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An Appraisal of Tetraethylsulfamide as Plasticizer for Poly(ethylene oxide)−$LiN(CF_3SO_2)_2$ Rubbery Electrolytes

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ABSTRACT: Tetraethylsulfamide (TESA), $(CH_3CH_2)_2NSO_2N(CH_2CH_3)_2$, is a nonvolatile liquid of moderate permittivity ($\epsilon = 29$) that exhibits a good stability toward reducing agents. This glass-forming liquid ($T_g = -111$ °C) is compared to propylene carbonate (PC, $\epsilon = 65$, $T_g = -110$ °C) as diluent for PEO−$LiN(CF_3SO_2)_2$ electrolytes based on high molecular weight ($M = 4 \times 10^6$) poly(ethylene oxide) (PEO). This study concerns amorphous mixtures with salt weight fractions fixed near the eutectic composition ($W_{salt} = 0.37$) of the PEO−salt binary system. It shows that, at 0 °C and up to 30% diluent (with respect to PEO), the conductivity elevation produced by TESA is about half that produced by PC. This difference is mainly due to the small T_g depression produced by TESA. This latter feature suggests that TESA is not as competitive as PC for lithium cation solvation. This situation is more severe at higher TESA contents where less and less PEO is available for cation solvation. Over this range, a neutral or a charged complex of very low mobility forms with TESA. Also examined is the effect of PC and TESA on the crystallization behavior of these salt-rich mixtures.

Introduction

Over the last decade, polyether rubbery electrolytes have found many applications, particularly as thin-film separators in all-solid lithium rechargeable batteries.[1,2] These electrolytes, however, are considerably less conductive than the aprotic, liquid electrolytes currently used in primary batteries. The reasons for this difference are twofold. First, polyethers have permittivities lower than polar aprotic solvents. This results in stronger ion−ion interactions that affect both salt dissociation and ion mobility. Second, rubbery polyether electrolytes have glass transition temperatures (T_g) much higher than their liquid counterparts. This leads to a situation where ion mobility decreases markedly with decreasing temperature. This feature is such that even the most dissociated of these electrolytes, for example those containing $LiN(CF_3SO_2)_2$ or $LiClO_4$, must be maintained at temperatures above 60 °C to allow efficient battery operation under high-power demands.[1]

The addition of low molecular weight solvating diluents has been considered as a viable solution to circumvent these limitations of polyether-based electrolytes.[3,4] Diluents with high permittivities such as propylene carbonate (PC, $\epsilon = 65$) or ethylene carbonate (EC, $\epsilon = 90$), which can simultaneously decrease T_g and promote salt dissociation, were among the first to be tested.[3−7] These dipolar diluents, however, are more aggressive toward lithium metal and insertion electrodes than aprotic ethers and polyethers ($\epsilon < 8$).[4,8] This drawback of PC or EC has stimulated research on nonvolatile diluents either of low polarity, such as oligoethers[9−11] and crown ethers,[12] or of intermerdiate polarity, such as aliphatic or aromatic diesters[13] and hybrid compounds based on oligoether-substituted EC.[14] Armand *et al.*[15] have suggested that tetraalkylsulfamides, which are known to be stable toward Grignard reagents and alkyllithium compounds,[16] could also act as less aggressive plasticizers in lithium rechargeable batteries. This work concerns tetraethylsulfamide, $(CH_3CH_2)_2NSO_2N(CH_2CH_3)_2$ (TESA, $\epsilon = 29$), which is a nonvolatile, glass-forming liquid having a T_g comparable to that of PC (−110 °C). The effect of this diluent on both T_g and conductivity will be compared to that of PC.

The polyethers currently used in solvent-free lithium rechargeable batteries are either high molecular weight copolymers or cross-linked networks, both containing a large fraction of ethylene oxide (EO) units.[1] Although high molecular weight PEO ($M > 1 \times 10^6$) is better suited for a basic study than random copolymers or networks that could be difficult to replicate from one laboratory to another, the main problem encountered with this polymer is crystallization.[17] Depending on the nature of the salt, intermediate crystalline compounds of various stoichiometries can form and persist over a temperature range well above the PEO melting point (69 °C). This feature is exemplified by the PEO−$LiCF_3SO_3$ system, in which a 3/1 (EO/Li) compound of high melting point (173 °C) partakes in a eutectic equilibrium at 58 °C with PEO.[18] For salt contents above the eutectic composition (EO/Li = 40), the liquidus curve of this compound precludes any conductivity study on diluent-free homogeneous mixtures at moderate temperatures. Less severe constraints are encountered with the PEO−$LiN(CF_3SO_2)_2$ and PEO−$LiClO_4$ systems, in which a 6/1 compound of low melting point (comparable to that of PEO) forms at moderate salt contents.[18] Furthermore, over the range from EO/Li = 8 to EO/Li = 12, the mixtures of theses systems, and particularly those containing $LiN(CF_3SO_2)_2$, are considerably less prone to crystallize than those of the PEO−$LiCF_3SO_3$ system. This feature is the main reason why we opted for the PEO−$LiN(CF_3SO_2)_2$ system in the present study.

