Ionic Interactions in Polymeric Electrolytes Based on Low Molecular Weight Poly(ethylene glycol)s

W. Wieczorek,* P. Lipka, G. Żukowska, and H. Wyciślik

Warsaw University of Technology, Faculty of Chemistry, ul. Noakowskiego 3, 00-664 Warszawa, Poland

Received: March 5, 1998; In Final Form: June 26, 1998

It is shown that ionic conductivity of polymeric electrolytes based on low molecular weight amorphous polyglycols can be modified by the addition of α-Al$_2$O$_3$ fillers containing surface groups of the Lewis acid type. An enhancement of conductivity over pure PEG−LiClO$_4$ electrolyte is observed for PEG−α-Al$_2$O$_3$−LiClO$_4$ composite electrolytes containing from 0.5 to 3 mol/kg of the lithium salt. This increase in conductivity is coupled with the lowering of the viscosity of composite electrolytes and increasing chain flexibility when compared to the PEG−LiClO$_4$ system as shown by rheological and DSC experiments. A decrease in the fraction of ionic aggregates is also seen from the FT-IR experiments for composite electrolyte in this salt concentration range. FT-IR studies of the C−O−C stretching mode has shown reduction in the transient cross-link density obtained after the addition of α-Al$_2$O$_3$ in the salt concentration range corresponding to the conductivity enhancement. The phenomena observed are explained in view of ion−ion and ion-polymer interactions, involving dispersed filler particles, which are of the Lewis acid−base origin.

Introduction

The interest in studies of polymeric electrolytes arises from the possibility of their applications in various electrochemical devices such as batteries, electrochromic windows, displays and fuel cells working from subambient, e.g., −50 °C, to moderate, e.g., 200 °C, temperatures.[1,2] Despite intensive search, the mechanism of ionic transport in polymeric electrolytes as well as the electrode−electrolyte interfacial behavior are still under discussion.[3] Owing to the low dielectric constant of polymer matrices, ion−ion interactions are equally important to polymer−ion interaction in polymer ionic conductors. Ionic interactions have been thoroughly studied in model low or medium molecular weight polymer systems owing to their simplicity over high molecular weight counterparters.[4−10] These investigations confirmed a high degree of ionic association in polyether-based systems evidenced by the formation of solvent-separated or contact ion pairs, triplets, or higher aggregates. Studies of low molecular weight systems enable also one to establish the viscosity of the polymer solvent and hence to use the Fuoss−Krauss relation[11] in the discussion of ionic transport in polymer matrices.[4−7] This formalism has previously been successfully used for the variety of liquid electrolytes based on low- or medium-permittivity solvents.[11] Vincent et al.[5] as well as Salomon et al.[7] used the Fuoss−Krass procedure to calculate the association constants for electrolytes based on low molecular weight polyethers.

On the other hand, it has been demonstrated by several authors that conductivity and ion−polymer and/or ion−ion interactions can be modified by the addition of inorganic fillers to high molecular weight polyether electrolytes.[12−14] For these semicrystalline systems, the increase in conductivity has been attributed to the lowering of their degree of crystallinity resulting in the formation of a highly conducting amorphous phase. A similar effect of various fillers has recently been observed in amorphous oxymethylene linked PEO systems and was attributed to the changes in polymer−ion interactions leading to the increase in the flexibility of the polymer host.[15,16] Scrosati and co-workers demonstrated that the addition of fillers to polymeric electrolytes leads to the improvement of the electrode−electrolyte interfacial behavior and suppression or limitation in the formation of passive layers with the resistance growing in time.[14,17] Therefore, such composite electrolytes are important for their application in microbatteries owing to the enhancement of conductivity and improved electrochemical stability over the pure polyether-based systems. However, so far there is a lack of complex studies of the ionic transport in low molecular weight polyglycols containing dispersed filler particles. The only attempts made by Scrosati's and Fedkiw's groups were limited to narrow filler and salt concentration ranges and did not show major differences between pure polyether electrolytes and those with dispersed filler particles.[18,19]

In the present work the ionic conduction is studied in PEG−LiClO$_4$ electrolytes over a wide salt concentration range. Two sets of electrolytes with and without α-Al$_2$O$_3$ (with Lewis acid type surface groups) are examined. Conductivity studies are coupled to viscosity and DSC experiments, which helps to establish the relation between salt concentration and viscosity (flexibility) of the polymer host. The ion−polymer and ion−ion interactions are studied on the basis of FT-IR spectroscopy and particularly the changes in the intensity of the IR modes characteristic for C−O−C and ClO$_4^-$ vibrations. These bands are characteristic of ion−polymer and ion−ion interactions, respectively. Finally, the ionic associations are discussed on the basis of the Fuoss−Krass formalism.[11]

Experimental Section

Sample Preparation. PEG (M_w = 350, Aldrich, monomethoxy-capped) was filtered and then dried on a vacuum line first at ~60 °C for 72 h and then, under a vacuum of 10^{-5} Torr, stringently freeze-dried using freeze−pump−thaw cycles. While

* Corresponding author: tel. +48 22 6607572; fax +48 22 6282741; e-mail: wladek@ch.pw.edu.pl.

Ionic Interactions in Polymeric Electrolytes

J. Phys. Chem. B, Vol. 102, No. 36, 1998 **6969**

still under vacuum, the polymer was transferred to an argon-filled drybox (moisture content lower than 2 ppm) where the salt was dissolved into the polymer using a magnetic stirrer. Salt concentration varied from 10^{-6} to 5 mol/kg of polymer. Samples of the salt concentration from 5 mol/kg down to 0.5 mol/kg were prepared by direct dissolution of the salt in a polymer. Samples of the highest salt concentration were heated to 50 °C to facilitate the dissolution process. Samples of lower salt concentration were prepared by successive dissolution of a batch containing the electrolyte with 0.5 mol/kg $LiClO_4$.

