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ION-PAIRING IN POLYETHER SOLID ELECTROLYTES AND ITS INFLUENCE ON ION TRANSPORT

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Vibrational spectroscopic and conductivity data are presented for complexes of NaBF_4 and NaBH_4 with poly(ethylene oxide). These studies indicate that extensive contact ion pairing occurs in the NaBH_4 complex but not in the NaBF_4 complex. As a result the ionic conductivity is considerably lower in the NaBH_4 complex, due to trapping of the mobile sodium cations by the anion. The effect of salt stoichiometry on the conductivity behavior is also reported.

1. INTRODUCTION

Poly(ethylene oxide), (PEO), is known to form solvent-free complexes with a large number of alkali metal salts. The Na^+ salt complexes are highly crystalline and typically exhibit ionic conductivities of about 10^{-7} (ohm-cm^{-1}) at room temperature, increasing to about 10^{-3} (ohm-cm^{-1}) at 120°C (1). The cation has been implicated as the mobile species in the $\text{PEO}\cdot\text{NaSCN}$ complex through transference number measurements using a sodium/mercury amalgam concentration cell (2). All of the Na^+ complexes have essentially the same polyether backbone conformation (3), and to date the reported conductivities at a given salt stoichiometry are very similar, providing evidence against contact ion pairing. In this paper we present vibrational spectroscopic and conductivity studies which indicate that ion pairing occurs in the $\text{PEO}\cdot\text{NaBH}_4$ complex. Previous work has also shown that a knee occurs in Arrhenius plots of $\ln\sigma T$ against $1/T$ for the Na^+ complexes. The origin of this phenomenon is discussed.

2. EXPERIMENTAL

Preparation and characterization of the $\text{PEO}\cdot\text{NaBF}_4$ complex has been described elsewhere (3). The $\text{PEO}\cdot\text{NaBH}_4$ complex was prepared by suspending films of pure PEO (m.w. 600,000 purified by ion exchange and filtration (3)) in a saturated isopropylamine/ NaBH_4 solution. The isopropylamine (Aldrich, 99%) was refluxed over CaH_2 under dry N_2 and distilled before use. Care was taken to exclude all traces of water and the samples were handled using standard inert atmosphere techniques (4). The complexes were characterized by infrared and Raman spectroscopy, differential scanning calorimetry, (DSC), visual observations using a hot stage polarizing microscope and x-ray diffraction. The stoichiometry of the complexes is indicated by the ratio of ether oxygens to sodium cations, i.e. 4:1 etc.

The stoichiometry of the $\text{PEO}\cdot\text{NaBH}_4$ complex was determined by protolysis of the BH_4^- using aqueous HCl followed by PVT measurement of the evolved H_2 . The fully complexed stoichiometry thus established was about 3.4:1. The absence of regions of uncomplexed PEO or excess NaBH_4 was established through x-ray diffraction and differential scanning calorimetry. The maximum stoichiometry of the $\text{PEO}\cdot\text{NaBF}_4$ complex was shown to be about 4:1 at room temperature by x-ray diffraction. The maximum stoichiometry decreases slightly with increasing temperature up to the complex melting range of $105\text{--}115^\circ\text{C}$.

Complexes of NaBF_4 and NaBH_4 salts at less than maximum stoichiometry, (4.5:1), were also studied; these are two phase systems below 60°C , as demonstrated through x-ray diffraction and DSC. Apparently small regions of crystalline PEO are interdispersed with the fully complexed phase.

Conductivities were measured on hot pressed pellets of the polymer complex using the complex admittance technique over the frequency range of 5 Hz to 500 kHz. Reversible sodium/mercury amalgam liquid electrodes were used as electrical contacts in a sealed cell filled with dry nitrogen (2).

3. RESULTS AND DISCUSSION

3.1 Spectroscopic Evidence for Ion Pairing

Vibrational spectroscopic techniques have been used to deduce a reasonable polyether conformation for the PEO -sodium salt complexes (3). The $\text{PEO}\cdot\text{NaBH}_4$ and $\text{PEO}\cdot\text{NaBF}_4$ have virtually identical polyether conformations, both complexes are highly crystalline, and the only physical difference between the complexes is their melting ranges, $170\text{--}177^\circ\text{C}$ and $105\text{--}115^\circ\text{C}$, respectively. Comparisons of spectroscopic and conductivity data were therefore limited to temperatures below 90°C .

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The internal vibrational modes of the BH_4^- and BF_4^- anions provide a convenient and powerful spectroscopic probe to study the local environment about the anion. If no cation-anion interactions are observed, then the anion is expected to reside outside of the helical polyether conformation proposed earlier (3), in essentially a hydrocarbon-like environment. The internal vibrational bands observed would then be expected to correspond closely to those for an unperturbed 'free ion' symmetry; in this case an anion of tetrahedral (T_d) symmetry (5). Any significant cation-anion interactions would result in a lower symmetry accompanied by a splitting of degenerate vibrational modes.

