Binding of Electrolytes to Poly(ethylene oxide) in Aqueous Solutions

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Received October 3, 1989; Revised Manuscript Received January 25, 1990

ABSTRACT: Ion selective electrode and ultrafiltration measurements have been employed to investigate the extent of electrolyte binding to poly(ethylene oxide) in aqueous solution. Although lithium chloride does not interact measurably with the polymer, significant binding is verified for sodium, potassium, rubidium, and cesium chlorides and for a series of other potassium salts. For the chlorides, operational binding constants, whose magnitudes depend on electrolyte and polymer concentrations, follow the sequence lithium $\ll$ sodium $<$ rubidium $\approx$ potassium $\approx$ cesium. These results are consistent with primary association of the alkali-metal cation with the polymer chain, creating a net positive potential that attracts the anions electrostatically to the vicinity of the polymer molecule.

Introduction

The binding of electrolytes to poly(ethylene oxide) (PEO) is a matter of current interest, partly due to the similarity of this process to the binding of cations to crown ethers.[1] The binding of electrolytes to PEO in nonaqueous solvents such as methanol has been investigated by a variety of techniques, including viscosimetry,[2-5] conductivity,[6-10] calorimetry,[11] and fluorescence.[12] Ono et al.[6-10] have established that the association is driven by a primary cation/PEO interaction. Studies employing different potassium salts indicate that the anion is also concentrated in the vicinity of the macromolecule, but in a manner that cannot be ascribed solely to electrostatic interactions,[12] suggesting that association and/or polarization of the anion also play a significant role.

Association of electrolytes to PEO in aqueous solution has been studied considerably less and is not well established. Bailey and Callard[3] reported that no interaction, other than a very small salting-out effect, occurs when PEO is added to potassium iodide solutions. Similarly, the decrease in conductivity of potassium chloride solutions upon addition of PEO has been explained in terms of models that disregard specific interaction between the ions and the polymer.[13] The interaction of inorganic salts with PEO derivatives in aqueous solution has also been investigated by proton magnetic resonance techniques.[14] Although the complexation capacity of open-chain PEO derivatives was found to be much smaller than that of crown ethers, the poly(ethylene glycol) derivatives employed were species of very low molecular weight. On the other hand, it has been established that amphipathic ions such as ionic surfactants can be strongly adsorbed on PEO, leading to the formation of small surfactant-rich aggregates on the polymer.[15] Also, differences observed for the capacity of various salts to form two-phase systems in concentrated poly(ethylene oxide) solutions have been explained in terms of specific interactions of the ions with the polymer.[16]

The aim of the present work is to evaluate the capacity of PEO to adsorb ions from solutions containing an alkali-metal cation and a series of different anions, ranging from hydrophilic (e.g., fluoride) to those with hydrophobic alkyl chains (e.g., pentanoate). In order to evaluate the capacity of the added PEO to decrease the concentration of the free ions, measurements were performed directly on the PEO-containing solutions with ion-selective electrodes. The concentration of the free salt was also evaluated in PEO-free filtrates obtained by ultrafiltration techniques.[17]

Experimental Section

Commercial PEO (nominal molecular weight 2×10^4) from Merck was employed. All inorganic salts (reagent grade) were dried under vacuum prior to their use. Potassium pentanoate was prepared as previously described.[18]

Ultrafiltration experiments[12,17] were carried out in a 50-cm^3 Amicon stirred ultrafiltration cell (Model 52) fitted with a PM-10 membrane. Solutions of each salt prepared in the presence of different PEO concentrations were ultrafiltrated until equilibration had been attained. The concentrations of the salts in the ultrafiltrate (UF) were measured by flame spectroscopy (an Oppendorf flame spectrometer was employed) and/or with ion-selective electrodes calibrated against solutions of known concentration. Free-ion concentrations in the PEO-containing solutions were evaluated by employing commercial potassium (Radiometer) and chloride (Ruzicka Selectrod) ion selective

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0024-9297/90/2223-3878$02.50/0

Table I
Total Salt and Chloride and Potassium Ion Concentrations in the PEO-Containing Solutions and the Salt Concentration in the Ultrafiltrate

[PEO],[a] mM	$[\text{salt}]_{\text{anal.}}$, mM	$[\text{Cl}^-]$, mM	$[\text{K}^+]$, mM	$[\text{salt}]_{\text{UF}}$, mM
5	2.4	1.8	1.65	1.73
50				1.43
100		1.1	0.8	1.0
200		0.6	0.4	0.68
5	7.5	4.8	4.3	4.5
50				2.6
100		2.3	1.5	1.5
200		1.2	0.9	1.04

[a] Concentrations expressed in monomer units.

