Selective conduction of alkali metal ions in poly(diaza-crown ether)

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(Received 24th July 1992; revised 11 September 1992)

Poly(diaza-18-crown-6) (**1**) was mixed with alkali metal perchlorates ($MClO_4$; M = Li, Na, K, Rb and Cs). Curved Arrhenius plots for ion conductivity were found for all dry samples, suggesting that ion migration occurs with segmental motion in **1**. The potassium cation showed the lowest ion conductivity, reflecting a stronger interaction with the crown ether structure.

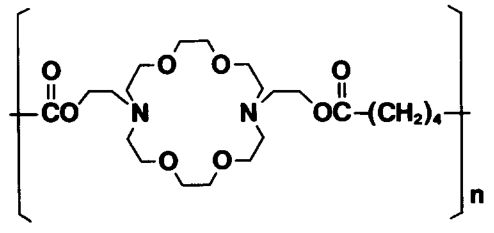
(Keywords: poly(crown ether); ion conduction; cation selectivity; alkali metal ion)

Introduction

Ion-conductive polymers are potential candidates for converting wet ionic devices into dry ones. Solid state batteries and solid electrochromic displays have already been prepared with these polymers[1–5]. Recently, attempts have been made to introduce higher functions into ion-conductive polymers, such as photo-sensitivity[6] and non-linear temperature response[7]. We have previously reported that larger cations migrate faster in polyether derivatives because of a weaker interaction force with the ether oxygens[8–11]. It was then suggested that ion-selective transport should be carried out with a suitable design of polymer matrix. The present communication reports the design of ion selectivity in ion conductivity with the use of a specific interaction between crown ether structure and alkali metal ions[12].

Experimental

Poly(7,16-diethylene-1,4,10,13-tetraoxa-7,16-diazacyclooctadec-7,16-ylene-adipate) (**1**) was synthesized by the reaction of adipoylchloride and *N,N'*-(dihydroxyethyl)-diaza-18-crown-6 (yield 70%) according to the method reported previously[13]. The average molecular weight was estimated to be about 2000–5000 by g.p.c. measurement.



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Polymer **1** was dissolved in dehydrated chloroform, and then alkali metal perchlorate ($MClO_4$) was further dissolved in it. The ratio of crown unit structure to metal cation was set at 10:1. Polymer film was prepared by evaporating chloroform and was dried *in vacuo* for 3 days at room temperature.

Ion conductivity was measured in the temperature range from 10 to 60°C with a computer-controlled impedance analyser (Solartron, Schlumberger). The dynamic impedance measurement was carried out with specially designed apparatus[14,15] at the heating and cooling rate of 3.0°C min^{-1}.

The cation binding property of the parent diaza-18-crown-6 was semiquantitatively assessed using FAB mass spectrometry competition technique. An aqueous solution of a diaza-18-crown-6 (0.01 M) and five metal chlorides (0.05 M each) was mixed with two-fold volume of glycerol. The averaged relative peak intensities of $[\text{diaza-18-crown-6-metal complex}]^+$ ion were as follows: Li^+, 0; Na^+, 58; K^+, 100; Rb^+, 47; and Cs^+, 19. This sequence reflects the relative bonding affinities[16,17].

Results and discussion

The Arrhenius plots of ion conductivity for **1** containing $MClO_4$ (M = Li, Na, K, Rb or Cs) were analysed. Data for Na and K systems are shown in *Figure 1*. All of these data plotted on curved lines, suggesting that the segmental motion of **1** supports the ion transport. Ion conductivity is generally a function of carrier ion radius[8–11]. Larger alkali metal ions have been revealed to migrate faster in polyether derivatives[8–11], because larger cations, with lower surface charge density, received weaker ion–dipole interaction with ether oxygen units.