The aqueous BH_4^- (BD_4^-) anion is representative of the unperturbed anion; its vibrational frequencies and assignments are shown in Tables 1 and 2. Only the symmetric and asymmetric deformation modes, ν_3 and ν_4 respectively, are formally infrared active and Fermi resonance has been invoked to explain the position of the totally symmetric $\nu_1(A_1)$ stretching mode (5). In contrast the BH_4^- (BD_4^-) vibrational bands for the PEO complexes are strongly perturbed. From a comparison of the number and intensity of the vibrational bands indicated in Tables 1 and 2 it is clear that the symmetry of the BH_4^- (BD_4^-) anion has been lowered from tetrahedral. For example, vibrational bands which are normally expected to be degenerate in a T_d symmetry, such as $\nu_4(F)$, are no longer degenerate in the BH_4^- complexes, and the large number of vibrational bands observed in the B-H and B-D stretching regions ($2150\text{--}2450\text{ cm}^{-1}$ or $1570\text{--}1750\text{ cm}^{-1}$, respectively) are due in part to a lifting of degeneracies. Tentative vibrational assignments have been made for some of these bands; these are indicated in Tables 1 and 2.

The symmetry of the anion may be lowered through cation-anion interactions or through solvent interactions. However, solvent interactions with BH_4^- or BD_4^- are likely to be weak in this case, and are not consistent with experimental observations. Far infrared data also support the hypothesis of cation-anion pair interactions. Cation-dependent vibrational bands have been observed in the far infrared for the PEO-alkali metal salt complexes (3), these correspond to the motion of the alkali metal cations relative to their counter anions and surrounding ether oxygens. A number of the sodium salt complexes, including the $\text{PEO}\cdot\text{NaBF}_4$ complex, exhibit no anion dependence in their far infrared spectra. However significant changes are seen in the far infrared when BD_4^- is substituted for BH_4^- , which is strong evidence that ion-pair interactions occur in these complexes. There is no spectroscopic indication of ion pairing in the $\text{PEO}\cdot\text{NaBF}_4$ complex.

Table I. Infrared and Raman vibrational assignments for the BH_4^- anion.

PEO·NaBH ₄		NaBH ₄ in basic aqueous solution		Approximate Assignments
Raman	IR	Raman	IR	
		2460w,p		$2\nu_4$
2342w,sh	2347vs	2340w,p		$\nu_2 + \nu_4$
2313vs				ν_1
	2295m	2294s,p		ν_1
		2266w,dp	2272s	ν_3
2230w,b	2232vs			ν_3
		2196w,dp	2200sh	$2\nu_4(E \text{ or } F_2)$
2177m,sh	2178s			-
	2169s			-
2155ms		2146m,p		$2\nu_4(A_1)$
		1246w		ν_2
		1097w		ν_4

Band intensities: vw (very weak), w(weak), sh(shoulder), mw(medium weak), m(medium), ms(medium strong), s(strong), vs(very strong), b(broad), p(polarized), dp(depolarized).

Table II. Infrared and Raman vibrational assignments for the BD_4^- anion.

PEO·NaBD ₄		NaBD ₄ in basic aqueous solution		Approximate Assignments
Raman	IR	Raman	IR	
1750sh	1751vs			$\nu_2 + \nu_4(?)$
1730m	1731vs			$\nu_2 + \nu_4(?)$
		1723w,dp	1721s	ν_3
1713m	1710w			-
	1684s	1694m,p		$2\nu_4(A_1)$
	1679s			-
		1675w,dp	1666sh	$2\nu_4(E \text{ or } F_2)$
1653w	1650sh			-
1638w	1639s			-
1578s	1579m	1585vs,p		ν_1
	947vw	890w		ν_2
	853mw			ν_4
	830m	842vw	843w	ν_4

Band intensities: see Table I.

3.2 Ionic Conductivity Measurements

Detailed ionic conductivity measurements on the $\text{PEO}\cdot\text{NaBF}_4$ and $\text{PEO}\cdot\text{NaBH}_4$ complexes with varying salt stoichiometries have been made. The temperature range was from 20° to 90°C for the NaBF_4 complex, and 20° to 150°C for the NaBH_4 complex. A complex impedance diagram

representative of those obtained for these complexes with reversible liquid electrodes is shown in Figure 1; this arc may be modeled by a simple circuit consisting of an internal resistance in parallel with an internal capacitance.