$LiClO_4$ (Aldrich, reagent grade) was dried under vacuum at 120 °C prior to the dissolution. The composite electrolytes were obtained by the dispersion of α-Al_2O_3 in PEG−$LiClO_4$ solutions. The concentration of α-Al_2O_3 in the composite electrolytes was equal to 10 mass %. α-Al_2O_3 (Aldrich, reagent grade, with the surface rich with Lewis acid type groups) was dried under a vacuum of 10^{-5} Torr at 150 °C for over 72 h prior to addition to the polymer−salt mixture. All samples were equilibrated in a drybox at ambient temperature for at least a month before undertaking any experiments.

DSC Studies. DSC data were obtained between −110 and 150 °C using a UNIPAN 605M scanning calorimeter with a low-temperature measuring head and liquid nitrogen cooled heating element. Samples in aluminum pans were stabilized by slow cooling to −110 °C and then heated at 10 °C/min to 150 °C. An empty aluminum pan was used as a reference.

Conductivity Measurements. Ionic conductivity was determined using the complex impedance method in the temperature range from 20 to 90 °C. The samples were sandwiched between stainless steel blocking electrodes and placed in a temperature-controlled oven. The experiments were performed in a constant volume cylindrical cell of an electrode diameter equal to 7.8 mm and fixed electrolytes thickness equal to 1.6 mm. The impedance measurements were carried out on a computer-interfaced Solartron-Schlumberger 1255 impedance analyzer over the frequency range 1 Hz to 1 MHz.

FT-IR. Infrared absorption spectra were recorded on a computer-interfaced Perkin-Elmer 2000 FT-IR system with a wavenumber resolution of 2 cm^{-1}. FT-IR studies were performed at 25 °C. Electrolytes were sandwiched between two NaCl plates and placed in the FT-IR temperature-controlled cell; the accuracy of the temperature was estimated to be ±1 °C.

Rheological Experiments. Rheological experiments were conducted at 25 °C using a Bohlin Visco 88BV viscometer in a two coaxial cylinders geometry. The measurements were performed within a shear rate range of 24−1200 cm^{-1}.

Results

Figure 1 presents conductivity isotherms measured at 20 and 90 °C as a function of salt concentrations for PEG−$LiClO_4$ and PEG−α-Al_2O_3−$LiClO_4$ electrolytes. For $LiClO_4$ concentration up to 0.5 mol/kg, conductivities measured for both electrolytes are similar at each temperature measured. At higher salt concentrations up to ∼3 mol/kg, the conductivities measured for PEG−α-Al_2O_3−$LiClO_4$ electrolytes are higher than those for electrolytes not containing α-Al_2O_3. The maximum in the conductivity measured for PEG−$LiClO_4$ electrolytes occurs at lower salt concentration than for the PEG−α-Al_2O_3−$LiClO_4$ system. For both types of electrolytes the maximum of conductivity shifts to the higher salt concentration with an increase in temperature. The differences in conductivity between both systems studied, measured in the 0.5−3 mol/kg salt concentration range, are higher at 20 than at 90 °C.
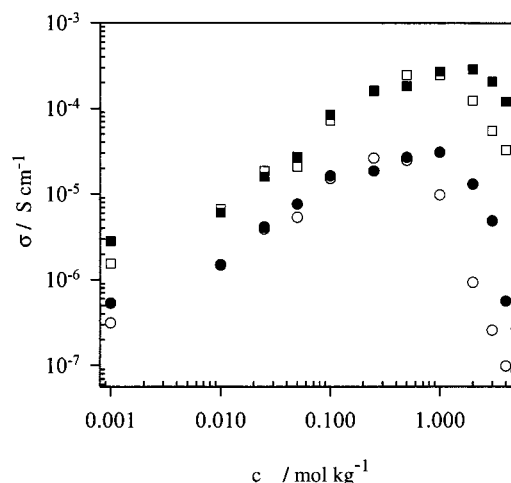

Figure 1. Changes in ionic conductivity as a function of salt concentration measured at 20 °C for (●) PEG−$LiClO_4$−α-Al_2O_3 electrolytes and (○) PEG−$LiClO_4$ electrolytes; at 90 °C for (■) PEG−$LiClO_4$−α-Al_2O_3 electrolytes and (□) PEG−$LiClO_4$ electrolytes.
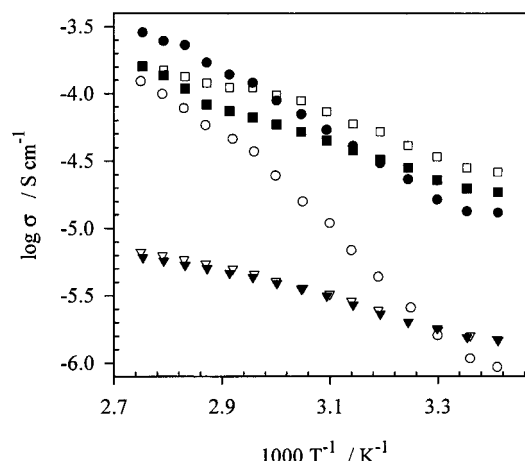

Figure 2. Changes in ionic conductivity of PEG−$LiClO_4$ electrolytes (open symbols) and PEG−α-Al_2O_3−$LiClO_4$ electrolytes (filled symbols) as a function of inverse temperature. Samples of various molal salt concentrations: (▽, ▼) 0.01 mol/kg; (□, ■) 0.25 mol/kg; (○, ●) 2 mol/kg.

