Effect of Salt Concentration on the Conductivity of PEO-Based Composite Polymeric Electrolytes

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The effect of salt concentration on the molal conductivity of various composite electrolytes was studied. Conductivity enhancement is achieved for composite electrolytes over the basic poly(ethylene oxide)−LiClO$_4$ system in the salt concentration range where the filler concentration corresponds to that of LiClO$_4$. On the basis of impedance spectroscopy, DSC, and FT-IR studies, it is concluded that changes in the conductivity result from acid−base type interactions involving polyether oxygens, filler acid or base centers, and alkali metal cations. The effect of a filler is to change the fraction of available oxygen sites which in turn results in changes in the formation of ionic aggregates. The region in which the enhancement of ionic conductivity is observed corresponds to a decrease in the fraction of contact-ion pairs and higher aggregates; this is due to the location of filler molecules in the vicinity of the coordination sphere of Li$^+$ cations.

Introduction

Poly(ethylene oxide) (PEO) based polymeric electrolytes are still among the most extensively studied polymer ionic conductors due to the beneficial structure of PEO in supporting fast ion transport.[1,2] PEO exhibits good complexation properties and high flexibility and retains good mechanical stability at temperatures up to its melting point i.e., ∼65−70 °C. Unfortunately, a high crystalline phase concentration limits the conductivity of PEO-based electrolytes; this is due mainly to the basic requirement for ionic mobility, i.e., ionic motions coupled to the segmental relaxations of a flexible amorphous polymer phase.[1−3] Various procedures have been applied to decrease the crystallinity of PEO-based electrolytes while maintaining their high flexibility and mechanical stability, which extends over a wide temperature range.[4] One of the most successful approaches relies on the preparation of polymer blends and composites.[4,5] These are systems in which inorganic fillers or high molecular weight polymers are added to PEO-based electrolytes.[5] These additives inhibit the crystallization of PEO-based electrolytes and often increase the polyether chain flexibility with the result that there is an increase in ambient and subambient temperature conductivity.[5−7] Scrosati and co-workers observed that the addition of LiAlO$_2$ or zeolites results in an improvement of electrode−electrolyte compatibility and electrochemical stability in comparison with pure polyether electrolytes.[8,9]

Although the macroscopic properties of composite electrolytes associated with an enhancement of ionic conductivity are widely discussed, a detailed microscopic picture of ionic conduction in these materials has not been achieved. Polyether ionic conductors have a low dielectric constant. This leads to extensive ion−ion interactions, resulting in the formation of ionic aggregates such as solvent-separated or contact ion pairs,

triplets, and higher aggregates. The fraction of these associated species varies with a change in the salt concentration. The ionic associations have been so far thoroughly studied for nonaqueous liquid electrolytes and low or medium molecular weight amorphous polymeric electrolytes based on polyether matrixes.[10−19]

On the other hand all of the to date studies devoted to composite polymeric electrolytes based on semicrystalline polyether matrixes have been limited to a narrow salt concentration range (usually for polyether oxygen-to-metal ratios equal to 8 or 10).[5,8,9] Assuming the crucial role of ionic associations on the conductivity of electrolytes based on low permittivity solvents, it is important to know whether the effect of the filler leading to the conductivity enhancement is limited only to this narrow salt concentration range or can be extended over larger salt concentration ranges. Therefore, the main goal of the present paper is to study the salt concentration dependence of the molal conductivity of various composite polymeric electrolytes in comparison with the salt concentration dependence of molal conductivity obtained for the base PEO−LiClO$_4$ electrolyte. An increase in conductivity observed for each composite system will be discussed in terms of the formation and redissociation of contact-ion pairs and higher ionic aggregates. These conductivity studies will be supported by FT-IR investigations of the C−O−C stretching vibrations as well as ν_4(ClO$_4^-$) vibrations; these are used to discuss respectively the formation of the polyether−LiClO$_4$ complexes and ionic aggregates. DSC investigations showing changes in the glass transition temperature (T_g) which reflect changes in the polymer flexibility give additional support. Changes in the degree of polymer host crystallinity and the formation of a polyether−LiClO$_4$ complex phase will also be discussed on the basis of the DSC data.

