

Neutron-Scattering Determination of the Li⁺ Environment in an Aqueous Poly(Ethylene Oxide) Solution

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Neutron diffraction with isotopic substitution was used to assess the relative solvation interactions near lithium ions in a D₂O/deuterated poly(ethylene oxide) (PEO) mixed solvent near 25 °C. Results for local structure near Li⁺ indicate a hydration structure very similar to that observed previously for Li⁺ in D₂O solution with no added polymer. For the mixed solvent ratio used, PEO does not compete effectively with D₂O for solvation sites near Li⁺. These results contribute to our understanding of reactivity and transport of ionic species in mixed aqueous polymer systems.

Introduction

Poly(ethylene oxide) (PEO) melts and solutions containing lithium salts have long been investigated in efforts to develop more useful electrolytes for batteries and other applications. Both the polymer and the salts are individually highly soluble in water at moderate temperatures but become less so in a ternary mixture. Experimental structural investigations^{1,2} and molecular dynamics simulations^{1,3} have established that in the polymer melt Li⁺ complexes with an average of 3–5 ether oxygen atoms. In the case of PEO in aqueous solutions, thermodynamic considerations⁴ and molecular dynamics simulations⁵ provide a picture of water molecules hydrogen bonding with the ether oxygens. In the ternary solutions, the complexation of Li⁺ observed in the Li⁺/PEO aqueous melts will reflect the competitive solvation of the ion by water and polymer. The ionic conductivity should be determined by the distribution of Li⁺ between the normal hydration spheres and complexation with the polymer chains. More broadly, fundamental aspects of ion transport and reactivity in mixed systems will depend on the solvation environment of the ions, which will in turn be determined by the relative strengths of the ion–water, ion–polymer, and water–polymer interactions. In this paper, we present a direct experimental determination of the Li⁺ environment in a ternary solution of D₂O/DPEO/LiI as an initial investigation of the structural evidence for the relative strengths of solvation interactions in aqueous polymer systems.

Method of Analysis

The neutron differential cross section (expressed in barns per steradian per atom) for a multicomponent amorphous sample may be written as

$$d\sigma/d\Omega = \sum_{\alpha} c_{\alpha} \frac{\sigma_{\alpha}^{\text{tot}}}{4\pi} (1 + P_{\alpha}(Q, \theta)) + \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} (S_{\alpha\beta}(Q) - 1) \quad (1)$$

where the first term is the self-scattering with a Placzek

correction, $\sigma_{\alpha}^{\text{tot}}$ is the sum of the coherent and incoherent cross sections, and c_{α} and b_{α} are the atom fraction and coherent-scattering length, respectively, of atoms of type α . The above is often referred to as the Faber–Ziman form. Q is the magnitude of the momentum transfer and is related to the scattering angle, θ , and neutron wavelength, λ , by $Q = (4/\pi) \cdot \sin(\theta/2)$. $S_{\alpha\beta}(Q)$ is a partial structure factor. The latter is related to the partial pair correlation function, $g_{\alpha\beta}(r)$ by

$$S_{\alpha\beta}(Q) - 1 = 4\pi\rho \int r^2 (g_{\alpha\beta}(r) - 1) \frac{\sin Qr}{Qr} dr \quad (2)$$

$$g_{\alpha\beta}(r) - 1 = \frac{1}{2\pi^2\rho} \int Q^2 (S_{\alpha\beta}(Q) - 1) \frac{\sin Qr}{Qr} dQ \quad (3)$$

with ρ being the total number density. The second term in eq 1 is referred to as the interference term and contains the structural information. Even for a simple binary system, it is generally difficult to extract detailed structural information from a single measurement. However, if two samples are prepared which differ only in the scattering length of one component, after subtraction of the self-scattering terms, the difference of the differential cross sections contains information on the pair correlations of all the other atoms with respect to the chosen species.