Figure 2 presents changes in the conductivity as a function of reciprocal temperature for PEG−$LiClO_4$ and PEG−α-Al_2O_3−$LiClO_4$ electrolytes. For each system the conductivity data are shown for samples with 0.01, 0.25, and 2 mol/kg $LiClO_4$. For PEG−$LiClO_4$ electrolytes below ∼40 °C, the conductivities measured for the electrolyte with the highest salt concentration are the lowest. At higher temperatures, the conductivities measured for this sample increase and are comparable to the PEG−0.25 mol/kg $LiClO_4$ electrolyte at ∼90 °C, but higher than for the PEG−0.01 mol/kg $LiClO_4$ electrolyte at above ∼40 °C. For the PEG− α-Al_2O_3−$LiClO_4$ electrolytes only at temperatures below ∼40 °C are the conductivities measured for the electrolyte with 2 mol/kg $LiClO_4$ lower than those for the PEG−α-Al_2O_3−$LiClO_4$ 0.25 mol/kg electrolyte. For electrolytes with 0.01 mol/kg $LiClO_4$, the conductivities measured for samples with and without Al_2O_3 are comparable over the entire range studied. For samples with 0.25 mol/kg $LiClO_4$, the conductivities measured for the pure PEG-based system are higher than those for electrolytes containing an inorganic filler up to ∼80 °C. For the sample of the highest salt concentration, the conductivities measured for PEG−α-Al_2O_3−$LiClO_4$ electrolytes are higher than those for the system based on pure PEG over the entire temperature range studied.
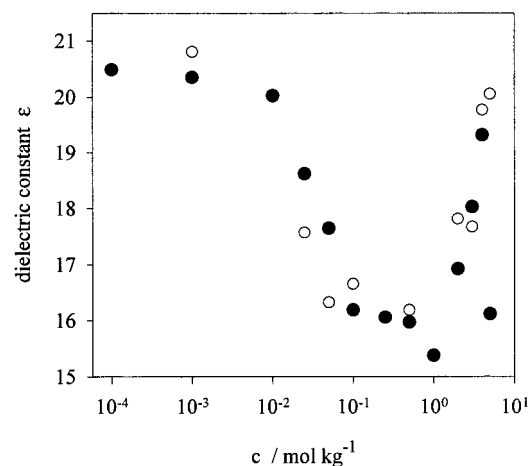
Figure 3. Changes in the electrolyte permittivity as a function of salt concentration. Data obtained at 20 °C for (○) PEG−LiClO$_4$ electrolytes; (●) PEG−α-Al$_2$O$_3$−LiClO$_4$ electrolytes.

Figure 3 presents changes in the electrolyte permittivity (ϵ) as a function of salt concentration. Data for PEG−LiClO$_4$ and PEG−α-Al$_2$O$_3$−LiClO$_4$ systems are compared. Permittivity has been calculated on the basis of impedance spectroscopy data using the following equation[20]

$$\epsilon = \frac{C_g d}{\epsilon_0 S} \qquad (1)$$

where C_g is the geometrical capacity, S is the electrolyte area, d is the electrolyte thickness, and ϵ_0 is the permittivity of the free space.

Permittivity initially decreases with an increase in the salt concentration reaching the minimum for LiClO$_4$ concentration equal to 0.5. For higher salt concentrations, an increase in permittivity is observed. For both sets of electrolytes, the permittivities measured for samples of the same salt concentration are very close. (The difference in the permittivity is usually smaller than the experimental error of the impedance spectroscopy technique.) Therefore, it can be concluded that the addition of α-Al$_2$O$_3$ does not result in a change in the electrolyte's permittivity.

DSC Studies. DSC traces display an endothermic phase transition occurring at about 260−265 K for samples of LiClO$_4$ concentration up to ∼0.5 mol/kg. This transition corresponds to the melting of the crystalline PEG phase. For higher concentrations of LiClO$_4$, the endothermic transition vanishes. The only other phase transition observed on DSC curves is the glass transition temperature (T_g) of the PEG phase. Changes in the T_g as a function of the salt concentration are depicted in Figure 4 for the PEG−LiClO$_4$ and PEG−α-Al$_2$O$_3$- LiClO$_4$ electrolytes. For salt concentration up to ∼0.01 mol/kg, T_g varied over a narrow temperature range of 193−198 K for both types of electrolytes. For higher salt concentration, T_g raises up slowly. It can be noticed that T_g values measured for PEG−α-Al$_2$O$_3$−LiClO$_4$ electrolytes at the 0.25−2 mol/kg salt concentration range are lower than for the PEG−LiClO$_4$ electrolytes. For some samples from the LiClO$_4$ concentration range above ∼0.1 mol/kg, the second T_g value was observed at around 200−205 K. The intensity of this transition was much lower than for the T_g's described above.

Rheology. Figure 5 displays changes in the viscosity of the PEG−LiClO$_4$ and PEG−α-Al$_2$O$_3$−LiClO$_4$ electrolytes as a function of salt concentration (data at 25 °C). It should be
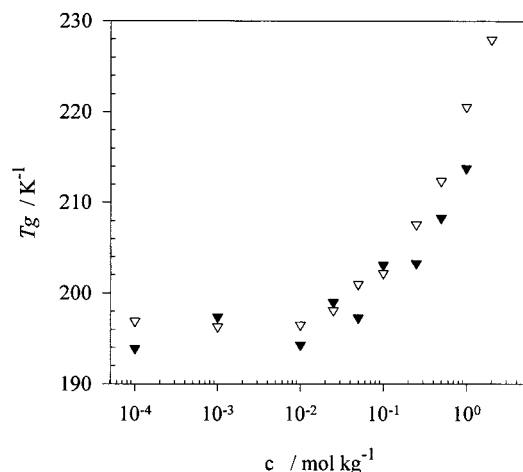

Figure 4. Changes in the T_g as a function of salt concentration. Data for (▽) PEG−LiClO$_4$ electrolytes; (▼) − PEG−α-Al$_2$O$_3$−LiClO$_4$ electrolytes.
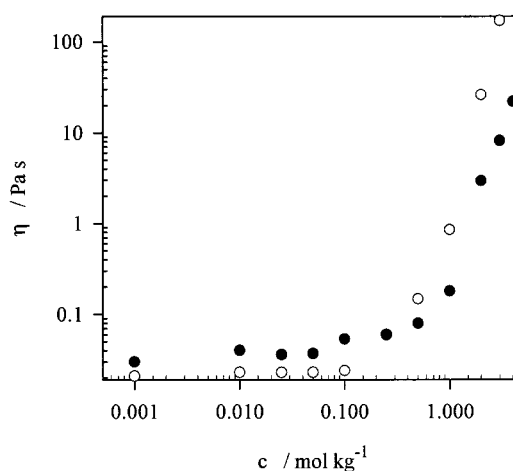

Figure 5. Viscosity (η) as a function of salt concentration. Data obtained at 25 °C for (○) PEG−LiClO$_4$ electrolytes; (●) PEG−α-Al$_2$O$_3$−LiClO$_4$ electrolytes.