Experimental Section

Sample Preparation. Poly(*N,N*-dimethylacrylamide) (PNND-MAA) ($M_w = 1.3 \times 10^5$, Polysciences, reagent grade), PEO (Aldrich, reagent grade, $M_w = 5 \times 10^6$), and AlBr$_3$ (Aldrich,

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TABLE 1: Conversion of O/M Ratios to the Molal Concentration[a] of Salts for PEO-Based Composite Electrolytes

O/M ratio	molal concn/mol·kg^{-1}			
	PEO$-$LiClO$_4$	PEO$-$LiClO$_4$$-$ α-Al$_2$O$_3$	PEO$-$LiClO$_4$$-$ PNNDMAA	PEO$-$LiClO$_4$$-$ AlBr$_3$[b]
3000	0.0076	0.00644	0.4236	0.00644
1000	0.0227	0.01932	0.4387	0.01932
300	0.076	0.0644	0.492	0.0644
100	0.227	0.1932	0.643	0.1932
25	0.909	0.7728	1.325	0.7728
16	1.420	1.2075	1.836	1.2075
10	2.272	1.932	2.688	1.932
8	2.841	2.415	3.257	2.415
6	3.788	3.220	4.204	3.220
4	5.682	4.830	6.098	4.830
3	7.576	6.440	7.992	6.440

[a] Molal concentration has been calculated with respect to the total concentration of PEO and filler (e.g., α-Al$_2$O$_3$ and PNNDMAA). [b] Molal concentration has been calculated with respect to the total concentration of LiClO$_4$ and AlBr$_3$. Molal concentration of additives calculated with respect to PEO are as follows: PNNDMAA, 1.782 mol·kg^{-1}; α-Al$_2$O$_3$, 1.730 mol·kg^{-1}; AlBr$_3$, 0.416 mol·kg^{-1}.

reagent grade) have been used without further purification and after drying under vacuum ($<10^{-4}$ Torr) at 50$-$70 °C for 48 h. α-Al$_2$O$_3$ samples with grain sizes less than 5 μm were prepared according to a procedure described elsewhere.[21] The fillers were chosen because of the different acid (base) groups included in their structure. PNNDMAA has lone electron pairs on the carbonyl oxygen or the nitrogen of the N(CH$_3$)$_2$ group which act as base centers. AlBr$_3$ is known as a strong Lewis acid. In the case of α-Al$_2$O$_3$, both Lewis acid centers and surface Lewis base oxygen centers coexist. Acetonitrile (Aldrich, reagent grade) was doubly distilled and stored over type 4A molecular sieves. All of the steps in the preparation procedure were performed in an argon-filled drybox (moisture content lower than 2 ppm). LiClO$_4$ (Aldrich, reagent grade) was dried under vacuum ($<10^{-4}$ Torr) at 120 °C prior to incorporation. The concentration of LiClO$_4$ is expressed as an O/M ratio, which is the molar ratio of ether oxygen to lithium cations. O/M ratios have been converted to molal concentration values, as are shown in Table 1. The solid components were mixed in appropriate amounts in a small glass reactor, and then acetonitrile was added to form an approximately 5 mass % suspension with respect to all solid components. The mixture was magnetically stirred until a homogeneous suspension was obtained. Excess acetonitrile was removed by vacuum distillation. The composite electrolytes obtained were dried under vacuum ($<10^{-4}$ Torr) for 48$-$72 h at 60 °C. The concentration of AlBr$_3$ in the composite electrolytes was equal to 10 mass %. The concentrations of PNNDMAA and α-Al$_2$O$_3$ were equal to 15 mass %. These are filler concentrations for which the highest enhancement of conductivity was previously observed for composite electrolytes based on the (PEO)$_{10}$LiClO$_4$ system.[7,22]

Experimental Techniques. *DSC Studies.* DSC data were obtained between -110 and 200 °C using a DuPont TA 2910 scanning calorimeter with a low-temperature measuring head and liquid nitrogen cooled heating element. Approximately 15 mg samples in aluminum pans were stabilized by slow cooling to -110 °C and then heated at 10 °C/min to 200 °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 0 to 100 °C. The samples were sandwiched between stainless steel blocking electrodes and placed in a temperature-controlled furnace. The accuracy of the temperature was
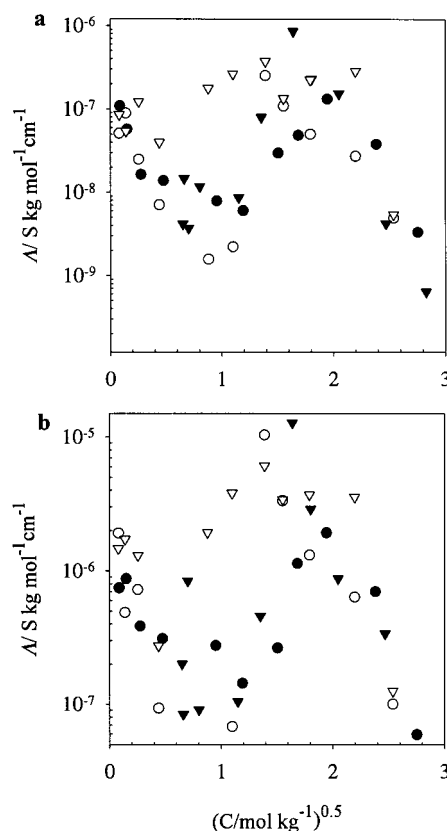

