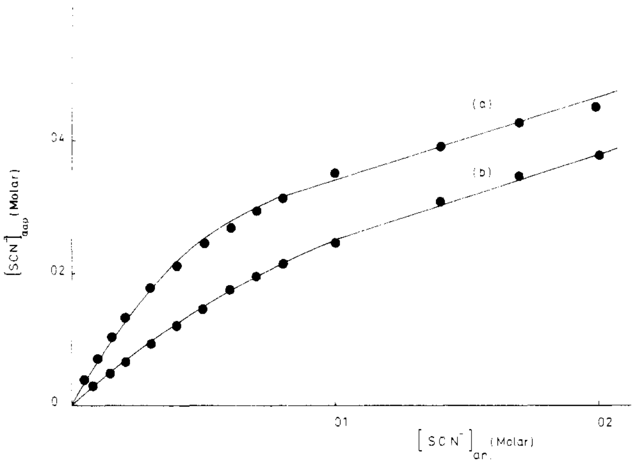

Figure 6. Plot of $[SCN^-]_{app}$ vs. $[SCN]_{an}$ (see text) obtained from the quenching of PEON by SCN^- salts: (a) KSCN; (b) NaSCN.

effect is larger for K^+ than for Na^+ salts is entirely in accord with the relative affinity of Li^+, Na^+, and K^+ to bind to PEO macromolecules.[2] These data conclusively show that as a result of ion-pair formation and/or more large-range electrostatic interactions, the anions are concentrated in the polymer surroundings upon binding to the alkali metal cations. The degree of anion accumulation (local concentration) can be evaluated from the relative quenching efficiences of lithium and sodium (or potassium) salts. In order to carry out an analysis of the factors that determine the local anion concentration, we define an apparent quencher concentration $[Q]_{app}$ given by the concentration of the lithium salt required to reduce the probe fluorescence to the same extent. The values of $[Q]_{app}$ as a function of the salt concentration for a given amount of PEO are shown in Figures 5 and 6. These figures show that $[Q]_{app}$ rises rapidly at low salt concentration and subsequently increases almost proportionally to the analytical quencher concentration. The fast rise takes place at salt concentrations where the major part of the Na^+ and K^+ cations occurs[2] and can be understood in terms of the accompanying increase in the charge density along the macromolecule.

The local concentration of the anion in the vicinity of the macromolecule is determined by the extent of cation binding, the anion concentration, and the solution ionic strength, μ. In order to isolate the effectsof each of these parameters, we have made use of a relative concentration factor f defined by

$$f = [Q]_{app}/[Q]_{an}$$

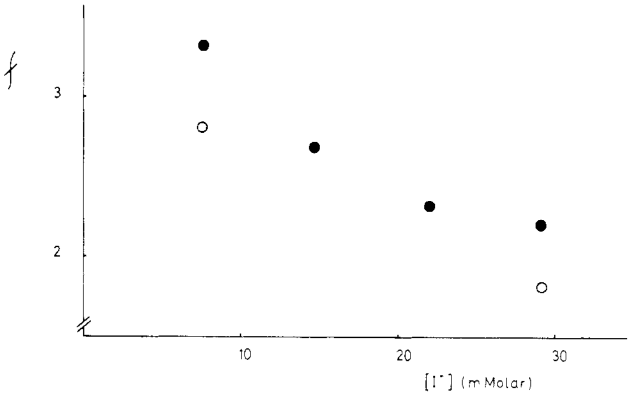

Figure 7. Values of the concentration factor f as a function of the I^- analytical concentration at fixed K^+ concentration and μ: (●) μ = 28.8 mM, K^+ = 28.8 mM; (○) μ = 28.8 mM, K^+ = 7.2 mM.