TABLE 1: Physicochemical Data Used for the Calculation of Ionic Association on the Basis of the Fuoss−Krauss Formalism[a,11]

	PEG−LiClO$_4$	PEG−LiClO$_4$−Al$_2$O$_3$
Λ_0^I/S cm^{-1} kg^{-1} mol	0.003 36	0.002 91
λ_0^T/S cm^{-1} kg^{-1} mol	0.002 24	0.001 94
d/g cm^{-3}	1.094[b]	1.382[b]
η/Pa s	0.020[c]	0.029[d]
K_I/mol^{-1} kg	9.4 × 10^4	4.5 × 10^4
K_T/mol^{-1} kg	48.8	42.4

[a] All calculations for 25 °C. [b] Density of PEG and PEG−Al$_2$O$_3$ found from picnometric determinations. [c] Data for PEG. [d] Data for the PEG−Al$_2$O$_3$ system.

noticed that the viscosity of PEG increases by about 50% after the addition of α-Al$_2$O$_3$ (see Table 1 for the viscosity data obtained for samples with 0 mol/kg concentration of LiClO$_4$). For salt concentration up to 0.25 mol/kg, the viscosities of PEG−LiClO$_4$ electrolytes are lower than for the PEG−α-Al$_2$O$_3$−LiClO$_4$ electrolytes. At salt concentrations higher than 0.5 mol/kg, the viscosities measured for PEG−α-Al$_2$O$_3$−LiClO$_4$ electrolytes are lower. At the highest salt concentrations, this difference is over 1 order of magnitude. For both electrolytes the viscosities increase with an increase in salt concentration, with the rise in viscosity for salt concentrations higher than ∼1 mol/kg.
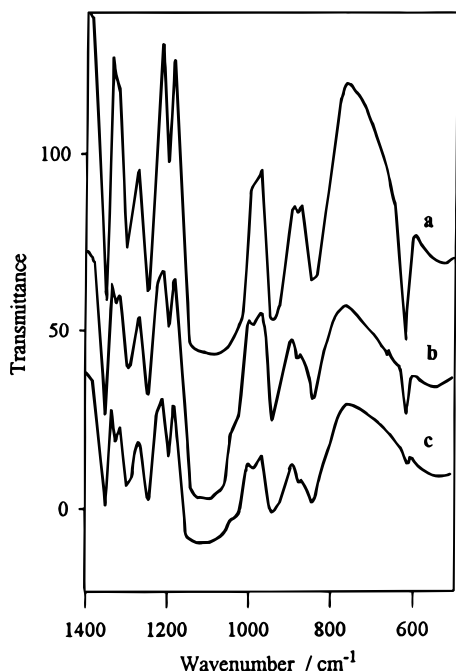
Ionic Interactions in Polymeric Electrolytes

J. Phys. Chem. B, Vol. 102, No. 36, 1998 **6971**

Figure 6. Exemplary FT-IR spectra depicted at 25 °C for PEG—α-Al₂O₃—LiClO₄ composite electrolytes. Samples of various LiClO₄ concentrations: (a) 0.01 mol/kg; (b) 0.25 mol/kg; (c) 2 mol/kg.
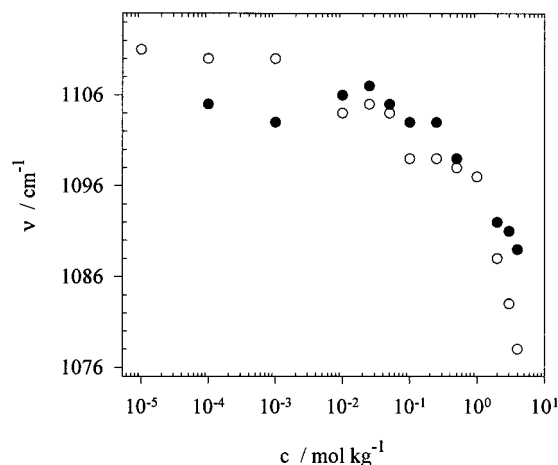

Figure 7. Changes in the maximum of the C—O—C stretching mode as a function of salt concentration. Data for (○) PEG—LiClO₄ electrolytes; (●) PEG—α-Al₂O₃—LiClO₄ electrolytes

FT-IR Studies. Figure 6 presents the exemplary FT-IR spectra depicted for the PEG—α-Al₂O₃—LiClO₄ electrolytes; samples of salt concentration equal to 0.01, 0.25, and 2 mol/kg. Two IR regions of C—O—C symmetric and asymmetric stretching vibrations observed at ∼1100 cm^{-1}, and ν_4 ClO₄$^-$ envelope ones occurring at ∼625 cm^{-1}, are of particular interest in our studies. Changes in the intensity, shape, and position of the C—O—C stretching mode are associated with the polyether—LiClO₄ interactions, whereas ν_4 ClO₄$^-$ stretch is associated with ion—ion interactions in these electrolytes. In Figure 6 the decrease in the position of the C—O—C stretch maximum can be noticed with an increase in the salt concentration. The broadening of this band, particularly at the highest salt concentration, is also observed.