Table II
Effect of Added Salts (7.5 mM) on the Viscosity of PEO Solutions at 25 °C

	η/η_0[a]	
salt	[PEO] = 0.003 M[b]	[PEO] = 0.05 M[b]
LiCl	0.97	0.88
KCl	1.06	1.01
KSCN	1.08	1.09
potassium acetate	1.06	1.04
potassium pentanoate	1.16	1.18

[a] Values relative to that measured in the absence of added salt. Estimated error: ±3%. The addition of salt barely modifies the viscosity in the absence of PEO. [b] Concentrations expressed in monomer units.

electrodes. The viscosities of the solutions were measured with an Ubbelohde type capillary viscometer thermostated at 25 °C.

Results and Discussion

Addition of PEO (3.2 mM to 0.1 M) to solutions of LiCl (2.4 or 7.5 mM) barely modifies the free chloride concentration, as measured directly by a chloride ion selective electrode in the solution. Similarly, the LiCl concentration measured in the ultrafiltrate was equal to the analytical salt concentration in the original solution. These results indicate that there is no significant interaction between the macromolecule and either the chloride or lithium ions. Furthermore, the fact that similar results are obtained in the PEO-free UF and with the ion-selective electrode in the PEO-containing solution indicates that the polymer does not interfere with the chloride ion selective electrode measurements.

When PEO is added to KCl solutions, however, the results are quite different from those obtained for LiCl. Both the potassium and chloride ion selective electrodes indicate a significant decrease in the ionic concentrations. Similarly, the salt concentrations measured in the UF were significantly smaller than the total analytical concentrations present in the whole solution. Typical results are shown in Table I. Other potassium salts (SCN^-, acetate, and pentanoate) exhibit behavior qualitatively similar to that found for KCl.

A strong interaction between the potassium salts and the PEO macromolecule is also indicated by the changes in the viscosity of the PEO solutions elicited by salt addition. For all the potassium salts considered, a viscosity increase is observed when the salt is added to PEO solutions. This behavior contrasts with the decrease observed when LiCl is added (see Table II), which can be explained[3] in terms of the coiling of the polymer chains provoked by a salt-dependent decrease in the solvent thermodynamic quality. On the other hand, the increase in the PEO solution viscosity produced by the potassium salts indicates net macromolecular expansion as a consequence of potassium adsorption.

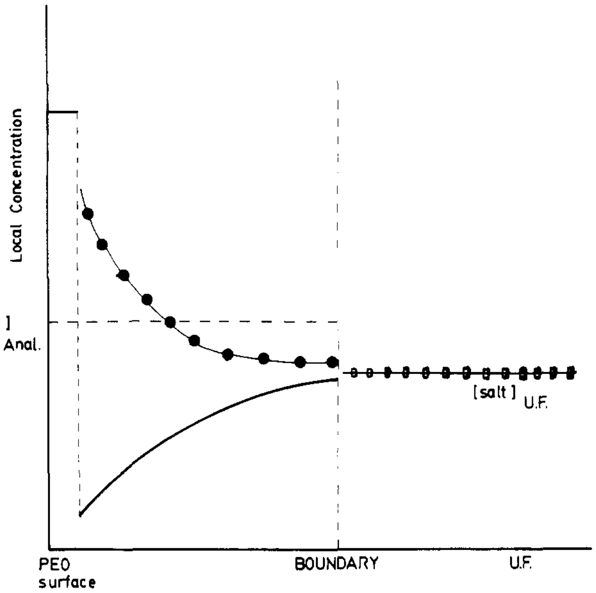

Figure 1. Schematic representation of concentration profiles from the PEO surface out to the boundary or midpoint between macromolecules and concentration in the ultrafiltrate: (—) cation; (●) anion; (□) salt.

The results in Tables I and II thus indicate that, while LiCl does not interact significantly with PEO, a strong interaction does take place with potassium salts. The data of Table I also show that the free concentrations of both potassium and chloride decrease in the presence of PEO, the effect being larger for the cation than for the anion. Furthermore, the product $[\text{Cl}^-][\text{K}^+]$ is found to be nearly equal to $[\text{salt}]^2$ in the UF. These results are consistent with primary association of the potassium ions with the PEO chains (as indicated by the different behavior of lithium and potassium salts), creating a net positive potential that attracts the anions electrostatically to the vicinity of the PEO molecule.

If the cation is primarily adsorbed, the concentration profiles from the PEO surface out to the boundary or midpoint between macromolecules can be qualitatively represented as in Figure 1. This figure shows that $[\text{anion}]_{\text{ads}} < [\text{anion}]_{\text{anal.}} - [\text{anion}]_{\text{bdy}}$ and $[\text{cation}]_{\text{ads}} > [\text{cation}]_{\text{anal.}} - [\text{cation}]_{\text{bdy}}$ (where bdy stands for boundary), being the concentration at the boundary as measured by the ion-selective electrode. Furthermore, this figure also shows that $[\text{cation}]_{\text{bdy}} < [\text{salt}]_{\text{UF}}$ and $[\text{anion}]_{\text{bdy}} > [\text{salt}]_{\text{UF}}$.