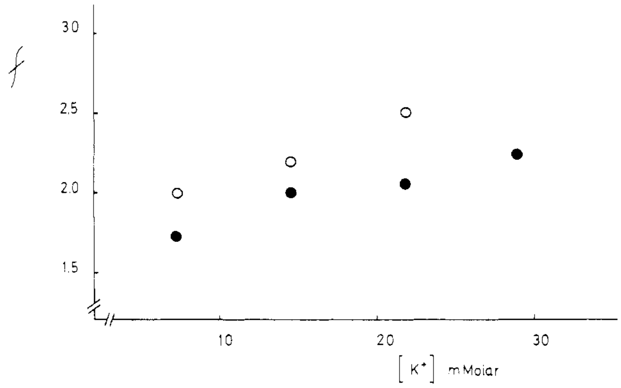

Figure 8. Values of the concentration factor f as a function of K^+ concentration at fixed μ and I^- concentration: (●) μ = 28.8 mM, I^- = 28.8 mM; (○) μ = 21.7 mM, I^- = 21.7 mM.

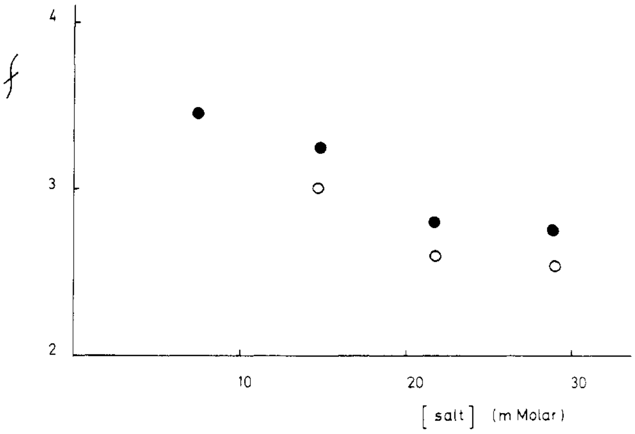

Figure 9. Values of the concentration factor f as a function of μ at fixed K^+ and I^- concentrations: (●) K^+ = 7.2 mM, I^- = 7.2 mM; (○) K^+ = 14.4 mM, I^- = 14.4 mM.

where $[Q]_{an}$ is the analytical concentration of the quencher. The variation of f with the K^+ concentration (at constant I^- and μ), with the I^- concentration (at constant K^+ and μ), and with μ (at constant K^+ and I^-) was measured in mixtures of LiI, LiCl, KCl, and KI. The results obtained are summarized in Figures 7–9.

If a simple model such as that proposed by Ono et al.[2] were operative, it could be expected that (i) the fraction of the occupied sites, θ, is only determined by the K^+ concentration and the solution ionic strength, μ, and (ii) the I^- anions are concentrated only by electrostatic attraction. Under these premises (and if $[Q]_{an} \approx [Q]_{\psi=0}$)

$$f = e^{Z\psi F/RT}$$

where ψ is the electrostatic potential generated on the

Table II
Data from Ultrafiltration Experiments

salt	PEO, M	C_{UF}, M	C_{bound}, M	C_{In}, M	C'_{bound}, M
KSCN	0.052	0.181	0.019	0.007	-0.002
	0.104	0.168	0.033	0.013	-0.002
	0.208	0.16	0.041	0.020	0.003
	0.052	0.090	0.010	0.006	0.002
	0.104	0.087	0.013	0.007	0.002
	0.208	0.074	0.027	0.015	0.005
	0.104	0.041	0.009	0.007	0.005
	0.208	0.034	0.017	0.013	0.010
	0.040	0.0036	0.0014	0.008	0.0000
	0.057	0.0027	0.0023	0.0015	0.0008
	0.104	0.0020	0.0030	0.0017	0.0006
	0.208	0.0019	0.0031	0.0018	0.0008
NaSCN	0.208	0.042	0.008	0.007	
	0.104	0.0044	0.0006	0.0003	
	0.208	0.0038	0.0012	0.0009	

polymer surface by the bound K^+ ions. Hence, at fixed K^+ and μ the value of f should have to be independent of I^-. Figure 7 shows, however, that f decreases when I^- increases. This type of behavior is more compatible with a specific binding of the I^- to the polymer-associated K^+ (i.e., ion-pair formation at the polymer surface). This type of specific interaction would also explain the different behavior of SCN^- and I^-, although in this case the comparison might be biased by the assumption that "free" and "bound" anions have the same quenching efficiency.

