

# Effect of Salt Concentration on the Ionic Conductivity of Amorphous Poly(ethylene oxide)-Sodium Salt Complexes

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**ABSTRACT:** Amorphous poly(ethylene oxide) (aPEO) is prepared by the oxy-methylene linkage of PEG400 and complexed with NaI and NaClO<sub>4</sub> with a range of stoichiometries, aPEO<sub>x</sub>NaAn,  $x = 15-150$ . Transmission IR spectra and X-ray diffraction data indicate that the aPEO and all salt complexes prepared are amorphous at ambient temperature. The complexes are characterized by impedance and dc methods, with bulk conductivities determined from 263 to 343 K. A broad conductivity maximum is obtained at low salt concentrations for each series. Ionic conductivities on the order of  $10^{-4}$ – $10^{-5}$  S cm<sup>-1</sup> are observed at ambient temperature. Arrhenius plots of the data indicate VTF behavior between  $T = 293$  and 343 K.

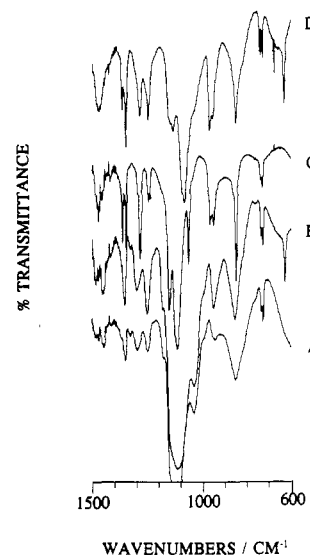
## Introduction

Poly(ethylene oxide) (PEO) forms salt complexes which exhibit high ionic conductivities above 333 K, but this conductivity rapidly decreases at lower temperatures due to the formation of a crystalline phase.<sup>1</sup> The utility of the complexes as electrolytes in ambient temperature cells is therefore limited. Booth and co-workers<sup>2,3</sup> and others<sup>2,4,5</sup> have demonstrated that high molecular weight polymers, [OCH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>m</sub>]<sub>n</sub>, can be produced by the oxy-methylene linkage of poly(ethylene glycol) to form amorphous salt complexes over a broad temperature range. Optimal properties for an amorphous-phase poly(ethylene oxide) (aPEO) are obtained from PEG400 ( $m \approx 8$ ). Complexes of aPEO with alkali-metal salts have been found to exhibit ionic conductivities on the order of  $10^{-4}$ – $10^{-5}$  S cm<sup>-1</sup> at ambient temperature, which is 1–2 orders of magnitude greater than that in comparable PEO complexes. Research on sodium salt complexes of aPEO has indicated that ionic conductivities comparable to those observed in the Li complexes may be obtained,<sup>3-5</sup> but a systematic study of the effect of concentration on conductivity has not yet been reported for the sodium complexes. This work describes the preparation and characterization of a range of stoichiometries for two sodium salt complexes, aPEO<sub>x</sub>NaClO<sub>4</sub> and aPEO<sub>x</sub>NaI with  $x = 15-150$ .

## Experimental Procedures

Amorphous PEO was prepared by a modification of the method published by Booth and co-workers.<sup>3</sup> PEG400 (50 g; Aldrich) was added to a suspension of finely-ground KOH (Ashland Chemical; high-purity grade) in dry CH<sub>2</sub>Cl<sub>2</sub> and mechanically stirred under N<sub>2</sub> for approximately 30 min until the solution became too viscous to stir. Another 50 mL of CH<sub>2</sub>Cl<sub>2</sub> was then added, and the mixture was allowed to react overnight. Excess CH<sub>2</sub>Cl<sub>2</sub> may be subsequently removed by evacuation. The crude product was dialyzed against distilled water (Spectrum cellulose tubing, MW cutoff = 3000) for 10 days to remove impurities of low molecular weight. Excess water was distilled away at reduced pressure and the product dried by heating under vacuum. A typical yield was 10 g of tacky, faintly yellow, polymer. <sup>13</sup>C and <sup>1</sup>H NMR spectra obtained closely matched those reported previously for the high molecular weight polymer.<sup>1</sup> All subsequent manipulations were performed in a drybox or under dry N<sub>2</sub> to exclude moisture.

Salt complexes were prepared by codissolving stoichiometric quantities of the polymer and salt in CH<sub>3</sub>CN and then removing the solvent by evacuation. The complexes were further dried by evacuation at 70 °C for several hours. Cylindrical samples (diameter = 6 mm, thickness = 1.6 mm) for electrical measurements were formed in air-tight Kel-F cells and annealed at 70 °C



**Figure 1.** Transmission IR spectra of thin films of (A) aPEO, (B) aPEO<sub>50</sub>NaClO<sub>4</sub>, (C) PEO, and (D) PEO<sub>50</sub>NaClO<sub>4</sub>.