Walker and Salomon[13] have already reported a comparative study performed on PEO−$LiN(CF_3SO_2)_2$ and PEO−$LiCF_3SO_3$ electrolytes diluted by PC, EC, dioctyl sebacate, and diethyl phthalate. As in other recent works devoted to PEO−diluent-salt mixtures,[10,12,14] the conductivity enhancement at low temperatures was quantified with respect to the semicrystalline PEO−salt mixtures. Since this enhancement was mainly due to the change in crystallinity, its magnitude (several orders in the case of $LiCF_3SO_3$) cannot help to understand the basic features associated with the presence of the diluent in the conducting phase. In this work, special attention was paid to the phase behavior of the binary

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and ternary systems involving PEO, and then a conductivity study was performed on homogeneous amorphous mixtures only. This study covers a temperature range (from 0 to 120 °C) wide enough to allow the separation of the plasticizing effect (T_g depression) from those related to the solvation properties of TESA and PC. The initial objective of this work was to investigate rubbery materials only, that is, electrolytes in which diluent diffusivity is small compared to that in highly swollen polyether networks.[19] However, due to a peculiar effect observed for the PEO−TESA−salt system (its conductivity at $T - T_g = 70$ °C exhibits a maximum near 30% diluent), the full range of compositions (up to 100% diluent) was examined for both diluents.

Experimental Section

Materials. $\mathrm{LiN(CF_3SO_2)_2}$ (3M) was dried under high vacuum for 24 h at 150 °C and for an additional 1 h at 170 °C. Before drying, the DSC curves of this salt exhibited a dehydration endotherm at 166 °C (40 J/g) followed by a fusion endotherm at 234 °C (46 J/g). The PEO samples (Aldrich, $M = 4 \times 10^6$ and 4×10^3) were dried under high vacuum for 48 h at 50 °C. PEO−salt binary mixtures were prepared under a dry atmosphere by mixing weighed quantities of 1−2% acetonitrile solutions of each component. Solvent evaporation was carried out in ampules connected to a vacuum system and the solvent-free mixtures were dried for 48 h at 140 °C. PEO−diluent binary mixtures were prepared by adding dried propylene carbonate (Aldrich 99.7%) or tetraethylsulfamide (Fluka 99%) to the melted polymer at 80 °C. After mechanical stirring under a dry atmosphere, aliquots of the mixtures were dissolved in deuterated acetonitrile and the diluent contents with respect to the polymer were determined by ^{1}H NMR analysis. PEO−diluent−salt ternary mixtures were prepared by adding PC or TESA to stirred acetonitrile solutions containing PEO (1−2%) and the salt. The ampules were connected to a vacuum system, and acetonitrile was slowly evaporated under reduced pressure (40 mmHg) over a period of 2−3 h at room temperature. This was followed by a second pumping under lower pressure (2 mmHg) for 48 h. As in the case of the PEO−diluent mixtures, the PC or TESA contents were determined by ^{1}H NMR analysis. After trial and error, this procedure allowed the preparation of a series of mixtures with fixed salt weight fractions ($W_{\mathrm{salt}} = 0.45 \pm 0.02$ for PC and $W_{\mathrm{salt}} = 0.35 \pm 0.02$ for PC and TESA).

DSC Measurements. The calorimeter (Perkin-Elmer DSC-4) was flushed with dry helium, and sample pans were filled and sealed under a dry atmosphere in a glovebox. Melting (or dissolution) endotherms and glass transition features were recorded at 10 and 40 °C/min, respectively. Melting (or dissolution) temperatures were read at the peak of the endotherms. Supercooled specimens were obtained by melt quenching at a cooling rate of 320 °C/min. The values of T_g were read at the intersection of the tangent drawn through the heat capacity jump with the base line recorded before the transition. T_g reproducibility was within ±1 deg.