The considerations given above emphasize the difficulties in obtaining "binding" constants from ion selective electrode measurements and/or from the concentrations measured in the UF. Nonetheless, operational binding constants can be defined by the relationship

$$K_{\text{binding}} = \frac{[\text{K}^+]_{\text{anal.}} - [\text{K}^+]_{\text{bdy}}}{[\text{K}^+]_{\text{bdy}}[\text{PEO}]} \tag{1}$$

or

$$K_{\text{binding}} = \frac{[\text{K}^+]_{\text{anal.}} - [\text{salt}]_{\text{UF}}}{[\text{salt}]_{\text{UF}}[\text{PEO}]} \tag{2}$$

Values of K_{binding} obtained from eq 1 for several potassium salts are collected in Table III. Values obtained from UF data for a variety of salts are given in Table IV. The K_{binding} values for potassium salts increase as the salt concentration increases. Nevertheless, this is not a general effect since the values for sodium salts show the opposite

Table III
Values of K_{binding} for Different Potassium Salts

		K_{binding}[a]				
[PEO],[b] mM	[salt], mM	KF[c]	KCl[d]	KSCN	potassium acetate	potassium pentanoate
1	2.4		263 (263)	412	600	550
	7.5		470 (470)	530	630	1700
5	2.4	80	90 (80)	120	173	182
	7.5	130	150 (133)	175	241	460
10	2.4				78	85
	7.5				121	210
50	2.4		(14)	33	31	38
	7.5		(37)	50	59	84
100	2.4	14	20 (14)	30	24	28
	7.5	40	40 (40)	60	40	48
150	2.4		12	28	20	20
	7.5		38	65	55	50
200	2.4		13 (13)	26	21	23
	7.5		40 (31)	70	58	58

[a] Obtained from eq 1. [b] Concentrations expressed in monomer units. [c] Obtained from eq 2. [d] Values in parentheses were obtained from eq 2.

Table IV
Values of K_{binding} for Chlorides of Alkali-Metal Ions

		K_{binding}[a]			
[PEO],[b] mM	[salt], mM	NaCl	KCl	RbCl	CsCl
1	2.4	90	260		200
	7.5	64	470		270
5	2.4	29	80	82	140
	7.5	18	140	113	165
50	2.4	2.9	14	17	
	7.5	2	37	34	
100	2.4	2	14	12	20
	7.5	1.2	40	25	26
200	2.4	1.15	12	14	19
	7.5	0.60	31	24	18

[a] From eq 2. [b] Concentrations expressed in monomer units.

Table V
Values of K_{binding} for Different Salts at Constant Salt and PEO Concentrations[a]

	salt concn, mM	
salt	2.4	7.5
[PEO] = 5 mM[b]		
KF	80	130
LiCl		
NaCl	29	18
KCl	80	137
RbCl	82	113
CsCl	140	165
NaSCN	53	29
KSCN	120	175
potassium acetate	160	270
potassium pentanoate	200	460
[PEO] = 100 mM[b]		
KF	14	40
LiCl	<0.4	<0.9
NaCl	2	1.2
KCl	14	40
RbCl	12	25
CsCl	20	21
NaSCN	2.8	1.5
KSCN	30	61
potassium acetate	24	40
potassium pentanoate	28	48

[a] From eq 2. [b] Concentrations expressed in monomer units.

trend, and those for CsCl are almost independent of the salt concentration. On the other hand, at fixed total salt concentration, a decrease in K_{binding} is observed in all cases as the PEO concentration is increased. Both of these trends, i.e., the salt concentration dependence observed with potassium salts and the decrease in binding constant with increasing polymer concentration, are opposite to the behavior expected for a simple "site-specific" interaction with a constant number of equivalent binding sites per macromolecule.