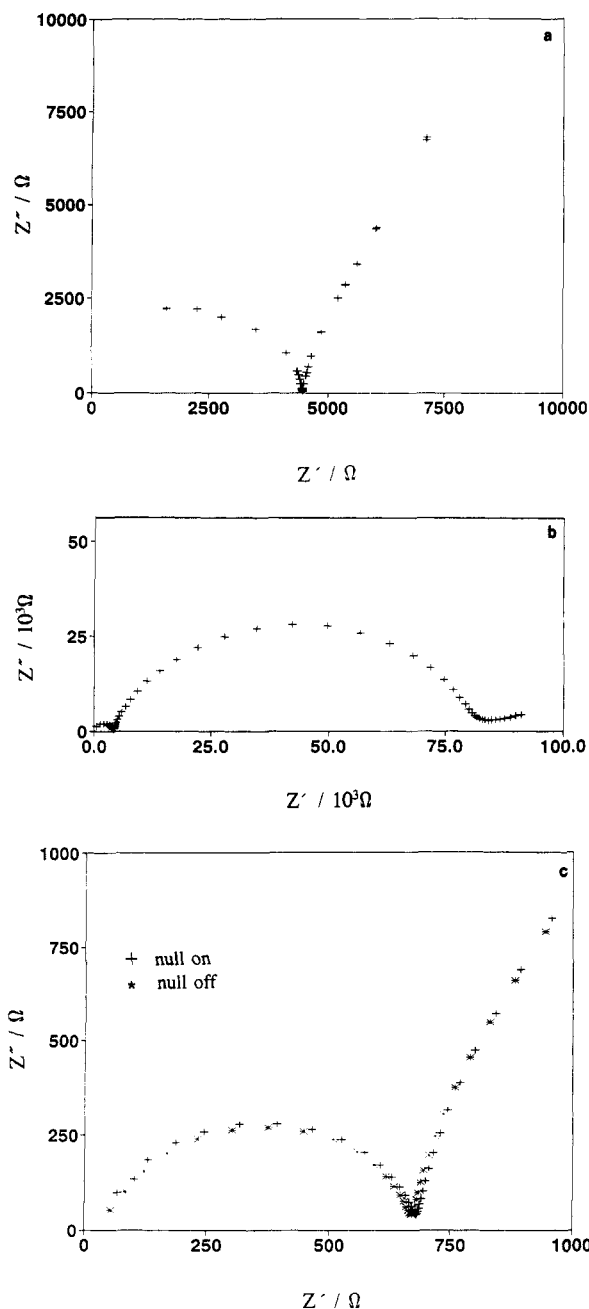
prior to data collection. Some samples were cast into films (approximate diameter = 1.2 cm; thickness = 150 μm) from a CH<sub>3</sub>CN solution, dried under vacuum, and pressed between disk electrodes in an air-tight cell. Stainless steel (irreversible) electrodes were generally employed, although some data were acquired with Na metal (reversible) electrodes.

Variable-temperature impedance spectra were collected using a computer-controlled Solartron 1260 impedance analyzer and Sun ECO1 environmental chamber. Impedance measurements were acquired in the frequency range 15 MHz to 1 Hz, applying a 1-V sine wave. A computer-controlled PAR362 potentiostat/galvanostat was used for dc measurements. Transmission IR spectra were acquired on a Nicolet 510P FTIR (64 scans averaged, resolution = 2 cm<sup>-1</sup>). Samples for IR spectroscopy were cast onto polyethylene films and dried under vacuum. The FTIR sample chamber was purged continuously with dry air. X-ray diffraction data, collected on a D5000 Siemens powder diffractometer ( $2^\circ < 2\theta < 60^\circ$ , scan rate  $2^\circ/\text{min}$ ), showed no evidence of a crystalline phase in aPEO or any of its complexes.

NaClO<sub>4</sub> (EM; reagent grade) and NaI (Mallinckrodt; analytical reagent, recrystallized from ethanol/water) were evacuated for several days at 70 °C and stored under N<sub>2</sub>. CH<sub>3</sub>CN (Mallinckrodt; HPLC grade) was distilled over P<sub>2</sub>O<sub>5</sub> prior to use. PEO (Aldrich; MW = 100 000) was used as received for comparison studies.