Conductivity Measurements. The electrolytes were contained in cells consisting of two stainless steel solid cylinders encapsulated at both ends of a Teflon ring.[20] The temperature of the electrolytes was measured with an accuracy of ±0.2 deg by means of a thermocouple inserted in a well dug in the body of the cells. The real part, Z', and the imaginary part, Z'', of the complex impedance of the cells were measured over the frequency range 5 Hz to 13 MHz by using a Model 4192A Hewlett-Packard impedance analyzer. The bulk dc resistance of the electrolyte was determined as the point where the high-frequency semicircle in the plot of Z'' as a function of Z' cuts the Z' axis. For each electrolyte, measurements were made in duplicate on distinct cells. For the rubbery materials, the reproducibility was better than 5% and no hysteresis was observed upon heating and cooling the cells. More accurate data were obtained for the liquid materials containing large amounts of diluent. In that case, as well as for standard KCl aqueous solutions, the reproducibility was better than 1%.

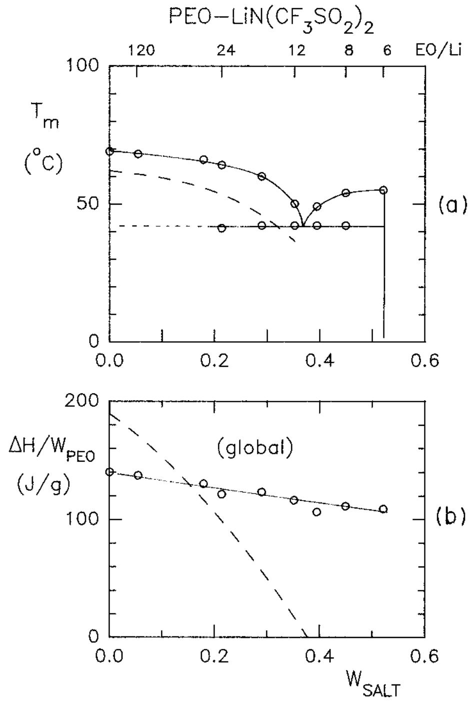

Figure 1. (a) Partial phase diagram showing the eutectic equilibrium between PEO ($M = 4 \times 10^6$) and the 6/1 ($W_{\mathrm{salt}} = 0.52$) intermediate compound characteristic of $\mathrm{LiN(CF_3SO_2)_2}$. (b) Global enthalpy of fusion/dissolution per gram of PEO recorded on the same mixtures. Dashed lines in (a) and (b) correspond to the single solid−liquid equilibrium (PEO liquidus curve) previously reported for a low molecular weight PEO ($M = 4 \times 10^3$).[18]

Results and Discussion

1. Physical Behavior. (a) Crystallinity. A complete phase diagram of the PEO−$\mathrm{LiN(CF_3SO_2)_2}$ system has been reported in a former work dealing with a low molecular weight PEO ($M = 4 \times 10^3$, $T_m = 62$ °C).[20] This diagram displayed solid−liquid equilibria related to PEO and to 6/1, 3/1, and 2/1 (EO/Li) intermediate compounds of low melting points (46, 85, and 110 °C, respectively). Although the mixtures were allowed to crystallize for a long period at room temperature, those over the range from EO/Li = 64 to EO/Li = 12 consisted of a decreasing amount of crystalline PEO in equilibrium with an amorphous phase of invariant stoichiometry (EO/Li = 11). As shown in another work,[18] mixtures with global compositions just above this range (EO/Li = 10 and 8) were noncrystallizable even at 5 °C. However, a sharp change occurred once the 6/1 stoichiometry was reached. This composition and those with more salt yielded highly crystalline materials, allowing the characterization of the three intermediate compounds.

The upper plot in Figure 1 shows a partial phase diagram constructed over the range from the neat polymer to EO/Li = 6 with a high molecular weight PEO ($M = 4 \times 10^6$, $T_m = 69$ °C). After a long standing at room temperature, no T_g features could be recorded on the mixtures of this system. Futhermore, over the range from EO/Li = 24 to EO/Li = 8, an endotherm recorded at 42 °C could be attributed to a eutectic equilibrium between PEO and the 6/1 compound. It may be seen that the eutectic liquid has the same composition (EO/Li = 11) as the amorphous phase in the former system. The PEO liquidus curve related to the present polymer is shifted to temperatures 7−12 deg higher than those reported in the former work (dashed line). This feature, which also applies to the melting point of the 6/1 compound (55 °C instead of 46 °C), is due to the increase in the thickness of the crystalline lamellae with increasing PEO molecular weight.