Figure 7 summarizes the change in the position of the maximum of C—O—C stretch as a function of salt concentration for the PEG—LiClO₄ and PEG—α-Al₂O₃—LiClO₄ electrolytes. For both samples the maximum in the C—O—C stretch band is in the 1100—1110 cm^{-1} range for salt concentrations up to

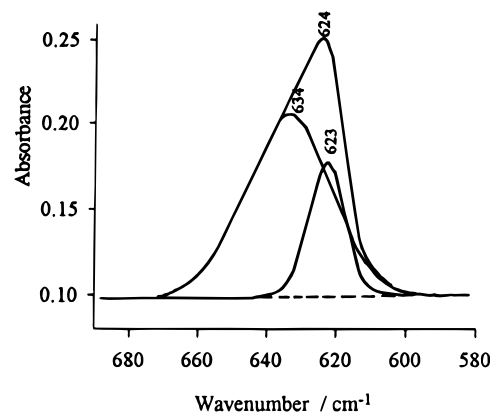**Figure 8.** Peak fitting for the ν(ClO₄$^-$) FT-IR region for the PEG—LiClO₄ (4 mol/kg) sample at 25 °C.

∼0.01 mol/kg. In this salt concentration range the maximum for PEG—LiClO₄ electrolytes occurs at higher wavenumbers than for the PEG—α-Al₂O₃—LiClO₄ system. At higher salt concentrations up to ∼1 mol/kg, the maximum of the C—O—C stretch shifts down to lower wavenumbers, and in this concentration range the position of the maximum for the PEG—α-Al₂O₃—LiClO₄ electrolytes is comparable to that for the PEG—LiClO₄ system. At salt concentrations higher than 1 mol/kg, the maximum for PEG—α-Al₂O₃—LiClO₄ system occurs at higher wavenumbers than for unmodified electrolytes. It is widely described in the literature that the changes in the position of the C—O—C stretch are connected with the polymer—cation interactions.[1,2] The downshift in the frequency of the C—O—C stretch evidenced the formation of the polymer—salt complex, which, on the other hand, is connected with the formation of the transient cross-links in the electrolyte, thus lowering the flexibility of the polymer chains.

In Figure 8 the exemplary spectrum obtained for the PEG—LiClO₄ (4mol/kg) electrolyte in the 600—650 cm^{-1} range is shown. The ν_4 ClO₄$^-$ envelope can be separated in two contributions with the maxima at ∼623 and 635 cm^{-1}. Salomon and co-workers attributed the 623 cm^{-1} band to the spectroscopically free anions and the 635 cm^{-1} mode to the bound or contact ClO₄$^-$ anions.[7] According to them, the 623 cm^{-1} mode probably constitutes the solvent-separated ion pairs Li$^+$(S)ClO₄$^-$ (where S stands for the solvent) and solvent-separated dimers. The 635 cm^{-1} band may also contain contributions from the contact or bound dimers. As is shown in Figure 8, the ν_4 ClO₄$^-$ envelope has been separated into the 623 and 635 cm^{-1} modes using the Grams 386 procedure.[21] For the salt concentrations up to ∼0.25 mol/kg, only single modes with a maximum at ∼623 cm^{-1} exist. For higher salt concentrations the fraction of bound anions can be calculated as the ratio of the area under the 635 cm^{-1} mode to the total area under the ν_4 ClO₄$^-$ envelope.

Figure 9 shows the fraction of the contact ion pairs as a function of salt concentration for the PEG—LiClO₄ and PEG—α-Al₂O₃—LiClO₄ electrolytes in the 0.5—5 mol/kg salt concentration range. The fraction of contact ion pairs increases with an increase in salt concentration and levels off for the salt concentration equal to 2 mol/kg for the PEG—α-Al₂O₃—LiClO₄ system and equal to 3 mol/kg for the PEG—LiClO₄ electrolyte. Over the entire salt concentration range shown in Figure 9, the fraction of contact ion pairs calculated for the PEG—LiClO₄ electrolyte is higher than for the PEG—α-Al₂O₃—LiClO₄ system.

Studies of Ionic Association Using the Fuoss—Krauss Formalism. According to the previous studies,[5-7] owing to the low dielectric constant of polyglycol matrixes, the following
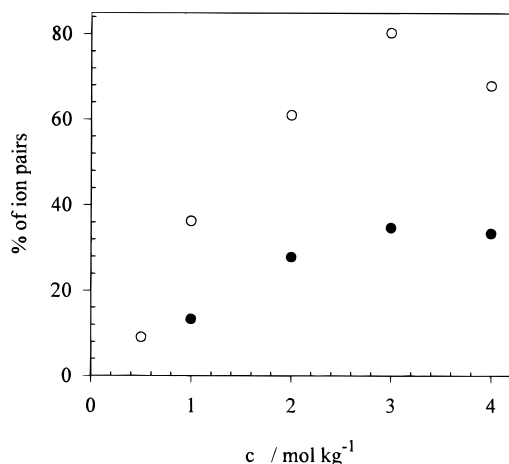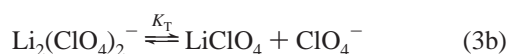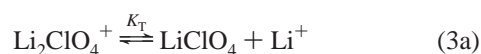
Figure 9. Changes in the fraction of $Li^+ClO_4^-$ contact ion pairs as a function of $LiClO_4$ concentration. Data are obtained at 25 °C in the 0.5−4 mol/kg $LiClO_4$ concentration range for (○) PEG−$LiClO_4$ electrolytes; (●) PEG−α-Al_2O_3−$LiClO_4$ electrolytes.

ion−ion equilibria exist in polyglycol-based electrolytes (eqs 2, 3a, and 3b).