Although the K_{binding} values obtained by applying eqs 1 and 2 are not true thermodynamic binding constants, the observed variations in K_{binding}, particularly when the PEO concentration is changed, are much too large to be ascribed to simple deviations from ideality. Presumably, then, these reflect changes in the binding forces and/or conformation of the macromolecules, with concomitant changes in the number and/or affinity of the "binding sites". In this context, increasing the salt concentration (at fixed PEO) should increase the number of adsorbed cations per ethylene oxide unit. The resultant increase in charge density causes, in turn, a polymer coil expansion, which can be partly counterbalanced by the screening effect of the increased ionic strength. Conversely, increasing the PEO concentration at fixed salt must decrease the mean number of adsorbed cations per macromolecule, the average conformation of the macromolecule being determined by both a polymer concentration effect and a charge density effect. Changes in polymer shape resulting from changes in the charge density will modify the surface potential and the availability of the binding sites, whose affinity must be dependent on polymer shape. The interplay of all of these factors will thus determine the final value of K_{binding}. Given the variety and complexity of the interactions involved, attempts to make a quantitative interpretation of the observed trends are premature. Nevertheless, qualitative trends can be verified by comparison of K_{binding} values obtained at the same salt and PEO concentrations in Table V. These data show that the magnitude of the binding constant is determined mainly by the cation, following the order $\text{Li}^+ \ll \text{Na}^+ < \text{Rb}^+ \approx \text{K}^+ \approx \text{Cs}^+$. The low binding capacities of lithium and sodium salts are particularly noteworthy. This overall order obtained is quite similar to that observed in methanol[6] and to that reported for complexation with crown ethers in water.[14] Also, it is worth mentioning that the ordering $\text{Li}^+ \ll \text{Na}^+ < \text{K}^+$ has also been reported for the capacity of the corresponding sulfates to form aqueous phases[16] and for the chlorides to lower the cloud point of PEO solutions.[3] These results would suggest that both two-phase formation and lowering of the cloud point in PEO solutions are, for a given anion, determined by the capacity of the cation to interact with the PEO chain.

The dependence of K_{binding} on the nature of the anion is considerably smaller than that observed for the cations, in spite of the fact that they range from very hard small anions (such as fluoride) to anions bearing sizable hydrophobic alkyl chains (such as pentanoate). This small dependence implies that the binding is mostly determined by the cation. Nevertheless, some contribution of the anion is evidenced by the differences observed. In particular, under all the conditions employed, SCN^- salts "bind" stronger than chlorides. This result is similar to that obtained from ion-exchange experiments in cationic micellar systems[19] and cationic polysoap monolayers[20] and can be explained in terms of the lower polarizability of the chloride ion.

Comparison of the K_{binding} values for potassium acetate and potassium pentanoate permits an estimation of the importance of hydrophobic interactions in the binding. The data given (Table V) indicate that hydrophobic interactions make only a minor contribution to the binding of pentanoate ion. This suggests that the anions remain mainly outside the polymer coil, such that their interaction with the polymer results in little or no shielding from contact with the solvent. In this regard, it is interesting to note that hydrophobic molecules adsorbed onto PEO remain exposed to a very polar environment.[21]

Acknowledgment. Financial support of this work by FONDECYT (Grant 520/87) and DICYT (Universidad de Santiago de Chile) is acknowledged.

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Registry No. PEO, 25322-68-3; SCN^-, 333-20-0; LiCl, 7447-41-8; KCl, 7447-40-7; KF, 7789-23-3; NaCl, 7647-14-5; RbCl, 7791-11-9; CsCl, 7647-17-8; NaSCN, 540-72-7; acetate, 127-08-2; pentanoate, 19455-21-1.

Liquid Crystalline Phosphazenes Bearing Biphenyl Mesogenic Groups

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Received December 6, 1989; Revised Manuscript Received February 20, 1990

ABSTRACT: New thermotropic liquid crystalline phosphazene cyclic trimers and high polymers have been prepared by the incorporation of biphenyl derivative units connected to the skeleton by oligomeric ethyleneoxy spacer units. The cyclic trimer $[NP\{O(CH_2CH_2O)_2C_6H_4C_6H_4CN\}_2]_3$ showed monotropic nematic schlieren texture between 102 and 59 °C. The phosphazene cyclic trimers and high polymers $[NP\{O(CH_2CH_2O)_3C_6H_4C_6H_4R\}_2]_{3\text{ and }n}$, where R = OMe, OEt, OPr-*n*, OPr-*i*, and OBu-*n*, have been synthesized. None of these cyclic trimers were liquid crystalline, but all the polymers showed enantiotropic liquid crystallinity.

Introduction

The widespread current interest in liquid crystalline polymers is connected with the possibility that polymeric systems can be prepared with unusual properties, combining the unique characteristics of a small-molecule liquid crystalline system with those of high molecular weight polymers.[1–3] Most of the known side-chain liquid crystalline macromolecular systems are derivatives of carbon-backbone organic polymers or polysiloxanes.[4,5]

Polyphosphazenes with the general formula $[NPR_2]_n$ have a highly flexible phosphorus–nitrogen inorganic backbone, and their properties can be varied by the incorporation of the suitable substituent R.[6–16] Recently,

0024-9297/90/2223-3881$02.50/0