Above a certain salt content (EO/Li = 24), all the mixtures depicted in Figure 1 could be supercooled by melt quenching. In their fully amorphous state, their T_g data were only 2 deg higher than those of the low molecular weight PEO. On this basis, it may be argued that the shift of the solid−liquid equilibrium to higher temperatures has opened a temperature window above T_g that is now favorable to a eutectic crystallization between PEO and the 6/1 compound. Note that the PEO−$LiClO_4$ system, whose the 6/1 compound melts at a higher temperature than the present one (70 °C for a $M = 4 \times 10^3$ PEO), is free from this complication.[18] In a recent work by Fauteux and McCabe,[21] mixtures of a high molecular weight PEO ($M = 9 \times 10^5$) with LiN(CF_3SO_2)$_2$ were also claimed to exhibit a eutectic melting over the range below the 6/1 stoichiometry. However, the endotherms recorded by these authors were located at lower and more dispersed temperatures (10−25 °C) than the present ones (42 °C). This departure is probably due to moisture contamination since they misintrepreted the dehydration endotherm of LiN(CF_3SO_2)$_2$ as the melting point of this salt.

The lower plot in Figure 1 shows the global enthalpy of fusion/dissolution per gram of PEO recorded over the range from 30 to 70 °C for the present mixtures. The finite value of this quantity (110 J/g) near the composition EO/Li = 11 confirms that the peaks recorded at 42 °C correspond to a eutectic equilibrium. Strong T_g features were previously reported over the range from EO/Li = 12 to EO/Li = 8 for PEO−LiN(CF_3SO_2)$_2$ mixtures prepared with a $M = 9 \times 10^5$ high molecular weight PEO.[22,23] The present study shows that after a long standing at room temperature such mixtures can reach a degree of crystallinity comparable to those of the PEO/$LiClO_4$ system. Furthermore, as will be shown shortly, and as exemplified by Fauteux and McCabe for an unknown diluent,[21] a sizable cristallinity can develop in these mixtures even in the presence of a diluent.

The PEO−diluent and PEO−diluent−salt mixtures were also allowed to crystallize for a long period (1−2 months) at room temperature. Figure 2 shows that for diluent contents up to 75% by weight, the melting point lowering of PEO due to the presence of PC or TESA in the PEO−diluent binary systems does not exceed 20 °C. At the same time, the enthalpy of fusion per gram of polymer increases toward the value of 203 ± 4 J/g expected for a 100% crystalline PEO.[24] This rise in crystallinity results from chain disentanglement due to the dilution. In their neat form, neither of the present diluents did crystallize upon slow cooling in the DSC apparatus. However, TESA exhibited a crystallization exotherm (near −75 °C) and subsequent endotherms (at −45 and −35 °C) when heated from the vitreous state. The same features applied to the mixtures containing more than 40% TESA.

For the physical study of the PEO−diluent−salt ternary systems, we opted to vary the diluent content while keeping the salt weight fraction constant at 0.45 for PC and 0.35 for TESA. In diluent-free PEO, these salt contents correspond to molar ratios EO/Li = 8 and EO/Li = 12, respectively. They are located on either side of the eutectic composition in the phase diagram of the PEO−salt system. Figure 3 shows that the dissolution temperature of the polymeric phases in the PC-based ternary system remains invariant at 55 °C up to a diluent in polymer content of 25%. Further addition of PC contributes to lower the dissolution temperature, and above the 45% composition no endotherms could be recorded on the DSC curves. The calorimetric diagram shows that the enthalpy of dissolution per gram of polymer first exhibits a small decrease (at 7% PC) and then re-increases to exhibit a maximum near 12% PC. This latter effect, which is probably due to chain disentanglement, is followed by a sharp decrease in crystallinity over the range 15−25%.

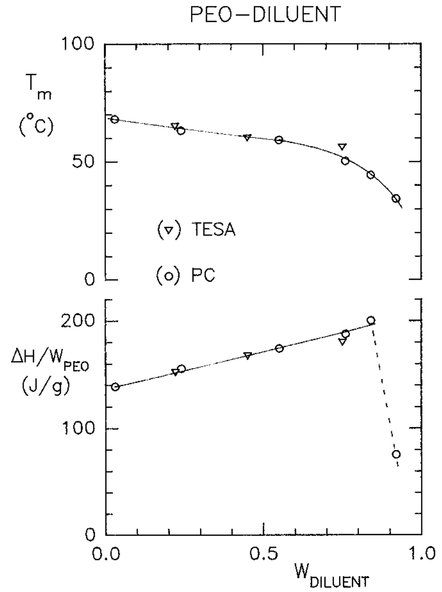

Figure 2. PEO liquidus curve and enthalpy of dissolution per gram of PEO for the binary systems PEO−PC and PEO−TESA.