For example, in the present case of two D₂O/DPEO/LiI solutions differing only in the proportion of ⁶Li and ⁷Li, we obtain

$$\Delta I(Q) = A(S_{\text{LiO}}(Q) - 1) + B(S_{\text{LiD}}(Q) - 1) + C(S_{\text{LiC}}(Q) - 1) + D(S_{\text{LiI}}(Q) - 1) + E(S_{\text{LiLi}}(Q) - 1) \quad (4)$$

with $A = 2c_{\text{Li}}c_{\text{O}}b_{\text{O}}\delta b_{\text{Li}}$, $B = 2c_{\text{Li}}c_{\text{D}}b_{\text{D}}\delta b_{\text{Li}}$, $C = 2c_{\text{Li}}c_{\text{C}}b_{\text{C}}\delta b_{\text{Li}}$, $D = 2c_{\text{Li}}c_{\text{I}}b_{\text{I}}\delta b_{\text{Li}}$, $E = c_{\text{Li}}^2((b_{\text{Li}}^{\text{nat}})^2 - (b_{\text{Li}}^{\text{nat}})^2)$. The scattering lengths for Li with the natural abundance of isotopes or enriched in ⁶Li are expressed by $b_{\text{Li}}^{\text{nat}}$ and b_{Li}^{e} , respectively, and $\delta b_{\text{Li}} = b_{\text{Li}}^{\text{e}} - b_{\text{Li}}^{\text{nat}}$.

From eq 3, a total, weighted pair correlation function for all the atoms about a Li atom may be written

$$G_{\text{Li}}(r) - 1 = \frac{1}{2\pi^2\rho} \int Q^2 \left(\frac{\Delta I(Q)}{\Sigma} \right) \frac{\sin Qr}{Qr} dQ \quad (5)$$

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or

$$G_{\text{Li}}(r) = \frac{A}{\Sigma} g_{\text{LiO}}(r) + \frac{B}{\Sigma} g_{\text{LiD}}(r) + \frac{C}{\Sigma} g_{\text{LiC}}(r) + \frac{D}{\Sigma} g_{\text{LiI}}(r) + \frac{E}{\Sigma} g_{\text{LiLi}}(r) \quad (6)$$

with $\Sigma = A + B + C + D + E$. The total number of atoms within a sphere of radius R about a Li atom is given by

$$N(R) = 4\pi\rho \int_0^R r^2 G_{\text{Li}}(r) dr \quad (7)$$

Experimental Information

The neutron-scattering data were obtained from the GLAD instrument at the Intense Pulsed Neutron Source at the Argonne National Laboratory. To reduce absorption corrections, annular cells constructed of coaxial vanadium cylinders with wall thicknesses of 0.15 mm were used to contain the samples. The cells had an outer diameter of 9.2 mm and provided a sample thickness of about 1.4 mm and were used for both samples. A 4-cm beam height was chosen. The experimental series consisted of scattering measurements from an empty cell to establish background, a standard vanadium rod to normalize the results, and measurements on the natural-abundance and enriched ⁶Li samples. Scattering data were obtained from the normal and enriched samples for approximately 36 and 50 h, respectively, to establish appropriate statistics for the difference experiment. The standard suite of GLAD correction programs was used, and the self-scattering corrections were obtained from the PLATON program.⁶

Measurements were done at instrument ambient temperature ($\sim 25^\circ\text{C}$). The ⁶LiI (95.96% ⁶Li) was obtained from Isotec (Miami, OH), and the ^{nat}LiI (7.5% ⁶Li) came from Aldrich. The deuterated PEO had a deuterium content greater than 99% and was prepared by Polymer Source, Inc. (Dorval, Quebec, Canada). The average molecular weight M_n was 25 800 with a polydispersity of 1.04. D₂O used in these experiments (Aldrich) had a deuterium content greater than 99.9%. Solutions were handled in syringes prior to cell filling to minimize contamination of D₂O with H from atmospheric exchange. The atom fractions of the components in the solutions prepared for this work were Li, 0.0362; I, 0.0362; D, 0.597; O, 0.266; and C, 0.0648. The molar ratio of D₂O to DPEO was 7.21/1 and for D₂O/LiI, 6.45/1. A solution density at laboratory ambient temperature ($\sim 22^\circ\text{C}$) of 1.645 g/cm³ was measured in our laboratory.