A comparison of the conductivity values for these complexes is shown in Figure 2. The 4.5:1 PEO:NaBF₄ complex exhibits a conductivity similar to that reported for other sodium salt complexes at this stoichiometry (1). If a slight excess of NaBF₄ is present in the PEO:NaBF₄ complex to prevent the formation of small regions of crystalline PEO, the overall conductivity falls by roughly a factor of 3 relative to the 4.5:1 complex, and a knee is not observed in the conductivity plot for the unannealed complex prepared at room temperature (see Figure 2). The absence of a knee at roughly 60°C for the salt-rich PEO electrolyte has been observed independently by P.V. Wright (6). The temperature range over which this knee occurs is coincident with the melting range of pure PEO and suggests that the melting of small regions of uncomplexed PEO or

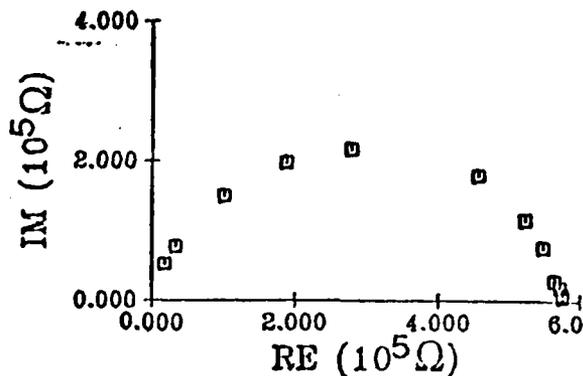


Figure 1. Representative complex impedance diagram for a PEO:NaBF₄ complex at 41°C from 100 Hz to 5×10^5 Hz, RE = real axis, IM = imaginary axis.

PEO with a low salt content may result in the observed conductivity behavior. This interpretation is consistent with our DSC and x-ray observations for complexes of varying salt

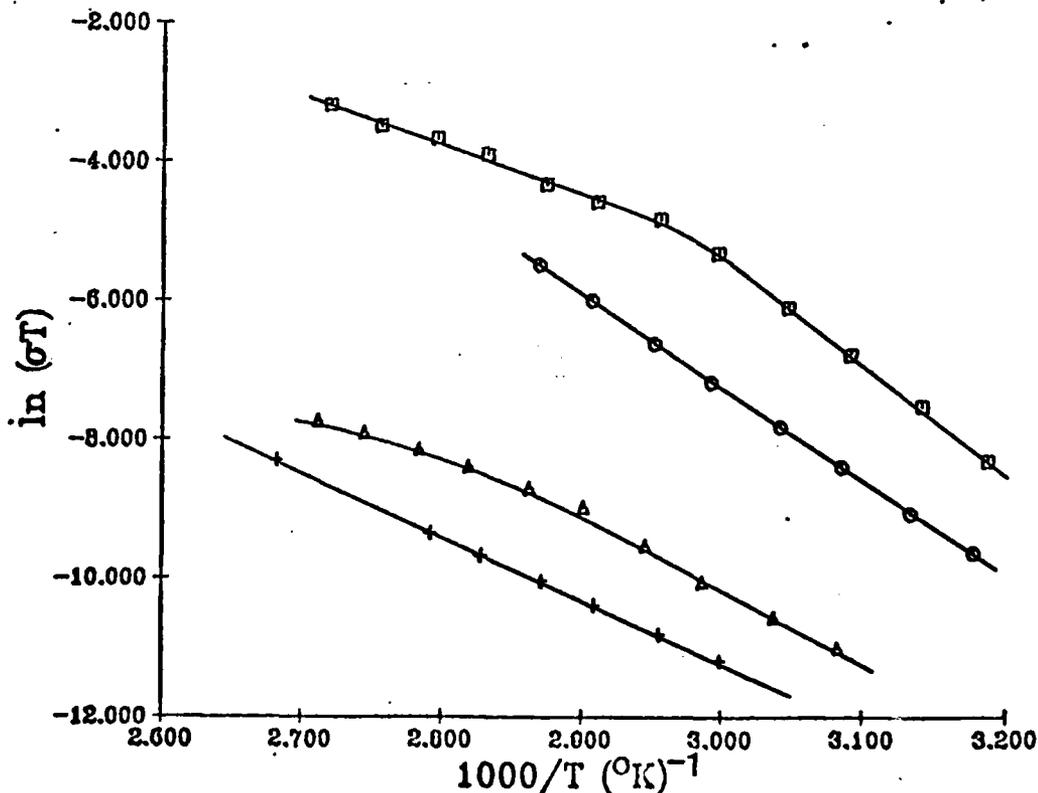


Figure 2. Variable temperature conductivity values for PEO:NaBF₄ complexes at 4.5:1 (□) and 3:1 (○), stoichiometry, and PEO:NaBH₄ complexes at 4.5:1 (Δ) and 3.4:1 (+) stoichiometry.

stoichiometry. An alternative hypothesis suggested by Wright to explain the thermal behavior he observed near 60°C in the PEO·NaX complexes involves the disordering of a complexed interlamellar phase at 60°C (6).

The conductivity of the 4.5:1 PEO·NaBF₄ complex is about 1.2×10^{-7} (ohm-cm)⁻¹ at 30°C and increases to 7.0×10^{-5} (ohm-cm)⁻¹ at 90°C. A linear Arrhenius type behavior is observed both above and below the knee at roughly 60°C. In contrast, the 4.5:1 PEO·NaBH₄ complex has a conductivity lower by roughly 10² over the same temperature range, and the conductivity plot is slightly curved. This sharp decrease in ionic conductivity, supported by the spectroscopic data presented above, indicates that ion pairing is likely to be the principal origin of the lower conductivity in the PEO·NaBH₄ complex.

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