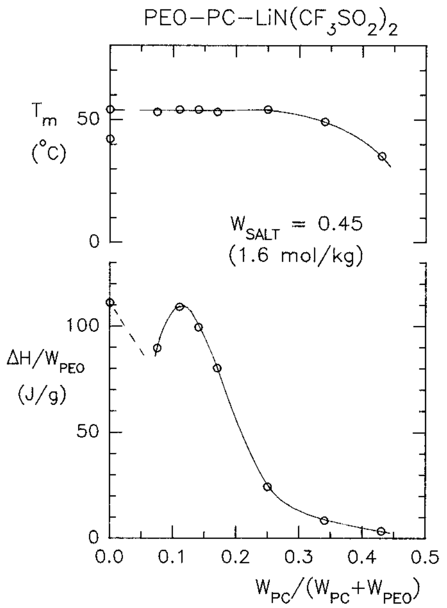

Figure 3. Liquidus curve and enthalpy of dissolution per gram of PEO for the PEO−PC−LiN(CF_3SO_2)$_2$ ternary system with $W_{salt} = 0.45$. The data are plotted as a function of diluent weight fraction with respect to PEO. The diluent-free mixture is defined according to the data in Figure 1.

A similar but more accentuated initial decrease in crystallinity occurs for the PEO−TESA−salt system (Figure 4). Although this feature is followed by a maximum near the 30% composition, the amplitude of this maximum is about half that observed for the PEO−PC−salt system. At the same time, the dissolution

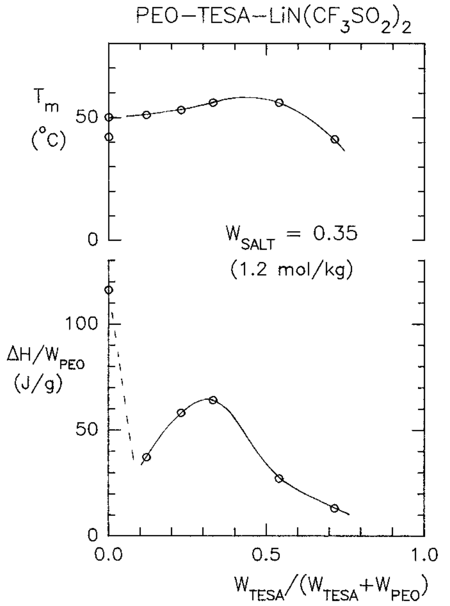

Figure 4. Liquidus curve and enthalpy of dissolution per gram of PEO for the PEO−TESA−LiN(CF$_3$SO$_2$)$_2$ system with W_{salt} = 0.35. Same remarks as in Figure 3.

temperature, which is initially the same as that of the PEO phase in the PEO−salt sytem (50 °C), increases progressively to pass through a maximum (57 °C) near the 50% composition. Note that the main thermal event in the related diluent-free mixture (EO/Li = 12 in Figure 1) is the eutectic equilibrium at 42 °C. This suggests that a small amount of diluent (less than 10%) hinders eutectic crystallization. This feature probably applies to both PC and TESA. The difference, however, is that a much larger amount of TESA (85% compared to 45% for PC) is required to inhibit all crystallization at room temperature. This latter effect results from the fact that above a certain diluent content the liquidus curves of these systems exhibit an abrupt fall below room temperature. Therefore, at any composition and temperature where a crystalline phase is present, this phase is in equilibrium with a liquid phase and its relative amount decreases with increasing diluent content. This effect, which opposes the crystallinity increase due to chain disentanglement, accounts for the crystallinity maximum in Figures 3 and 4.

A crystallinity maximum is also observed for the PEO−PC binary system (Figure 2). This maximum takes place at a much higher diluent content (85%) than in the foregoing ternary systems because the abrupt fall in the PEO liquidus curve is located near 100% PC. A similar feature probably applies to the PEO−TESA system which was studied up to 75% diluent only. Thermodynamically, this feature does not mean that PC and TESA are poor solvents for PEO. Comparable liquidus curves have been reported for polymer−diluent systems (e.g., polyethylene−xylene) in which the diluent is a good solvent for the polymer.[25] Such a small depression in melting point up to a large amount of diluent is essentially due to the large enthalpy of fusion of the polymer on a molar basis.