Figure 1. Molal conductivity as a function of the square root of the total molal concentration of salt for various PEO-based electrolytes. Data were obtained at (a) 0 °C and (b) 25 °C for (●) PEO$-$LiClO$_4$, (○) PEO$-$LiClO$_4$$-$PNNDMAA, (▽) PEO$-$LiClO$_4$$-\alpha$-Al$_2O_3$, and (▼) PEO$-$LiClO$_4$$-$AlBr$_3$ electrolytes.

estimated to be ±1 °C. The impedance measurements were carried out on a computer-interfaced HP 4192 impedance analyzer over the frequency range 5 Hz to 13 MHz. The peak-to-peak voltage in impedance experiments was equal to 1 V. The reproducibility of impedance spectroscopy results was checked by multiple experiments performed at room temperature. All measurements for samples of the same composition are within 5%.

FT-IR Experiments. Infrared absorption spectra were recorded on a computer-interfaced Nicolet FT-IR system 4.4 instrument with a wavenumber resolution of 2 cm^{-1} in the frequency range from 4000 to 400 cm^{-1}. Thin-film electrolyte membranes 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.

Results

Conductivity Studies. Figure 1 shows changes in the molal conductivity versus square root of molal concentration of salt at 0 °C (Figure 1a) and 25 °C (Figure 1b). In Figure 1a,b three conductivity regions can be distinguished. After an initial decrease in the conductivity down to a minimum (region I) an increase in the conductivity is observed with the maximum in the conductivity detected at salt concentrations around 2$-$5 mol·kg^{-1} (region II). This increase is followed by a decrease in the conductivity for higher salt concentrations (region III). The position of the conductivity minima and maxima measured for composite systems appears at lower salt concentrations than for the base PEO$-$LiClO$_4$ electrolyte. Also the conductivity maxima measured for composite electrolytes are higher than

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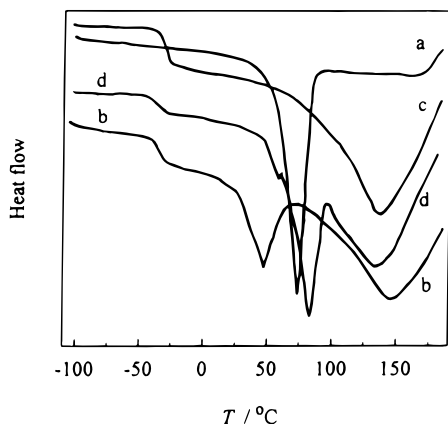*J. Phys. Chem. B, Vol. 102, No. 44, 1998* **8727**

Figure 2. DSC traces obtained for PEO−LiClO₄−PNNDMAA composite electrolytes with samples of O/M ratios equal to 25 (a), 8 (b), 6 (c), and 3 (d).

Figure 3. Changes of the T_g of composite polymeric electrolytes as a function of salt concentration. Data are for (●) PEO−LiClO₄, (○) PEO−LiClO₄−PNNDMAA, (▽) PEO−LiClO₄−α-Al₂O₃, and (▼) PEO−LiClO₄−AlBr₃ electrolytes.

for the PEO−LiClO₄ system. Sharp conductivity maxima measured for the composite systems containing AlBr₃ and PNNDMAA are in contrast to broader maxima observed for the system with α-Al₂O₃ as an additive. The position of the small conductivity minimum for composite electrolytes containing α-Al₂O₃ occurs at a lower salt concentration than the minima for other electrolytes. The conductivity minima observed for composite systems with AlBr₃ and especially with PNNDMAA are deeper than for the base PEO−LiClO₄ electrolyte. The minimum conductivity measured for the composite system with α-Al₂O₃ is higher than for the other electrolytes.

The most significant difference between the conductivities measured for PEO−LiClO₄ electrolytes and composite systems is in region II in which the conductivities measured at 0 and 25 °C for most of composite systems are higher than for unmodified PEO−LiClO₄ electrolytes of the same salt concentration. In the first region conductivities measured for the PEO−LiClO₄ electrolytes are higher or comparable to those measured for electrolytes containing AlBr₃ and PNNDMAA but still lower than for composite electrolytes with α-Al₂O₃. At high salt concentrations (e.g. in the IIIrd region) conductivities measured for the pure PEO-based electrolytes are slightly higher than for composite systems.