In order to further investigate the role of the anions, we have carried out a comparative analysis of the effect of adding different K^+ salts (KCl and KF). The results obtained, presented in Figure 10, show that at a given μ, I^-, and K^+, the value of I^0/I (and hence the value of f) is anion dependent and is greater for Cl^- than for F^-. This difference shows that specific anion effects (in the formation of pairs and/or in the activity coefficients of the ions) must be taken into account. The observed difference may be explained by assuming that Cl^- binds better to the positively charged polymer than does F^-, decreasing the net charge of the chain. Under these conditions the degree of coiling may also increase, further increasing the "local" counterion concentration in the vicinity of the labeled chain end.

The effect of K^+ concentration upon f (at fixed μ and I^-) is shown in Figure 8. The data show that f increases as K^+ increases. This effect is a consequence of the increase in the number of K^+ ions bound to the polymer. A larger value of θ implies a higher potential ψ at the polymer surface and hence a larger value of f.

The effect of μ upon f at constant K^+ and I^- is more difficult to interpret since the solution ionic strength can modify several relevant factors: (i) An increase in μ increases θ as a consequence of the charge screening (this would increase f). (ii) An increase in μ decreases (at fixed θ) the value of ψ; if ion pairs are formed, an increase in μ can also decrease the number of K^+I^- pairs due to Cl^-/I^- competition (this would decrease f). (iii) The charge screening and/or the increase in the number of ion pairs should tend to favor coiling of the macromolecule (this would increase f). The data in Figure 9 show that f decreases markedly as μ increases, pointing to a predominance of effect ii. Nevertheless, changes in μ might also change the ionic activity coefficients, introducing an additional factor whose magnitude is difficult to predict a priori.

Ultrafiltration Experiments. Ultrafiltration techniques have been extensively employed to determine the binding of solutes to microphases in solution,[10] but this method has not been previously applied to the study of ion binding to PEO. We have applied this technique, coupled with conductivity measurements, in order to evaluate whether the anions are able to move freely in the solution or are "bound" to the positively charged macromolecule.

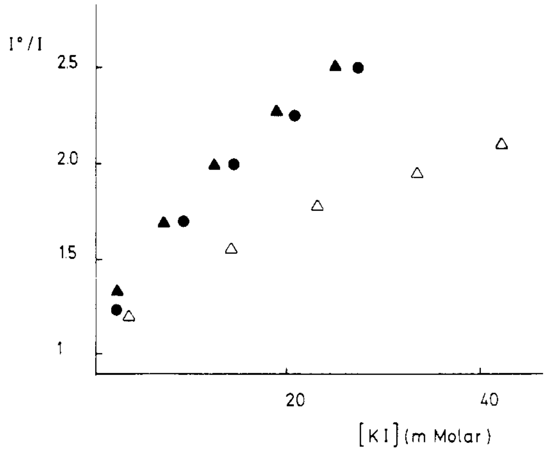

Figure 10. Values of I^0/I as a function of KI concentration: (▲) without added salt; (●) 7.23 mM KCl added; (○) 7.23 mM KF added.

The solution containing the PEO and a given concentration of added salt was equilibrated as described in the experimental section. After equilibration, the conductivity of the ultrafiltrate (λ_{UF}) and that of the PEO solution (λ_{PEO}) were measured. From λ_{UF}, the salt concentration in the ultrafiltrate can be directly evaluated by interpolation from a calibration curve of λ vs. salt concentration. From this value, the initial concentration of added salt, the volume of the initial solution, and the volume of the ultrafiltrate, the analytical concentration in the PEO solution in equilibrium with the ultrafiltrate (C_{PEO}), can be obtained by simple mass balance. The difference between C_{PEO} and C_{UF} can be equated to the concentration of "bound" salt

$$C_{\mathrm{bound}} = C_{\mathrm{PEO}} - C_{\mathrm{UF}}$$

The values of C_{UF} and C_{bound} for several salt and PEO concentrations are given in Table II.