Results and Discussion

Figure 1 shows the difference function $\Delta I(Q)/\Sigma$, and Figure 2 gives the resulting $G_{\text{Li}}(r)$. The first two peaks in $G_{\text{Li}}(r)$ at 1.9–2.0 Å and 2.5–2.6 Å are very similar to those obtained by Yamaguchi et al.⁷ and Howell and Neilson⁸ for LiCl in D₂O. In those studies, the peaks were identified with the Li–O and Li–D correlations of the nearest-neighbor water molecules. For Li/D₂O ratios in the range of 3.6–5.4 coordination numbers of 3.2 to 4 were reported^{7,8} with mean separations of 1.96–2.12 Å and 2.52–2.61 Å for Li–O and Li–D, respectively. Assuming these identifications also apply to the present case and that there are two D atoms to one O atom, numerical integration of $G_{\text{Li}}(r)$ between $r = 1.45$ and 2.90 Å results in a coordination number of 3.8 water molecules per Li.

An alternative approach is to assume an analytical form and fit it to the data. Here a peak in $g_{\alpha\beta}(r)$ is approximated by the form $(n_{\alpha\beta}/r)\exp(-(r-R_{\alpha\beta})^2/2l_{\alpha\beta}^2)$ where $n_{\alpha\beta}$ is the number of

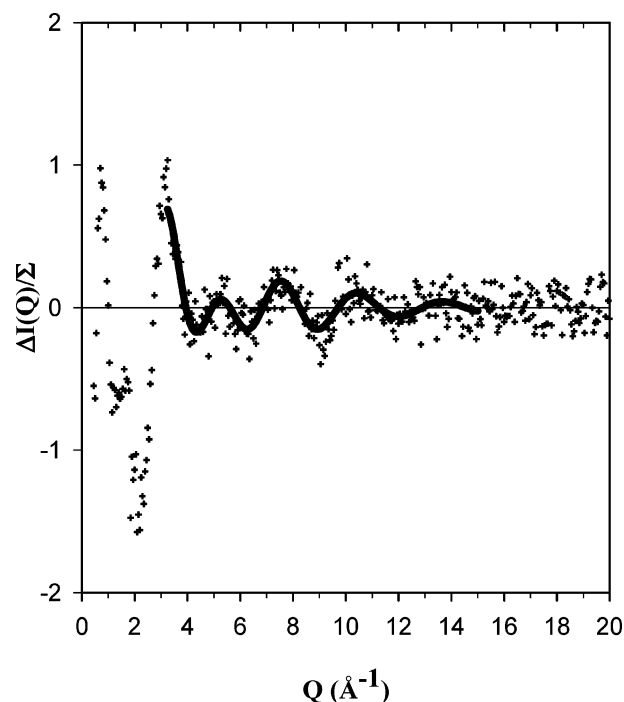


Figure 1. Q space difference function. +, from experiment. The solid line is the result of a fit of the data in the range 3.25–15 Å^{−1} as described in text.

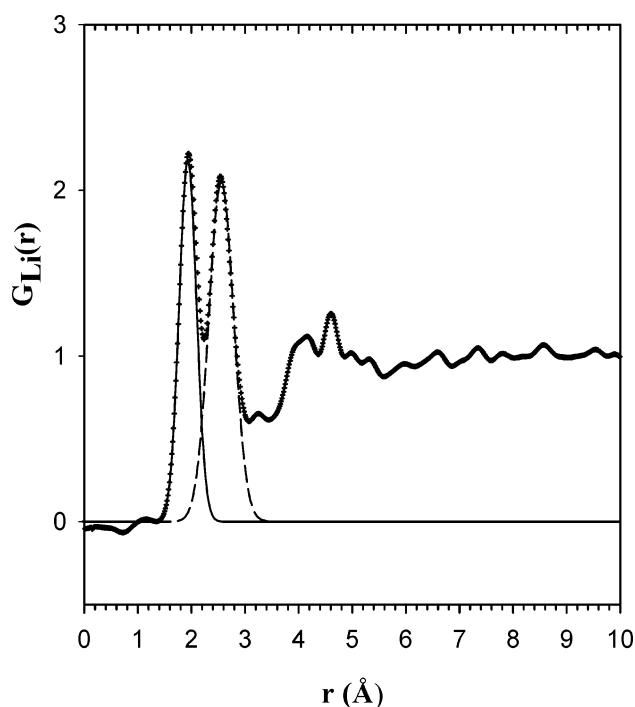


Figure 2. Total pair correlation function. +, from experiment. The solid line is a fitted Li–O peak, and the dashed line is for fitted Li–D.