DSC Studies. Figure 2 presents examples of DSC curves obtained for PEO−LiClO₄−PNNDMAA composite electrolytes; samples with O/M ratio equal to 25 (curve a), 8 (curve b), 6 (curve c) and 3 (curve d). Similar curves have been obtained for other electrolytes. Up to two endothermic first order transitions can be seen. For samples of O/M = 25 (curve a) only one first-order transition is recorded with a maximum at ∼70 °C. As the concentration of the salt increases, the intensity of this transition decreases and a second endothermic feature develops with a maximum around 140−150 °C. For the sample with O/M = 6 only the high-temperature endotherm is observed. For O/M = 3 the position of the low-temperature endotherm shifts to higher temperatures (at ca. 85 °C). It is suggested that the high-temperature endotherm is due to the melting of the crystalline complex phase formed between PEO and LiClO₄, whereas the low-temperature one is due to the melting of the eutectic formed between the crystalline PEO and the crystalline complex phase. Similar behavior has been observed for all electrolytes studied.

Changes of the T_g as a function of the salt concentration are presented in Figure 3. T_g values increase with an increase in LiClO₄ concentration; this is due to the formation of transient cross-links between the salt and the polyether phase. However
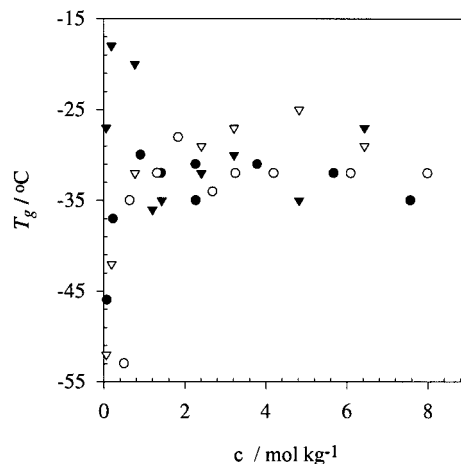
for O/M ratios lower than 25 the T_g's varied in a rather narrow range, e.g. between −35 and −25 °C, showing that further addition of the salt has a rather minor effect on T_g. Slightly different behavior is recorded for the electrolytes containing AlBr₃. For this system the electrolytes with a low LiClO₄ concentration have higher T_g values. This could be due to the presence of AlBr₃, which is also capable of interaction with the polyether phase.[22]

Figure 4a,b presents the fraction of the pure crystalline PEO phase (X_c) (see Figure 4a) and the fraction of the PEO−LiClO₄ complex phase (X_{mc}) (see Figure 4b) as the function of salt concentration. X_c is calculated by comparing the heat of melting of the crystalline polyether phase with the heat of melting found for the pure crystalline PEO phase (=213.7 J·g⁻¹).[23] X_{mc} is calculated from the comparison of the heat of melting of the crystalline complex phase with the heat of melting measured by us for the pure crystalline (PEO)₆LiClO₄ complex phase (∼136 J·g⁻¹). It can be noticed from Figure 4b that in the case of composite systems containing PNNDMAA and α-Al₂O₃ the complex phase is observed for samples with an O/M ratio lower than 16, whereas for the other two systems the presence of the complex phase is already evident for the sample with O/M = 25. The fraction of this complex phase (see X_{mc} values in Figure 4b) is lower for samples with PNNDMAA and α-Al₂O₃ than for the base PEO−LiClO₄ electrolyte. The highest differences can be noticed for samples of O/M = 16 and O/M = 10. Also the presence of the pure crystalline PEO phase is not observed for samples characterized by an O/M ratio lower than 6. For electrolytes containing AlBr₃ the onset of the high-temperature endotherm occurs at higher temperatures than that for the other electrolytes, and the intensity of this endotherm is lower as compared to the other systems studied (see X_{mc} data in Figure 4b). From the DSC data (see Figure 4a) it can also be noticed that the fraction of the crystalline PEO phase for composite electrolytes containing PNNDMAA and α-Al₂O₃ (samples with O/M = 16 and 25) is higher than for the base PEO−LiClO₄ electrolytes.