Comparison of the λ_{PEO} conductivity values with the calibration curve obtained in methanol provides an "apparent" concentration of free salt in the PEO solution, $(C_{\mathrm{PEO}})_{\mathrm{app}}$. The difference between $(C_{\mathrm{PEO}})_{\mathrm{app}}$ and the analytical concentration of salt in the solution C_{PEO} can provide the apparent concentration of the inmobilized salt which we define as

$$C_{\mathrm{In}} = C_{\mathrm{PEO}} - (C_{\mathrm{PEO}})_{\mathrm{app}}$$

These values are also included in Table II.

If it is accepted that the cation is the main species bound to the polymer (either alone or as an ion pair with the anion), the values of C_{bound} are a measure of the amount of cations bound to the PEO. As expected, the amount of bound ions increases with the PEO and salt concentration and is considerably larger for KSCN than for NaSCN.[2] Furthermore, the data also show that at a given PEO concentration, the ratio $C_{\text{bound}}/C_{\text{UF}}$ decreases with increasing salt concentration, as expected for a process involving adsorption of a solute to a fixed number of sites with strong (Coulombic) repulsion between the adsorbed species.[2-6]

The values of C_{bound} are consistently larger than those of C_{In}. Equal values of both quantities would be expected if the whole salt were adsorbed as tight ion pairs onto the PEO chains. The data thus imply that one of the species (the cation) is preferentially adsorbed and that at least a fraction of the counterions is capable of contributing to the net conductivity of the solution. An evaluation of this fraction requires several assumptions: (i) The mobilities of the small ions are not affected by the polymer. (ii) The bound ions do not contribute to the solution conductivity.[2] (iii) The average free cation concentration in the PEO solution is equal to the ultrafiltrate concentration (i.e., to the salt concentration at the boundary). (iv) The relative mobilities of both the anion and the cation of the salt are independent of the solute concentration, and the mobilities themselves are influenced only by the ionic strength of the solution.

The first two assumptions are supported by previous data.[2] The third one probably overestimates the average cation concentration, due to depletion of the cations in the diffuse double layer, but can be expected to hold at high salt and low PEO concentrations. Unfortunately, those are the conditions of maxima errors in the evaluation of C_{bound} and C_{In}. The fourth should be valid at low salt concentrations.

If these assumptions hold, the concentration of bound ions C'_{bound} can be expressed as

$$C'_{\text{bound}} = \frac{C_{\text{In}} - f_+ C_{\text{bound}}}{1 - f_+}$$

where f_+, is the transference number of the cation in methanol. Taking f_+ to be equal to 0.44 for KSCN,[4] we obtain the C'_{bound} values given in Table II. These values provide an average value of $C'_{\text{bound}}/C_{\text{bound}}$ of 0.2 ± 0.2 without a clear dependence on either the salt or polymer concentration. Although these values involve large uncertainties due to the scatter of the data and to the assumptions involved in their evaluation, we can conclude that most of the anions are free, with only a minor portion inmobilized by (or trapped within the electrostatic field of) the positively charged PEO macromolecules.

Acknowledgment. Thanks are given to the Depto. Investigaciones y Bibliotecas de la Universidad de Chile, to the Dirección de Investigaciones de la Universidad de Santiago, and to the Fondo Nacional de Ciencias (Gran 011-02/84) for supporting this work.

Registry No. PEO (SRU), 25322-68-3; KSCN, 333-20-0; NaSCN, 540-72-7; LiSCN, 556-65-0; LiI, 10377-51-2; NAAM, 2876-78-0; KI, 7681-11-0; NaI, 7681-82-5.

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