## Results and Discussion

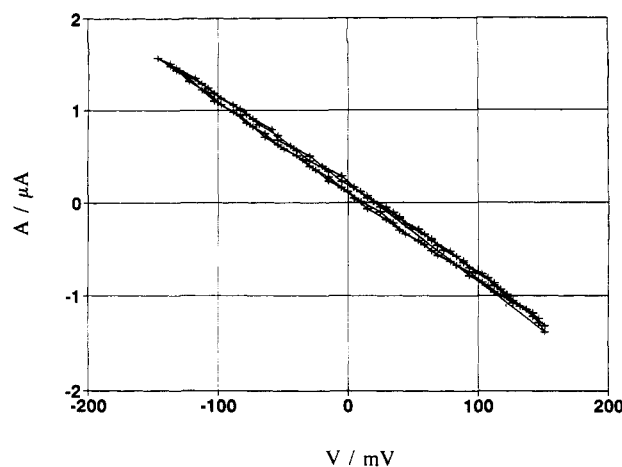
Transmission IR data for aPEO, PEO, and salt complexes are presented in Figure 1. Previous studies<sup>6</sup> have



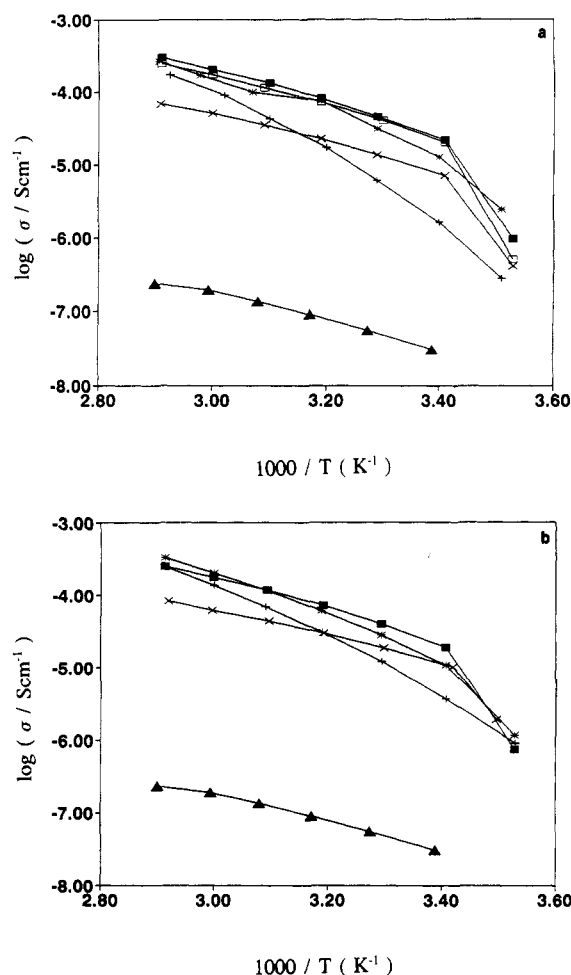
**Figure 2.** Cole-Cole plots of impedance data from aPEO<sub>75</sub>-NaClO<sub>4</sub>; (a) pellet sample with steel electrodes at 323 K, (b) pellet sample with Na electrodes at 323 K, and (c) 150- $\mu$ m film sample with steel electrodes at ambient temperature. In c, pluses indicate data corrected with a null circuit and asterisks indicate uncorrected data.

ascribed the splitting of the peak near 1390  $\text{cm}^{-1}$  to the presence of a symmetric and asymmetric  $-\text{CH}_2$  wag and found that this peak is split only in a crystalline phase.<sup>7</sup> The split peak is readily observed in the spectra of PEO and its complexes but is not split in ambient temperature spectra of aPEO and its complexes, indicating the amorphous nature of the latter. This result is confirmed by X-ray diffraction, which shows no diffraction peaks for aPEO or its complexes.

Representative impedance spectra obtained on pellets and thin films are shown in Figure 2a-c. The Cole-Cole plots obtained have a single arc for cells with irreversible electrodes. Measurements of samples with different geometries confirm that this arc corresponds to a bulk conduction process, and the bulk ionic conductivity was taken to be the touchdown of the high-frequency arc.



**Figure 3.** Cyclic voltammogram using two Na metal electrodes (scan rate = 20 mV/s,  $T = 323$  K) and a thin film of aPEO<sub>75</sub>-NaClO<sub>4</sub> as electrolyte. The inverse slope =  $R = \Delta V / \Delta I = 1.0 \times 10^5 \Omega$ .



**Figure 4.** Arrhenius plots for (a) aPEO<sub>x</sub>NaClO<sub>4</sub> and (b) aPEO<sub>x</sub>NaI: (+)  $x = 15$ , (\*)  $x = 25$ , (■)  $x = 50$ , (□)  $x = 75$ , (×)  $x = 150$ , and (▲) uncomplexed aPEO.