The main effect due to the presence of the salt is to displace the abrupt fall in the liquidus curves to lower amounts of diluent. This effect, which results from a change in the activity of the polymer in the liquid phase, strongly depends on the salt content. For instance, the solid phase in 35% PC mixtures with W_{salt} = 0.45, 0.35, and 0.26 (EO/Li = 18 in neat PEO) exhibited enthalpies of dissolution of 7, 19, and 62 J/g of polymer, respectively. Once melted, the latter mixture crystallized readily upon its cooling at 5 °C/min in the DSC apparatus. Such a rapid crystallization, which started near 20 °C, was not observed for the ternary mixtures depicted in Figures 3 and 4. All these mixtures remained supercooled for a period long enough to allow conductivity measurements down to 0 °C in the homogeneous state.

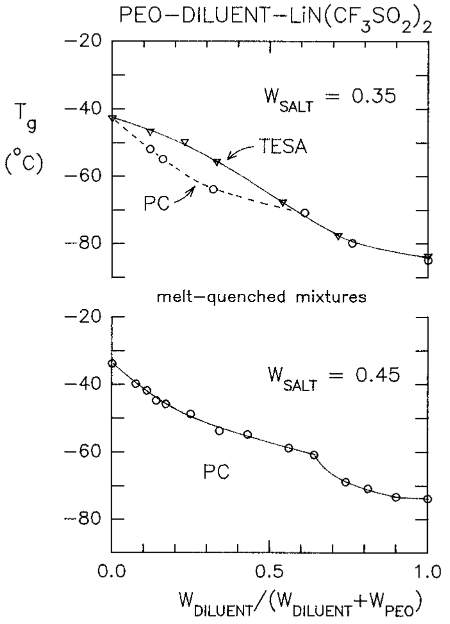

Figure 5. T_g−composition relationships for melt-quenched amorphous mixtures of the PEO−PC−salt and PEO−TESA−salt systems with W_{salt} = 0.35 (upper plot) and W_{salt} = 0.45 (lower plot, for PC only).

(b) T_g−Composition Relationships. Over the range from zero to 60% diluent, PC is a better plasticizer than TESA in the supercooled mixtures of the present systems. This may be seen in the upper part of Figure 5, where T_g data obtained for W_{salt} = 0.35 are plotted as a function of the diluent content. At this salt concentration, 33% of PC produces a T_g depression of 21 °C compared to 12 °C for TESA. The main difference between these two systems lies in the initial curvature of the plots, which is negative for TESA and positive for PC. Above 60% diluent, however, there is a change in both curvatures and the data merge on a common plot. A more detailed study performed on the PC-based system with W_{salt} = 0.45 is presented in the lower part of Figure 5. It may be seen that a sharp change in curvature occurs just above the 60% composition. This change was accompanied by a broadening of the T_g features over the range from 40% to 80% PC.

A similar feature, as well as a T_g splitting over a range of compositions, has been reported for optically clear mixtures of many polymer−diluent systems.[26−28] NMR and mechanical relaxation studies performed at moderate diluent contents (15−20%) on some of these systems have shown that a substantial fraction (more than 30%) of the diluent molecules still exhibited high mobility at temperatures well below the T_g measured by DSC.[28] This was evidenced by a fast and a slow component in the NMR relaxation data of the diluent, as well as by a broad peak at low temperatures in the loss component of the shear modulus data. For some of these systems [e.g., polystyrene (T_g = 103 °C)−tricresyl phosphate (T_g = −68 °C)], further dilution leads to a situation where the highly mobile diluent molecules form microdomains large enough to yield a separate low-T_g feature on the DSC curves.[26,27] At the same time, the high-T_g feature associated with the solvated polymer broadens and shifts toward the low-T_g feature to finally disappear above a certain diluent content.[27] For other systems [e.g., poly(vinyl chloride) (T_g = 85 °C)−dibutyl phthalate (T_g = −98 °C)], a T_g broadening instead of a T_g splitting takes place over a range of compositions.[27] As for the present systems, this broadening is accompanied by a sharp change in the curvature of the T_g−composition relationship.