nearest neighbor β atoms around an α . When two such terms were fitted to the data, values of 3.95 for the number of nearest-neighbor oxygen atoms and 8.14 for deuterium atoms resulted. The corresponding Li–O and Li–D distances were 1.95 and 2.58 Å. The peaks are shown in Figure 2 and the results listed in Table 1. For the case of Li⁺/DPEO melts,^{1,2} Li–O peaks that corresponded to interactions with ether oxygens were identified at 2.1 Å. Accordingly, a third peak was introduced at this distance but this did not improve the fit and led to a negligible contribution. Another means of analysis is to fit the

TABLE 1: Parameters Obtained from Fits to Data

	n_O	n_D	R_{LiO} (D)	R_{LiD} (D)	l_{LiO} (D)	l_{LiD} (D)
$G_{Li}(r)$	3.95	8.14	1.95	2.58	0.161	0.231
$\Delta I(Q)/\Sigma$	3.34	7.96	1.94	2.57	0.104	0.234

function, $\Delta I(Q)/\Sigma$, directly, under the assumption that this function is determined only by the nearest-neighbor contributions at larger Q values. An advantage of this approach is that it avoids the broadening effect of the Fourier transformation used in obtaining $G_{Li}(r)$. This procedure had previously been found to give useful results for simple aqueous solutions.⁹ For the present case, $\Delta I(Q)/\Sigma$ at higher Q was taken to be the first two terms of eq 4 with

$$S_{LiO}(Q) - 1 = (n_O/c_O) \frac{\sin QR_{LiO}}{QR_{LiO}} \exp(-l_{LiO}^2 Q^2/2) \quad (8)$$

and

$$S_{LiD}(Q) - 1 = (n_D/c_D) \frac{\sin QR_{LiD}}{QR_{LiD}} \exp(-l_{LiD}^2 Q^2/2) \quad (9)$$

A fit over the Q range 3.25–15 Å⁻¹ yielded nearest-neighbor numbers of oxygen and deuterium atoms of 3.34 and 7.96, respectively. Nearest-neighbor distances similar to the preceding were obtained and are listed in Table 1. As before, attempts to fit a third peak with a Li–O spacing of 2.1 Å did not lead to meaningful results. Consequently, the results show no indication of modification of the lithium hydration sphere due to the presence of PEO at this concentration. van der Maarel et al.¹⁰ arrived at a similar conclusion in a previous study of a Li–poly(acrylic acid) solution which had considerably lower Li and monomer concentrations than was the case here. In an investigation of chloride ion hydration also in a relatively more dilute aqueous solution of NaCl and PEO, Barnes et al.¹¹ found no evidence of change resulting from the PEO. In another study, Bieze et al.¹² concluded that on average six water molecules can be packed on the surface of a PEO monomer. With this in mind, for our solution with a concentration ratio of 7.2 water molecules per monomer, there is insufficient free water available to provide the 3.3–4 molecules involved in Li⁺ hydration and it is apparent that some sharing of water molecules between the monomers and Li⁺ must occur.

In Figure 1 for the difference function, a relatively sharp peak at $Q < 1$ Å⁻¹ is evident. A similar feature was observed in the Li⁺/PEO melt studies^{1,2} but is not present in the LiCl aqueous

solution data⁸ at higher concentration. At present, the origin of this feature is not understood.

Conclusions

From the perspective of an aqueous solution, the result is that the presence of PEO at this concentration has no effect on the hydration of Li⁺. However, from the perspective of Li⁺/PEO melts, the addition of water has a significant effect on the Li⁺–ether oxygen interaction. For the mixed solvent ratio of this study (approximately 1 PEO ether oxygen per lithium ion in solution), it is clear from the structural results that PEO does not compete effectively with water for solvation sites on the lithium ion. Additional experiments at higher PEO/D₂O ratios are anticipated to provide more quantitative information on the competitive solvation of Li⁺ in aqueous polymer melts.

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