Conductivities for the salt complexes are on the order of  $10^{-4}$ – $10^{-5}$  S  $\text{cm}^{-1}$  at ambient temperature. Cole-Cole plots with two arcs are observed with reversible electrodes, with the high-frequency arc corresponding to bulk conduction and the low-frequency arc ascribed to an interfacial process. Although a previous report has indicated that the aPEO<sub>x</sub>-LiAn/Li interface is highly unstable,<sup>8</sup> the measured aPEO<sub>x</sub>-NaAn interfacial impedance remained relatively constant over a period of several hours at 323 K. The alkali-metal electrode interface is highly vulnerable to air and especially

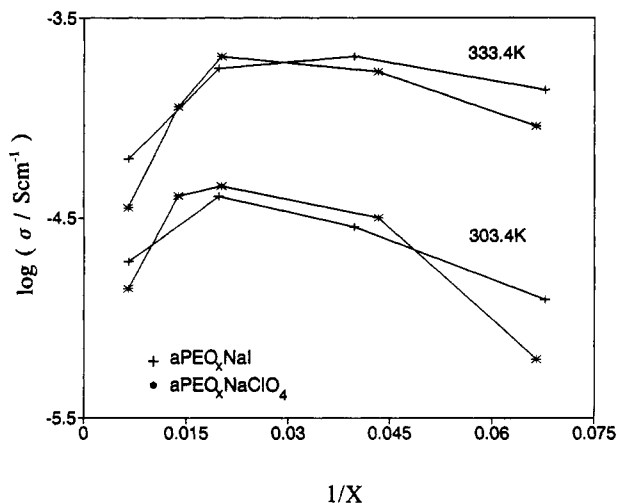


Figure 5. Conductivity vs composition at 303 and 333 K for  $\text{aPEO}_x\text{NaClO}_4$  and  $\text{aPEO}_x\text{NaI}$ .

moisture, and the differences in the results obtained here and previously may represent the experimental difficulty of maintaining an inert environment within the cell. In agreement with the above model, the impedance measured at the low-frequency touchdown is similar to the total cell resistance obtained by cyclic voltammetry (Figure 3).

Arrhenius plots of the impedance data for the  $\text{aPEO}_x\text{NaClO}_4$  and  $\text{aPEO}_x\text{NaI}$  (Figure 4) are similar, and the curved lines are consistent with the VTF behavior observed in many polymer electrolytes. The VTF equation may be expressed as

$$\sigma T = A \exp(-B/(T - T_0)) \quad (1)$$

and reasonable VTF parameters obtained from a fit of the data between 293 and 343 K are  $A = 0.47$ ,  $B = 0.091$  eV, and  $T_0 = 165$  K for  $\text{aPEO}_{150}\text{NaClO}_4$  and  $A = 3.0$ ,  $B = 0.096$  eV, and  $T_0 = 171$  K for  $\text{aPEO}_{15}\text{NaClO}_4$ . The onset of a rapid decrease in conductivity is observed at 293 K, but the conductivities at ambient temperature are far greater than those of corresponding PEO complexes. The general slope of the curves becomes gradually steeper with increasing concentration, indicating a small increase in the activation energy and/or glass transition temperature.

It is notable that the conductivity is not greatly affected by the salt concentration over the wide concentration range

studied, although a broad maximum can be observed near  $x = 25$ –50 for the complexes at 333 K with a somewhat sharper maximum near  $x = 50$  at 303 K (Figure 5). The conductivities obtained at low salt concentrations agree well with those found for  $\text{aPEO}_x\text{LiClO}_4$ ,<sup>4</sup> these results differ markedly from the conductivity-concentration relation of crystalline PEO complexes,<sup>1</sup> which exhibits a maximum near  $x = 8$ . This dissimilarity can be explained by the multiphase nature of the PEO complexes at these temperatures: the PEO complexes contain a crystalline phase,  $\text{PEO}_x\text{NaAn}$  ( $x = 3$ –6), of low conductivity along with an amorphous, conductive phase. The very shallow dependence of the conductivity of the salt concentration, resulting, for example, in a conductivity greater than  $10^{-5}$   $\text{S cm}^{-1}$  for at least a range of concentration for  $\text{PEO}_x\text{NaClO}_4$ ,  $150 < x < 25$ , may prove useful in cell applications where nonequilibrium processes result in an ion concentration gradient.

Further characterization of the  $\text{aPEO}_x\text{NaAn}$  complexes by NMR spectroscopy and differential scanning calorimetry is presently underway.

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## References and Notes

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