Electrical properties of a molecular ion channel


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Abstract. A.c. and d.c. electrical conductivities have been determined for complexes of either KCl or K picrate with a polymer of an isocyanide containing benzo-18-crown-6 rings. In both complexes, mixed ionic conductivity occurs. In the KCl complex, chloride ion conductivity predominates. The K-picrate complex has a low bulk ionic conductivity, but a substantial contribution of cations. The role played by anion-size effects is discussed.

Introduction

Ion transport across the membrane of the living cell is an important process, although the mechanism is not well understood. The triggering of nerve cells and heart-muscle cells is coupled with mechanisms which control diffusion of potassium and sodium ions through cell membranes. These ions are transported either coordinated to carrier molecules, which migrate from one side of the membrane to the other, or as free ions moving through ion-specific channels which span the membrane. The channels may represent a series of discrete ion-binding sites. Ion transport would then consist of a series of consecutive hops between these sites. In order to mimic this behaviour, we recently prepared an artificial molecular ion channel, 1, by polymerizing an isocyanide containing a benzo-18-crown-6 ring. Polymers of isocyanides, called poly(iminomethylenes) or poly(carbonimidoyls), have a rigid, helical structure. The side-chains are arranged in four stacks. When each side-chain contains a crown-ether ring, these rings form four channels which run parallel to the polymer helix axis (Fig. 1). These channels may transport cations since crown ethers have the ability to form complexes with a wide variety of cations such as Li⁺, Na⁺, K⁺, etc. Recently, we incorporated molecular-ion channel 1 into closed vesicles in order to mimic a channel-type ionophore present in biomembranes. We have now studied the electrical properties of solid-state compacts of potassium chloride and potassium picrate salts of compound 1.

Results and discussion

Figure 2 shows a perspective three-dimensional plot of the admittance response of a potassium picrate-polymer complex containing 51 mole % K picrate, mounted between ionically blocking stainless-steel electrodes. It is quite apparent that the low-frequency data extrapolate to the origin of the susceptance (Y″)−conductance (Y′) plane, indicating that in this polymer complex ionic conduction prevails. Similar admittance spectra were obtained for other compositions, and for the KCl−polymer complexes.
All the spectra reveal semi-circular arcs, whose centres invariably lie below the real conductance axis. The electrical equivalent circuit corresponding to the admittance spectrum of Fig. 2 not only comprises frequency-independent resistors and capacitors, but also constant-phase elements (CPE) of admittance $Y = A(i\omega)^n$ with $0 \leq n \leq 1$, indicating current inhomogeneities in the electrochemical system. While CPE interfacial response is frequently encountered in solid-state systems, ionic transport in the polymer complexes requires intramolecular hops, as well as intermolecular exchange. This may lead to non-uniform ionic diffusion, and hence bulk-CPE response. A detailed analysis of this CPE response will be the subject of a forthcoming paper.

Figure 3 shows the temperature dependence of the specific bulk ionic conductivity of several KCl-polymer complexes having KCl contents varying between 5 and 43 mole %. In addition, conductivity data for a potassium picrate (51 mole %)-polymer complex have been included. The slopes of the curves correspond to a conductivity activation enthalpy, $\Delta H$, of 1.2 eV for the KCl-, and 1.5 eV for the K-picrate-polymer complexes. While the ionic conductivity increases with KCl content, it is apparent that complexing with K picrate substantially lowers the bulk ionic conductivity. The question then arises as to whether the conductivity is cationic or anionic in nature. If the latter were to prevail, the data would suggest that the mobility of the chloride ion exceeds that of the picrate ion by several orders of magnitude, indicating strong ion-size effects.

To examine the contribution of potassium ions to the conductivity, the open-circuit voltage (OCV) of the concentration cell K-amalgam(I)/KCl (43 mole %)-polymer complex/Hg(II) was measured after intervals of utilization in the battery mode. The OCV progressively decreased from a starting value of approximately 2 V, this value being ill-defined because $\alpha_\text{K}(\text{II}) = 0$ at $t = 0$. After 25 h, the OCV had decreased to 1.40 V. In a subsequent 88 h period, the OCV decreased to 1.26 V. Subsequent replacement of the K-amalgam(I) electrode for Hg resulted in an OCV of $-0.13$ V. Similar results were obtained when the potassium picrate-polymer complex was utilized. These data qualitatively reveal that the potassium-salt-polymer complexes conduct potassium ions.

From open-circuit voltage (OCV), load-circuit voltages (LCV) and load-current ($I_L$) data for the concentration cells in the battery discharge mode, LCV/OCV vs. $I_L$ plots were constructed, and from the linear parts, $R_{dc}$ data were obtained.