FT-IR Studies. Figure 5 presents the IR spectra recorded for PEO−LiClO₄−α-Al₂O₃ electrolytes with O/M ratio = 300 (Figure 5a) and 6 (Figure 5b) in the frequency range 1400−600 cm⁻¹. For the sample with O/M = 300 the presence of a crystalline PEO phase is confirmed by the presence of the triplet peak of the C−O−C stretching vibrations with maxima at ∼1144, 1107, and 1062 cm⁻¹.[23,24] The CH₂ wagging mode
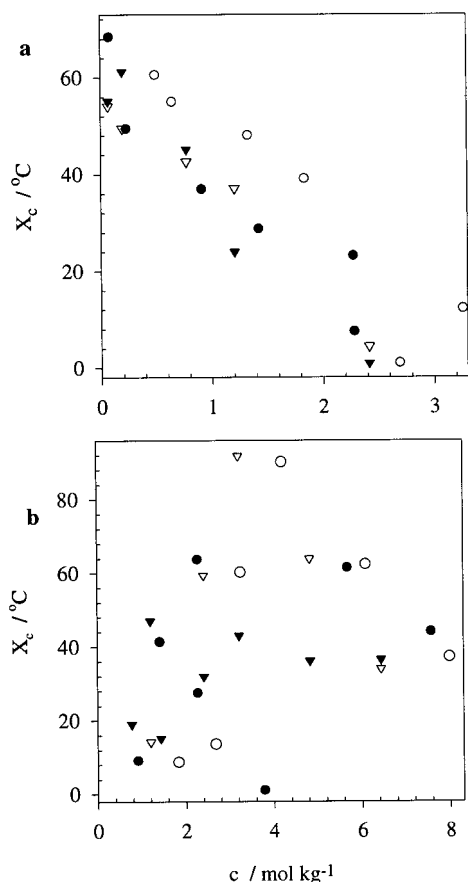
Figure 4. Changes of the X_c (a) and X_{cm} (b) for composite polymeric electrolytes as a function of salt concentration. Data are for (●) PEO–LiClO$_4$, (○) PEO–LiClO$_4$–PNNDMAA, (▽) PEO–LiClO$_4$–α-Al$_2$O$_3$, and (▼) PEO–LiClO$_4$–AlBr$_3$ electrolytes.
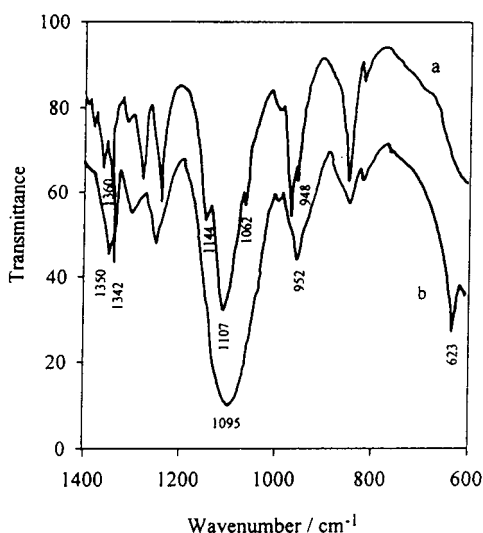
Figure 5. FT-IR spectra recorded for PEO–LiClO$_4$–a-Al$_2$O$_3$ composite electrolytes (O/M ratios equal to 300 (a) and 6 (b)) in the frequency range 1400–600 cm^{-1}.

observed at ∼ 1350 cm^{-1} is also split with two peaks at ∼1343 and 1360 cm^{-1}; this is evidence for the presence of a crystalline PEO phase.[23,24] For the sample with O/M = 6 single peaks observed at 1096 cm^{-1} (C–O–C region) and 1350 cm^{-1} (CH$_2$ wagging mode) suggest that the crystalline PEO phase is not present in this electrolyte. The downshift of the maximum of the C–O–C mode from the value of 1116 cm^{-1} recorded for the amorphous pure polyether phase[6,7,24] confirms interactions between PEO and salt leading to the formation of transient cross-

TABLE 2: Position of the Maximum of the C–O–C Stretch Vibration for PEO-Based Composite Electrolytes

O/M ratio	C–O–C stretch max/cm^{-1}			
	PEO–LiClO$_4$	PEO–LiClO$_4$–α-Al$_2$O$_3$	PEO–LiClO$_4$–AlBr$_3$	PEO–LiClO$_4$–PNNDMAA
300	1107	1107	1113	1108
100	1108	1107	1117	1108
25	1107	1106	1110	1108
16	1108	1108	1109	1108
10	1092	1095	1093	1097
8	1094	1099	1092	1092
6	1091	1096	1095	1097
4	1088	1099	1093	1098
3[a]	1114, 1080	1111, 1088	1108, 1088	1110, 1089

[a] A split of the C–O–C stretch vibration is observed for this salt concentration.
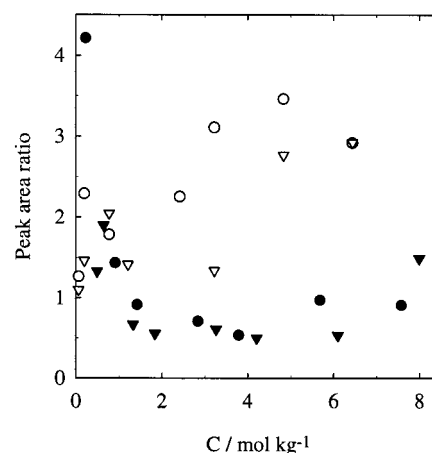
Figure 6. Ratio between the area of the peaks (in the C–O–C region) due to the uncomplexed PEO and PEO–LiClO$_4$ complex phase as a function of a salt concentration for (●) PEO–LiClO$_4$, (○) PEO–LiClO$_4$–PNNDMAA, (▽) PEO–LiClO$_4$–α-Al$_2$O$_3$, and (▼) PEO–LiClO$_4$–AlBr$_3$ electrolytes.