$$Li^+ + ClO_4^- \overset{K_I}{\rightleftharpoons} LiClO_4 \tag{2}$$

$$Li_2ClO_4^+ \overset{K_T}{\rightleftharpoons} LiClO_4 + Li^+ \tag{3a}$$

$$Li_2(ClO_4)_2^- \overset{K_T}{\rightleftharpoons} LiClO_4 + ClO_4^- \tag{3b}$$

Following Vincent and co-workers,[5] we define α_i and α_T as a fraction of solute existing as simple ions and triple ion complexes, respectively (see eqs 4a−4c)

$$c_{Li^+} = c_{ClO_4^-} = \alpha_I \cdot c \tag{4a}$$

$$c_{Li_2(ClO_4)^+} = c_{Li(ClO_4)_2^-} = \alpha_T \cdot c \tag{4b}$$

$$c_{LiClO_4} = c(1 - \alpha_I - 3\alpha_T) \tag{4c}$$

Therefore, in accordance with the law of mass action the ion pair and ion triple complexes formation constants can be calculated on the basis of eq 5 and eq 6, respectively.

$$K_I = \frac{LiClO_4}{Li^+ \cdot ClO_4^-} = \frac{(1 - \alpha_i)}{(\alpha_i^2 \cdot c)} \tag{5}$$

$$K_T = \frac{Li_2(ClO_4)_2^+}{Li^+ \cdot LiClO_4} = \frac{Li(ClO_4)_2^+}{LiClO_4 \cdot ClO_4^-} = \frac{\alpha_T}{\alpha_I(1 - \alpha_I - 3\alpha_T)c} \tag{6}$$

where c is the molal concentration of $LiClO_4$. The K_I and K_T constants can also be evaluated upon the Fuoss-Krauss relation for the molal conductivity (Λ) of electrolytes based on low-permittivity solvents (eq 7)[11]

$$\Lambda = \alpha_T \Lambda_0^I + \alpha_T \lambda_0^T \tag{7}$$

where Λ_0 is the limiting molar conductance of the free ions and λ_0^T represents that of the hypothetical electrolyte Li_2ClO_4 + $Li(ClO_4)_2^-$.

When α_i and α_T are small, eq 7 simplifies to eq 8

$$\Lambda \cdot c^{1/2} = \frac{\Lambda_0^I}{K_I^{1/2}} + \frac{\lambda_0^T K_T \cdot c}{K_I^{1/2}} \tag{8}$$

On the basis of eq 8, the values of K_I and K_T can be calculated if the $\Lambda \cdot c^{0.5}$ vs c relationship is linear for the low salt concentrations and the limiting molal conductances are known for $LiClO_4$ and Li_2ClO_4 + $Li(ClO_4)_2^-$ electrolytes. These limiting molal conductances can be calculated using the Walden product rule (eq 9)[11]

$$(\Lambda_0 \eta)_{solvent1} = (\Lambda_0 \eta)_{solvent2} \tag{9}$$

and the semiempirical relation between Λ_0^I and λ_0^T which is as follows (eq 10)

$$\lambda_0^T / \Lambda_0^I = (1/3 \text{ or } 2/3) \tag{10}$$

In the calculations presented below the value of 2/3 will be used.[5−7]

Following Vincent and co-workers,[5] a mean value of the Walden product for $LiClO_4$ at 25 °C is equal to 0.614 S cm² pmol⁻¹. For PEG(350) used in these studies, the experimentally determined viscosity η = 0.020 Pa·s, and therefore Λ_0^I = 0.003 36 S·cm⁻¹ kg·mol⁻¹. For the electrolytes with dispersed α-Al_2O_3 particles, η = 0.029 Pa·s, which leads to Λ_0^I = 0.002 91 S·cm⁻¹·kg·mol⁻¹.

By using the above Λ_0 values, λ_0^T parameters can be calculated from eq 10 and then used to calculate the K_I and K_T constants on the basis of eq 8 in the 0.1−0.001 mol/kg salt concentration range, in which the linear dependence of $\Lambda c^{0.5}$ vs c is observed for the PEG−$LiClO_4$ and PEG−α-Al_2O_3−$LiClO_4$ electrolytes. K_I and K_T values for both sets of electrolytes are presented in Table 1 together with the raw data used for their calculations. Knowing K_I and K_T, the α_i and α_T parameters are calculated after rearranging eqs 5 and 6 to the following form (eqs 11 and 12).

$$\alpha_I = \frac{-1 + \sqrt{1 + K_I \cdot c}}{2K_I \cdot c} \tag{11}$$

$$\alpha_T = \frac{K_T \cdot \alpha_I(1 - \alpha_I)c}{1 + 3K_T \cdot \alpha_I \cdot c} \tag{12}$$

This enables us to calculate the fraction of single ions, ion pairs, and triples (on the basis of eqs 4a−4c) over the range of concentrations including the values above and below those of the experimental $LiClO_4$ concentration range used for the determination of K_I and K_T on the basis of the Fuoss-Krauss relation (eq 8).

The comparison of changes in the fraction of single ions, ion pairs, and triplets for PEG−$LiClO_4$ and PEG−α-Al_2O_3−$LiClO_4$ electrolytes is shown in Figure 10. Up to the salt concentration range of 0.1 mol/kg, the differences between both sets of electrolytes are small. For higher salt concentrations, PEG−α-Al_2O_3−$LiClO_4$ electrolytes are characterized by a higher concentration of triple ions and lower concentration of ion pairs as compared to the PEG−$LiClO_4$ system. This is in agreement with the experimental conductivity data showing an enhancement in conductivity upon the addition of α-Al_2O_3 over this salt concentration range. Similarly to the previous study,[5]

Ionic Interactions in Polymeric Electrolytes

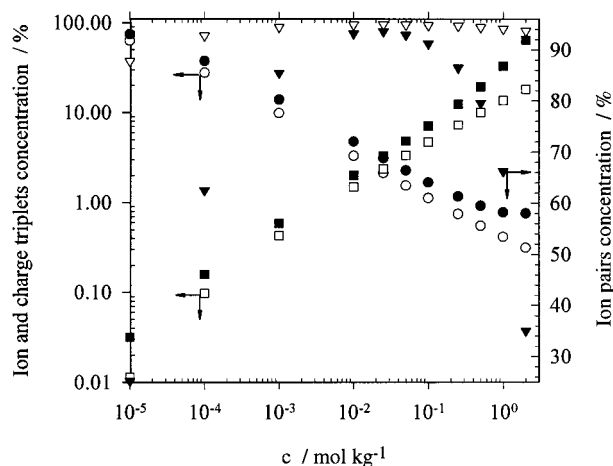*J. Phys. Chem. B, Vol. 102, No. 36, 1998* **6973**

Figure 10. Changes in the fraction of "free ions" (○, ●), contact-ion pairs (▽, ▼), and charged triplets (□, ■) as a function of $LiClO_4$ concentration calculated at 25 °C on the basis of the Fuoss-Krauss formalism for PEG−$LiClO_4$ electrolytes (open symbols) and PEG−α-Al_2O_3−$LiClO_4$ electrolytes (filled symbols).