Figure 4 shows the discharge characteristics of a concentration cell with the KCl-polymer complex as solid-state membrane. Similar results were obtained for polymers having other KCl contents and a K-picrate-polymer complex as membrane. In this configuration, $(R_{dc})^{-1}$ represents the conductance by potassium ions $G_k$. By comparison with the cell's high-frequency conductance, which represents the total ionic conductance $G_i$, we can calculate the
transference number \( t_{K^+} = (G_{K^+}/G_i) \) of the potassium ions in the polymer complexes. For the KCl (43 mole %)-polymer complex, \( R_{K^+} \) has the value of \( 1.6 \times 10^5 \) \( \Omega \), and \( R_{\text{pol}} \) the value of \( 1.9 \times 10^3 \) \( \Omega \) at 40°C. Hence, \( t_{K^+} \) has the value of 0.01. For a K-picrate (51 mole %)-polymer complex, the value 0.47 is obtained for \( t_{K^+} \). In general, \( t_{K^+} \) values of the KCl-polymer complexes range from \( 10^{-3} \) to \( 10^{-2} \), while for the K-picrate-polymer complex, a much larger value of 0.47 is found.

It may be concluded that in both complexes mixed ionic conduction occurs. In the KCl-polymer complex, chloride ion conduction predominates with a well-defined conductivity activation enthalpy of 1.2 eV. The value of 1.5 eV for the conductivity activation enthalpy of the K-picrate-polymer complex cannot be assigned to one specific charge carrier. However, for both \( K^+ \) diffusion via the pathway formed by the macrocyclic rings and for picrate-anion diffusion along the lipophytic mantle, a conductivity activation enthalpy larger than 1.2 eV is to be expected. A substantial anion-size effect is also reflected in the low bulk ionic conductivity of the K-picrate-polymer complex.

Electrical properties of monomeric crown ether metal halide complexes have recently been studied by Newman and Fujimoto. The complexes of 18-crown-6 with potassium and sodium iodide were found to exhibit anionic rather than cationic conduction. In addition, the dibenzo-18-crown-6 lithium halide complexes showed conductivities in the order \( \text{Cl}^- > \text{Br}^- > \text{I}^- \). These results are in line with our experiments. The occurrence of anionic conduction in complexes of 1, and in the above mentioned complexes, can be explained by the fact that the cations are strongly bound by the crown-ether rings. This is particularly true for the potassium ion whose size matches the cavity of the ring. The free energy of complexation of this ion by compound 1 is \( \Delta G_{\text{K}} = -42.7 \text{ kJ/mol} \).

The data presented in this paper suggest that appreciable cation transport through the channels of 1 can only be expected for ions having low free energies of complexation, i.e., small ionic radii, e.g., Co(II) ions. We have recently realized such an ion transport in a model membrane system consisting of closed vesicles in which 1 had been incorporated. Our experiments further suggest that in order to study cation transport in detail, anionic conduction should by suppressed by immobilizing the anions, e.g., by anchoring them onto the polymer backbone. Work along these lines is currently in progress.

**Experimental**

Polymer 1 was prepared as described previously. Its molecular weight amounted to \( M_w \approx 15,000 \). Complexes of the polymer and potassium chloride or picrate were prepared by stirring a solution of the polymer in dichloromethane with the solid salts at 25°C for 24 h. Clear solutions were obtained from which the solvent was removed by evaporation. The resulting complexes were analysed for their potassium content by elemental analysis. Disc-shaped compacts with a typical diameter of 5 mm, and a thickness of \( \approx 0.5-1 \) mm, were spring-loaded between stainless-steel discs in a teflon rod-shaped holder. This assembly was mounted between the platinum electrodes of a conventional conductivity cell. The small-signal a.c. response of the samples was recorded using a Solartron frequency response analyser (1174). The temperatures varied from \( \approx 293 \) to \( \approx 370^\circ \text{K} \) and the frequency from \( 10^{-2} \) to \( 10^5 \) Hz. Bulk conductances were obtained from analysing two- (2-D) and three-dimensional (3-D) complex–plane representations of the recorded admittance parameters. A detailed non-linear least-squares analysis, providing information on the electrode polarization phenomena, is beyond the scope of the present paper and will be reported elsewhere.

The potassium-salt–polymer complexes were investigated as membranes in concentration cells of the type K-amalgam(I)/K-salt–polymer complex/Hg(II), a potassium activity being established after discharge of the cell across an external load. In the discharge (battery) mode, the d.c. resistance \( (R_{dc}) \) of the membranes was determined from normalized load-circuit voltages (LCV/OCV) vs. load-current densities \( (I_L) \), the relation between these parameters being

\[
\frac{\text{LCV}}{\text{OCV}} = - \frac{R_{dc}}{\text{OCV}^2} \cdot I_L + 1,
\]

where OCV represents the open-circuit voltage of the concentration cell. The OCV is governed by the Nernst expression

\[
\text{OCV} = \frac{kT}{q} \ln \frac{a_{\text{K}_\text{pol}}}{a_{\text{K}_\text{amal}}},
\]

OCV and LCV data were recorded using a Keithley model 616 digital electrometer, while load currents were measured using a Keithley model 445 digital picoameter.