By analogy with these systems, it may be argued that the negative curvature observed over the range from zero to 60% TESA means that a larger fraction of the molecules of this diluent remain highly mobile at temperatures below the T_g measured by DSC. If this interpretation is correct, the higher T_g observed for the TESA-based system suggests a preferential solvation of the salt by the polymer. Therefore, TESA is not as effective as PC to destroy the transient network produced by the salt. It is also likely that above the 60% diluent composition, which roughly corresponds to the change in curvature for both PC and TESA, the T_g data no longer reflect the relaxation of the polymer moiety. In either case, T_g is only 5 deg higher for 75% diluent than for 100% diluent. For compositions over the range 80−100% diluent (studied for the PC-based system only), the T_g feature was as narrow as that of pure PC.

2. Conductivity Behavior. It is well-known that the conductivity (σ) of amorphous polyether electrolytes decreases exponentially with decreasing temperature toward T_g. This feature, which indicates that free volume plays a determinant part on the ion mobility, is successfully described by the empirical Vogel−Tammann−Fulcher (VTF) equation for fluidity of glass-forming liquids. When the VTF equation is applied to conductivity, it leads to the familiar equation:[2]

$$\sigma(T) = A \exp-[B/(T - T_o)] \qquad (1)$$

where A is a constant related to charge carrier density, B is a constant equivalent to a pseudoenergy of activation, and T_o is the ideal glass transition temperature.

As illustrated in Figure 6 for the PC-based system, fits of eq 1 to the conductivity data of the present electrolytes yield nearly parallel plots over the full range of diluent contents. In this illustration, T_o is adjusted to the quantity (T_g − 25) °C, which, within ±10 deg, corresponds to the best fits obtained for all the compositions, including those of the TESA-based system. In these best fits we noted no systematic variations in either B or (T_g − T_o) with increasing diluent content. The average value of B was 790 ± 90 K for the former system and 890 ± 110 for the latter. Recently, similar values of B (875 ± 90 and 801 ± 25 K) were reported by MacFarlane *et al.*[11] for $LiClO_4$ (1 mol/kg) in a PEO-cross-linked network containing various amounts of PC and tetraglyme. It thus appears that this quantity is roughly independent of the nature of the diluent in concentrated PEO−diluent−LiX electrolytes. If preferential solvation of the salt by the diluent or the polymer plays a part in the temperature dependence of σ, this effect is overwhelmed by the free volume effect related to T_g.

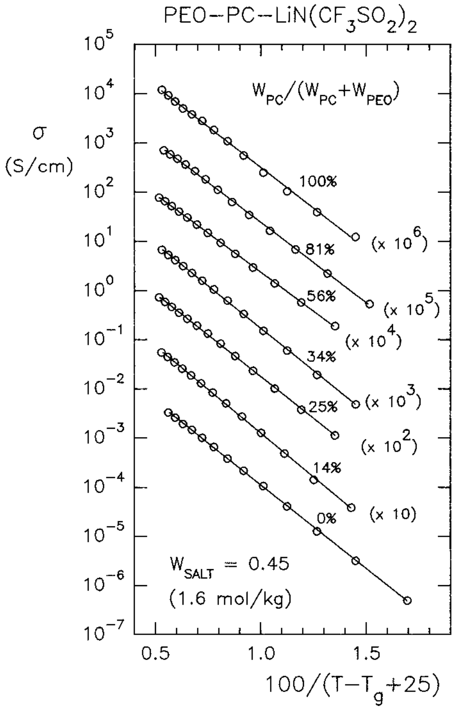

Figure 6. Fits of eq 1 to the conductivity data of the PEO−PC−salt system with W_{salt} = 0.45. In these fits, T_o is adjusted to the quantity T_g − 25 °C. See text for detail.

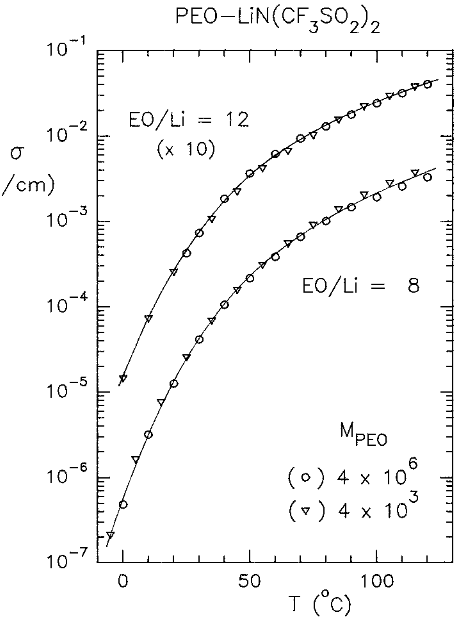

Figure 7. Conductivity data of PEO−LiN(CF_3SO_2)$_2$ amorphous mixtures of composition EO/Li = 12 (W_{salt} = 0.35) and EO/Li = 8 (W_{salt} = 0.45) for a high (M = 4 × 10^6) and a low (M = 4 × 10^3) molecular weight PEO.