links which weaken the C–O polyether bonds. The IR C–O–C stretching region has been analyzed for all of the systems studied in order to monitor the polyether–salt interactions with the maxima of the C–O–C stretching occurring between 1110–1105 cm^{-1} for O/M ratios higher than 10 and then the shift down to ∼1095–1090 cm^{-1} for lower O/M ratios (see Table 2). The positions of the maximum of the C–O–C band are similar for all electrolytes studied with the same O/M ratio.

To analyze the C–O–C stretching region in greater depth the spectral features were fitted with a Gaussian–Lorentzian function using Grams 386 deconvolution software.[25] On the basis of this fitting procedure the intensities of the peaks due to the uncomplexed or modified PEO phase (i.e. those with a maxima at ∼1144, 1107, and 1062 cm^{-1}) are compared to the intensity of the peak maximum ∼1090–1075 cm^{-1} due to the PEO–LiClO$_4$ complex phase. The ratio of the area under the 1144, 1107, and 1062 cm^{-1} peaks due to uncomplexed or modified complex phase to the area under the 1090 cm^{-1} peak due to complex polyether as a function of salt concentration is shown in Figure 6. For samples containing PNNDMAA and α-Al$_2$O$_3$ the peak ratio is higher than 1 for the entire salt concentration range studied whereas for the PEO–LiClO$_4$ base electrolytes and composite systems containing AlBr$_3$ the peak ratio decreases from values higher than 1 for samples of low salt concentrations to values 0.3–0.4 for the high salt concentration range.

To study the ion–ion interactions the ν_4(ClO$_4^-$) mode appearing at ∼620–640 cm^{-1} has been analyzed using the same

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Figure 7. Fraction of spectroscopically "free" anions as a function of salt concentration for (●) PEO−LiClO₄, (○) PEO−LiClO₄−PNND-MAA, (▽) PEO−LiClO₄−α-Al₂O₃, and (▼) PEO−LiClO₄−AlBr₃ electrolytes.

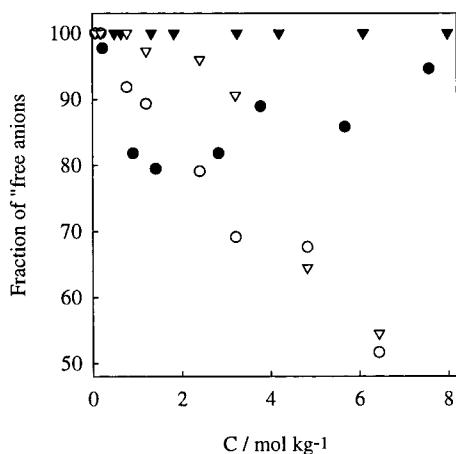procedure as previously applied to analyze the C−O−C stretch. The $\nu_4(ClO_4^-)$ envelope consists of two separate peaks with maxima at ∼624 and ∼632 cm⁻¹.[17] On the basis of previous studies[17] the 624 cm⁻¹ peak has been assigned to the ClO_4^- "free" anion vibrations and the 632 cm⁻¹ peak to the vibration of $Li^+ClO_4^-$ contact-ion pairs. In Figure 7 the ratio of the area under the 624 cm⁻¹ peak to the total area under the $\nu_4(ClO_4^-)$ envelope is shown as a function of salt concentration for all of the electrolytes studied (this ratio represents the fraction of spectroscopically "free" anions). For the base PEO−LiClO₄ electrolyte the peak ratio decreases with an increase in salt concentration for the samples of O/M ratio higher than 16 and then increases for higher salt concentrations. For the system with α-Al₂O₃ the peak ratio is over 0.9 for O/M ratios down to 6 and then decreases to ∼0.5−0.6 for the samples of O/M ratios equal to 4 and 3. A similar trend to that of the system with α-Al₂O₃ is observed for composite electrolytes containing PNNDMAA.