Figure 11. Schematic structure of ion−ion and ion-polymer interactions in the PEG−$LiClO_4$ (a and b) and PEG−α-Al_2O_3−$LiClO_4$ (c and d) systems.

the fraction of single ions for the salt concentrations higher than 10^{-3} mol/kg is negligible.

Discussion

The addition of α-Al_2O_3 results in a variation in conductivity, viscosity, ion−ion and ion−polymer interactions in PEG−α-Al_2O_3−$LiClO_4$ electrolytes in comparison with the pure PEG−$LiClO_4$ system. Conductivities for both electrolytes are comparable up to about 0.25 mol/kg $LiClO_4$, but in the salt concentration range 0.5−3 mol/kg $LiClO_4$, the conductivities measured for PEG−α-Al_2O_3−$LiClO_4$ electrolytes are higher than that for the PEG−$LiClO_4$ system of the same salt concentration (see Figure 1). This is connected with the lower viscosity (see Figure 5) and higher flexibility (lower T_g values, see Figure 4) of the PEG−α-Al_2O_3−$LiClO_4$ electrolytes in this salt concentration range. FT-IR studies showed that the ion−polymer interactions are weaker for the PEG−α-Al_2O_3−$LiClO_4$ system over this $LiClO_4$ concentration range, which is evidenced by a downshift of the maximum of the C−O−C mode as compared to the pure PEG to the higher frequencies than those measured for the PEG−$LiClO_4$ electrolytes (see Figure 7). Also, the fraction of bound or contact ionic species is lower for samples with the α-Al_2O_3 filler (see Figure 8).

Such behavior should be explained in terms of filler−polymer−salt interactions of the Lewis acid−base type.[12] α-Al_2O_3 has a surface enriched with Lewis acidic groups capable of interactions with Lewis base centers of polyether or ClO_4^- anionic oxygen. Therefore, α-Al_2O_3 competes with Li^+ cations, being a hard acid according to the Pearsons classification, in the complexation of PEG and (or) in the interaction with ClO_4^- anions. Similar type interactions with aluminas are widely described in the literature for the water solutions of alkali metal salts[22] as well as for the low molecular weight polyethers.[23]

In our case the addition of α-Al_2O_3 to pure PEG results in an increase in the viscosity of the polyglycol (see Table 1 for the viscosity data obtained for zero salt concentration). This increase might be due either to the steric hindrance of α-Al_2O_3 or to the coupling of acidic surface groups of the filler to the polyether base oxygens. Both result in the limitation of the segmental motion of polymer chains; viscosity increases. On the basis of the previous report,[24] the increase in the viscosity due to steric hindrance should be roughly 7−8% compared to the viscosity of the pure PEG for the volume fraction of α-Al_2O_3
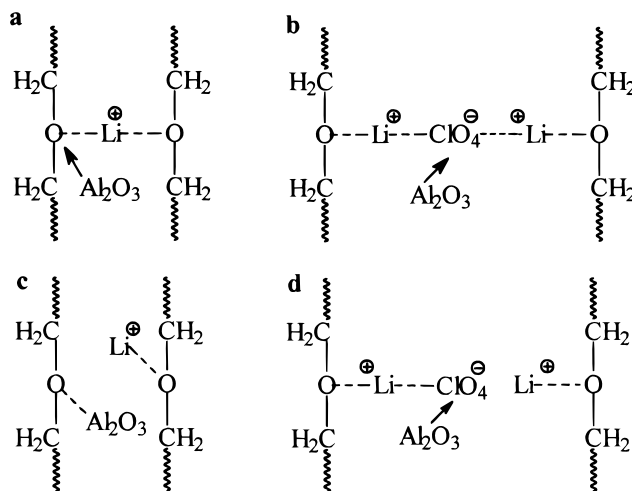
corresponding to one used in the present work. This is calculated under the assumption of spherical geometry of the filler grains. The viscosity enhancement found in our studies is about 50% (see Table 1), which suggests strong interactions between α-Al_2O_3 and the polyether.

After the addition of $LiClO_4$ the viscosities of the PEG−α-Al_2O_3−$LiClO_4$ systems are higher than those for the PEG−$LiClO_4$ electrolytes up to the salt concentration equal to 0.25 mol/kg. This is coupled with the larger downshift of the C−O−C maximum in the salt concentration range up to ∼0.01 as observed from FT-IR studies for PEG−α-Al_2O_3−$LiClO_4$ electrolytes (see Figure 7). The latter is evidence of the stronger coupling of Li^+, and/or also α-Al_2O_3 with the polyether oxygens.

It is known that the interaction between polyether and lithium salts leads to the formation of inter- or intramolecular transient cross-links of the polyether chains, thus limiting the flexibility (increasing viscosity) of the polymer solvent.[3,25,26] It is under discussion whether these cross-links might go directly through the Li^+ cations (see Figure 11a) or their formation might involve cation−anion interaction, as shown in Figure 11b.[27] Surface acidic groups of α-Al_2O_3 might either compete with Li^+ cation in the reaction with ether oxygens (see Figure 11c) or in the reaction with ClO_4^- anions (see Figure 11d). Both lead to the substitution of Li^+ by α-Al_2O_3. These reactions can explain the lowering of the viscosity of PEG−α-Al_2O_3−$LiClO_4$ electrolytes over the PEG−$LiClO_4$ systems and at the same time the decrease in the fraction of bound or contact species (see Figures 9 and 11d).