The ion conductivity for **1** at 30°C was plotted as a function of the dissolved cation radius, as shown in *Figure 2*. It is clear that a relatively higher ion conductivity was found for **1** containing Li, Na or Rb salts. The ion radius of K^+ is 1.33 Å and K^+ is known[12] to be trapped firmly in the domain of 18-diaza-crown-6. FAB mass spectrometry indicated the following sequence for the affinity of alkali metal ions with parent diaza-18-crown-6: $Li \ll Na \ll K \gg Rb \gg Cs$. Further, the stability constant

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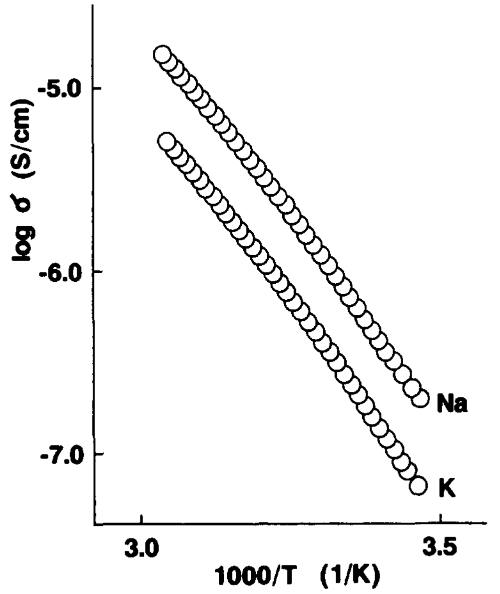

Figure 1 Arrhenius plot of ion conductivity for **1** containing $NaClO_4$ or $KClO_4$. $[MClO_4]/[\text{diaza-crown unit}] = 1/10$ (mol ratio)

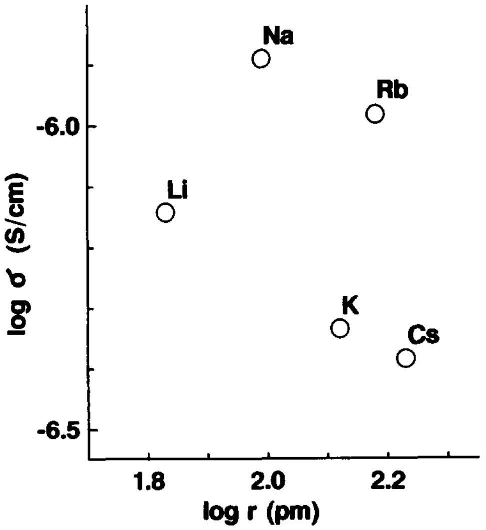

Figure 2 Relationship between carrier cation radius and observed ion conductivity (at 25°C) for **1** containing the corresponding perchlorate salt. $[MClO_4]/[\text{diaza-crown unit}] = 1/10$ (mol ratio)

($K_c \times 10^{-5}\ M^{-1}$) of **1** with a series of alkali metal ions in chlorofom has already been reported to be 1, 4 and 0.3, for Na^+, K^+ and Rb^+ species, respectively[13]. Potassium ion was confirmed to be well accommodated in the diaza-crown ring, providing lower ion conductivity. (^{13}C n.m.r. binding studies revealed that ester moieties were too far away to interact with the crown-bound metal cations in **1**.)

The observed ion conductivity for **1** containing $KClO_4$ should be due mainly to the ClO_4^- species. This tendency is generally found for the polyether derivative systems. The amount of ClO_4^- was proportional to the dissociation degree of the salt, which was also affected by the interaction force between cation and crown structure. If ClO_4^- ion was the only carrier ion, **1** containing $KClO_4$ should show higher ion conductivity due to a higher dissociation degree. The data obtained therefore showed the considerable contribution of the migration of cations. The conductivity found in the $KClO_4$ system may be attributed mainly to anion migration.

On the other hand, the ion radius of Cs^+ is larger than the cavity size of diaza-18-crown-6, so there should not be strong interaction between Cs^+ and diaza-18-crown-6 unit. However, the low Cs^+ ion conductivity could not be explained by this factor alone, and might be attributed to the lower solubility of $CsClO_4$ in **1**. Actually, Li, Na and K salts were dissolved in the chloroform solution of **1** under stirring within a day. However, when Rb and Cs salts were placed in chloroform solution under stirring for about a week, they were not homogeneously dissolved. Detailed data on the effect of cation size could be obtained if single ion-conductive poly(diaza-crown ether)s were synthesized, but their preparation and purification might be difficult.

The relation between the structure of a series of poly(diaza-crown ether)s and the ion radius of a series of alkali metal ions will be reported in a future publication.

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