Discussion

As can be noted in Figure 1 at ambient and subambient temperatures, composite polymeric electrolytes as well as the base PEO−LiClO₄ system display a Λ vs $c^{0.5}$ variation typical for electrolytes based on low or medium permittivity solvents ($\epsilon < 20$).[19,20] The enhancement of ionic conductivity observed for composite systems containing PNNDMAA or α-Al₂O₃ corresponds to the region in which the concentration of filler is in the range of the molal salt concentration (see Table 1). In this region the fraction of the crystalline complex phase found for composite systems containing PNNDMAA and α-Al₂O₃ is lower than for the PEO−LiClO₄ electrolytes, as is evident from the DSC data (see Figure 4b). Also for these two composite systems the fraction of the crystalline PEO phase is higher than for the PEO−LiClO₄ base system as seen in Figure 4a. This observation is considered in light of the competition among the various Lewis acid−base reactions, i.e., those involving the filler acid or base centers, the base centers on the polyether, and ClO_4^- anion and the Li^+ cations hard acid centers.[5−7] Note that the concentration of PNNDMAA and α-Al₂O₃ roughly corresponds to an O/M ratio of 10. For higher salt concentrations the effect of fillers is less important due to an excess of the salt. DSC and conductivity results (see Table 1 for conversion of molal concentration to O/M ratios) agree well with the FT-IR analysis of the C−O−C stretching vibrations, which shows that for the

systems containing PNNDMAA and α-Al₂O₃ the ratio between the area under the peaks corresponding to the uncomplexed or modified PEO to the area under the peak characteristic for the complex phase is higher than 1 and higher than for the PEO−LiClO₄ and PEO−LiClO₄−AlBr₃ electrolytes. The low value of this ratio observed for the PEO−LiClO₄−PNNDMAA system of the low salt concentration can be explained by the occurrence of the peak characteristic for the PNNDMAA itself at 1096 cm⁻¹.[7] This peak overlaps with the peak of the complex phase and therefore affects the quantitative analysis of the FT-IR spectra.

It is also important to note that for composite electrolytes containing α-Al₂O₃ and NNPAAM the fraction of ion pairs is lower than for the PEO−LiClO₄ electrolytes in the region II in which the enhancement in ionic conductivity was observed (see Figure 7). For the base PEO−LiClO₄ system the fraction of free ions is roughly constant for O/M ratios above 8 and then increases slightly for higher salt concentrations (see Figure 7). This might be due to the redissociation of "free" ions occurring at high salt concentrations due to an increase in the system permittivity or dipole−dipole interactions as previously suggested by several authors.[11] For composite electrolytes containing α-Al₂O₃ and PNNDMAA the fraction of spectroscopically "free" anions or solvent separated ion pairs is higher than for the base PEO−LiClO₄ system for salt concentration up to ∼2 mol·kg⁻¹ (O/M ratio = 10). For higher salt concentrations the relative intensity of the ∼632 cm⁻¹ peak increases; thus the fraction of contact-ion pairs in these composite electrolytes increases. The increase in the fraction of contact-ion pairs, or possibly higher ionic aggregates, corresponds to the region in which salt concentration is higher than the concentration of the filler.

For composite systems containing AlBr₃ only a single peak at ∼623 cm⁻¹ is observed. This might be due to the presence of AlBr₃ and its effect on the system permittivity which results in a higher fraction of spectroscopically "free" anions. AlBr₃ also has an effect on the formation of the PEO−LiClO₄ complex phase. The position of the onset of the melting point of the crystalline complex phase is different for these composite systems than for the PEO−LiClO₄ electrolyte.[22] Moreover, AlBr₃ is capable of interaction with ClO_4^- anions leading to the formation of complex anions acting as plasticizers for the polyether host.[22]

On the basis of the observations, the following mechanisms for changes in molal conductivity are proposed. In the PEO−LiClO₄−PNNDMAA system there is a possibility of the formation of three different types of complexes.[7]

Type I complexes: polyether−Li^+−polyether complexes involving Lewis base ether oxygens from the polyether chain. These complexes incorporate transient cross-links between the polyether chains via alkali metal cations which stiffen the polyether host and reduce the electrolyte conductivity. These cross-links can be either intra-or intermolecular.[2,26,27]

Type II complexes: mixed polyether−Li^+−PNNDMAA complexes involving Lewis base ether oxygens from the polyether chain and Lewis base carbonyl oxygens from the PNNDMAA chain.

Type III complexes: PNNDMAA−Li^+−PNNDMAA complexes involving the Lewis base carbonyl oxygens of PNNDMAA. These cross-links can be either intra- or intermolecular.