Therefore, in the low salt concentration there is an excess of α-Al_2O_3 over ClO_4^- anions and surface groups of the filler participate in the reaction with polyether oxygens, thus increasing the viscosity of these electrolytes (see Figure 5) and resulting in a larger downshift of the maximum of the C−O−C mode (see Figure 7). In the higher salt concentration range, the filler surface groups bound to the ClO_4^- anions reduce the number of transient cross-links (see the C−O−C position in Figure 7) and lower the fraction of contact ion pairs (see Figure 9). On the basis of experimental data, it can be postulated that the ClO_4^- anions have larger affinity to α-Al_2O_3 surface groups than to the Li^+ cations. The ClO_4^-−α-Al_2O_3 interactions do not result in the formation of a new anion mode.

On the basis of the above discussion, an increase in the conductivity of the PEG−α-Al_2O_3−$LiClO_4$ electrolytes over PEG−$LiClO_4$ systems should be related to the decrease in

viscosity resulting from the interaction of α-Al_2O_3 with ClO_4^- anions. However, the importance of α-Al_2O_3−polyether oxygens interactions cannot be excluded.

The experimental results are in good agreement with the ionic associations predicted from the Fuoss-Krauss relation[11] (see Figure 10). The increase in the fraction of charged triplets observed for the PEG−α-Al_2O_3−$LiClO_4$ electrolytes in the 0.5−5 mol/kg $LiClO_4$ concentration range might be due to the association of α-Al_2O_3−ClO_4^- complexes or "free" Li^+ cations with existing contact ion pairs.

Conclusions

It has been shown that the addition of α-Al_2O_3 results in an increase in the conductivity of PEG−α-Al_2O_3−$LiClO_4$ electrolytes over the PEG−$LiClO_4$ systems in the 0.5−3 mol/kg salt concentration range. This increase is coupled with the decrease in the viscosity and decrease in the fraction of contact ion pairs. It is suggested that the above changes result from the interaction of the α-Al_2O_3 surface acidic group with ClO_4^- anions and polyether oxygens leading to the lowering of the transient cross-link density and weakening of ion−ion interactions over the salt concentration range in which the increase in conductivity and decrease in viscosity are observed.

References and Notes

(1) *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman and Hall: London, 1993.

(2) *Solid State Electrochemistry*; Bruce, P. G., Ed.; Cambridge University Press: Cambridge, 1995.

(3) Bruce, P. G.; Shriver, D. F.; Gray, F. M. Reference 2, Chapters 5 and 6.

(4) Gray, F. M. *Solid State Ionics* **1990**, *40/41*, 637.

(5) MacCallum, J. R.; Tomlin, A. S.; Vincent, C. A. *Eur. Polym. J.* **1986**, *22*, 787.

(6) Xu, M.; Eyring, E. M.; Petrucci, S. *J. Phys. Chem.* **1995**, *99*, 14589.

(7) Salomon, M.; Xu, M.; Eyring, E. M.; Petrucci, S. *J. Phys. Chem.* **1994**, *98*, 8234.

(8) Albinsson, I.; Mellander B. E.; Stevens, J. R. *J. Chem. Phys.* **1992**, *96*, 681.

(9) Ferry, A.; Jacobsson, P.; Stevens, J. R. *J. Phys. Chem.* **1996**, *100*, 12574.

(10) Ferry, A. *J. Phys. Chem. B* **1997**, *101*, 150.

(11) Fuoss, R. M.; Accascina, F. *Electrolytic Conductance*; Interscience: New York, 1959.

(12) Wieczorek, W.; Florjanczyk, Z.; Stevens, J. R. *Electrochim. Acta* **1995**, *40*, 2251.

(13) Gray, F. M. *Solid Polymer Electrolytes-Fundamentals and Technological Applications*; VCH: Weinheim, Germany, 1991.

(14) Scrosati, B.; Neat, R. Reference 1, Chapter 6.

(15) Wieczorek, W.; Such, K.; Florjanczyk, Z.; Stevens, J. R. *J. Phys. Chem.* **1994**, *98*, 6840.

(16) Wieczorek, W.; Such, K.; Chung, S. H.; Stevens, J. R. *J. Phys. Chem.* **1994**, *98*, 9047.

(17) Capuano, F.; Croce, F.; Scrosati, B. *J. Electrochem. Soc.* **1991**, *138*, 1918.

(18) Panero, S.; Scrosati, B.; Greenbaum, S. G. *Electrochim. Acta* **1992**, *37*, 1533.

(19) Fan, J.; Fedkiw, P. S. *J. Electrochem. Soc.* **1997**, *144*, 399.

(20) Bruce, P. G. In *Polymer Electrolyte Reviews-1*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier: London, 1987; Chapter 8.

(21) Grams 386 is a commercially available product from Galactic Industries Corp. Marquardt's nonlinear least-squares-fitting algorithm is used. Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.

(22) Sposito, G. *The Surface Chemistry of Soils*; Oxford University Press: Oxford, 1984; Chapter 5.

(23) Lyth, E.; Ng, L. M. *J. Phys. Chem.* **1995**, *99*, 17615.

(24) Thomas, D. G. *J. Colloid Sci.* **1965**, *20*, 267.

(25) Latham, R. J.; Linford, R. G. *1-st Electronic Conference on Solid State Ionics*, June 1995; Paper 314.

(26) Oleander, R.; Nitzan, A. *J. Chem. Phys.* **1995**, *102*, 7180.

(27) Cruickshank, J.; Hubbard H. V. St. A.; Boden, N.; Ward, I. M. *Polymer* **1995**, *36*, 3779.