For low salt concentrations up to ∼1 mol·kg⁻¹ the formation of type I complexes is limited, due to strong interactions between the PNNDMAA carbonyl oxygens and Li^+ cations. This is confirmed by the changes in the C=O vibrations. FT-IR studies

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of the C=O carbonyl region show that the position of the maximum of C=O stretch vibrations shifts to lower frequencies ($\sim$1623 cm^{-1}) compared with the pure PNNDMAA ($\sim$1640 cm^{-1}).[7] The position of this mode increases with an increase in salt concentration up to $\sim$1634 cm^{-1} for samples of the highest salt concentrations. The shift in the position of the C=O vibration confirms the interaction between PNNDMAA and LiClO$_4$ and therefore the possibility of the formation of type II and type III complexes. Therefore for salt concentrations up to $\sim$1 mol$\cdot$kg^{-1} most of the Li$^+$ cations should be involved in the interaction with PNNDMAA, thus causing a decrease in the conductivity of this composite system below values measured for the pure PEO–LiClO$_4$ electrolyte. On the other hand these interactions leave the ClO$_4^-$ anion unaffected, which leads to an increase in conductivity. The maximum in the conductivity is observed for systems for which the salt and filler concentrations are comparable. For higher salt concentrations there is an excess of LiClO$_4$ which results in the formation of ionic aggregates (see Figure 7), thus lowering the ionic conductivity which in this concentration range is very close to the conductivity of the PEO–LiClO$_4$ electrolytes. In the IIIrd region an increase in the C–O–C peak ratio between the uncomplexed or modified PEO phase and the PEO–LiClO$_4$ complex phase is noticed for these electrolytes. This increase is higher than can be expected on the basis of X_{mc} values calculated from DSC data (see Figure 4b). This might be due to the formation of type II mixed complexes, which can change the position of the maximum of C–O–C vibrations, thus increasing the peak ratio calculated on the basis of the procedure applied by us. On the other hand type II complexes can be crystalline, which results in a higher value of X_{mc}.

A different explanation of the changes in the conductivity is proposed for the other composite electrolytes, for which the acidic centers are capable of interacting with the base centers of the polyether chains. In accordance with a recent paper by Ferry et al.[12] there are at least two different types of sites available for the coordination of cations in the PEO. One is in which cations are preferentially coordinated in a crown ether type configuration, and the other, where cations are less tightly bonded. It is suggested that both α-Al$_2$O$_3$ and AlBr$_3$ acidic centers compete with Li$^+$ cations in coordinating to the base ether oxygens. In the case of AlBr$_3$, which is a stronger Lewis acid than the Li$^+$ cation, this leads to a decrease in ionic conductivity which is followed by an increase for higher salt concentrations. For composite electrolytes containing α-Al$_2$O$_3$ the addition of the filler limits the availability of oxygen sites for the Li$^+$ cations forcing them to occupy the less preferential ether oxygen sites that are more labile. This competition results in a decrease in the formation of the PEO–LiClO$_4$ complex phase and an increase in the fraction of "free" anions. Only for very high salt concentrations is an increase in ion aggregation observed for the PEO–LiClO$_4$–α-Al$_2$O$_3$ electrolytes; this results in a decrease in the conductivity compared with the PEO–LiClO$_4$ electrolyte.

The effect of a filler is to change the fraction of available oxygen sites which in turn results in changes in the formation of ionic aggregates. The region in which the enhancement of ionic conductivity is observed corresponds to a lowering of the fraction of contact-ion pairs and higher aggregates, which is due to the placement of filler molecules in the vicinity of the coordination sphere of Li$^+$ cations. The interactions described also result in changes in the phase structure of PEO, particularly in the lowering of the crystallinity. This has been observed previously by several authors.[4,5,9]

For all PEO-based electrolytes a change in the conduction mechanism from the partially thermally activated conduction to the VTF type conductivity mechanism has been observed at around 60 °C which corresponds to the melting temperature of the crystalline PEO phase. Above the melting point the amount of amorphous polyether phase is high enough to carry the conduction process. This explains why there is no enhancement in conductivity for composite electrolytes compared to the PEO–LiClO$_4$ system at 100 °C. For electrolytes with low salt concentrations the melting of the crystalline PEO phase is connected with an abrupt increase in conductivity whereas for high salt concentration only the knee point on the conductivity curve is observed.

Conclusions

It has been shown that the conductivity of the PEO–LiClO$_4$ electrolytes changes upon the addition of various organic or inorganic fillers. The changes in the conductivity result from the Lewis acid base interactions between the filler, Li$^+$ cations, and base centers on polyether oxygens. The effect of a filler is to change the fraction of available oxygen sites which in turn results in changes in the formation of ionic aggregates. The region in which the enhancement of ionic conductivity is observed corresponds to a lowering in the fraction of contact-ion pairs and higher aggregates which is due to the placement of filler molecules in a vicinity of the coordination sphere of Li$^+$ cations. The highest enhancement in the conductivity has been achieved for filler concentrations corresponding to the molal salt concentration.

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