In Figure 6, the actual temperatures cover a range of 120 deg for each composition. The lowest temperature is 0 °C for 0%, 14%, and 25% PC, −10 °C for 34% and 56% PC, and −30 °C for 81% and 100% PC. Such low-temperature measurements could also be made on fully amorphous mixtures containing TESA. However, the diluent-free mixture (EO/Li = 12) related to this system did not remain supercooled for a time long enough to allow its study below 25 °C. Its crystallization gave rise to a negative departure from the linear VTF behavior observed at higher temperatures. We noted that under supercooling, PEO−salt mixtures prepared with the present PEO (M = 4 × 10^6) have conductivities nearly identical to those prepared with a M = 4 × 10^3 low molecular weight PEO. This feature, which is illustrated in Figure 7 for the compositions EO/Li = 8 and 12, also applied to a less concentrated EO/Li = 128 mixture. It shows that down to a salt concentration of

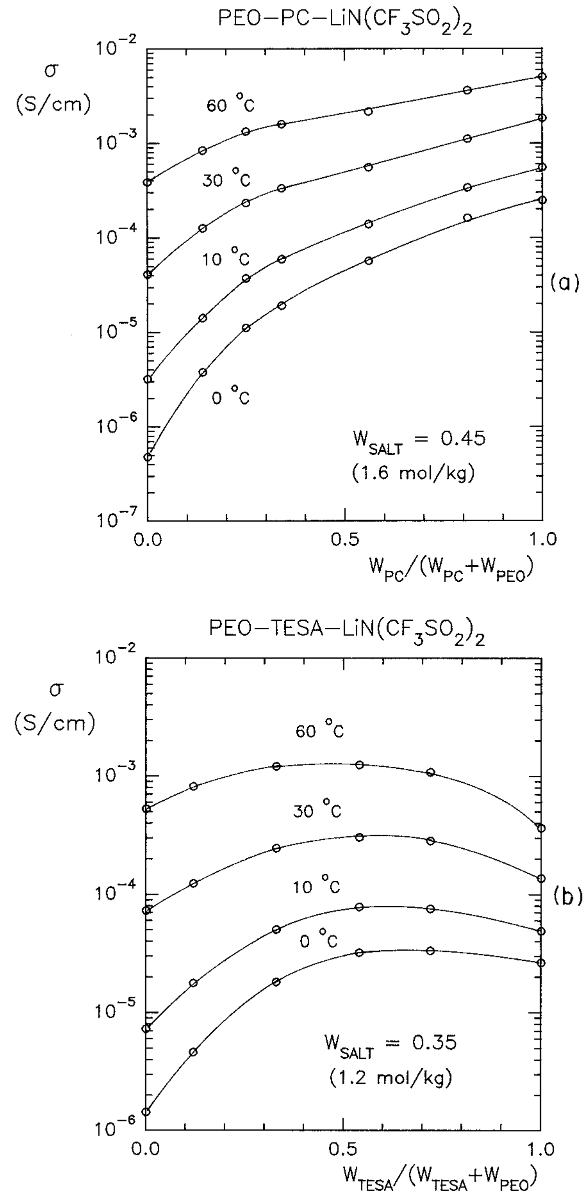

Figure 8. Conductivity isotherms of the PEO–PC–salt system with $W_{salt} = 0.45$ (a) and the PEO–TESA–salt system with $W_{salt} = 0.35$ (b). The data, which correspond to fully amorphous mixtures, are plotted as a function of diluent weight fraction with respect to PEO.

0.2 mol/kg (EO/Li = 128), the hydroxy end groups (2 mol %) in the low molecular weight PEO have no sizable effect on the conductivity. Since the EO/Li = 12 mixture prepared with this polymer remained supercooled for a long period even at 0 °C, its conductivity data at this temperature and at 10 °C will be used to quantify the effect produced by TESA under subambient conditions. Conductivity isotherms including these two temperatures are depicted in Figure 8 for both the PC-based and TESA-based ternary systems.

As a consequence of the VTF behavior of these two systems, the decrease in conductivity with decreasing temperature is strongly dampened with increasing diluent content. Near the 20% diluent composition, this dampening is roughly comparable to that produced by a shift of 10 deg to higher temperatures in the temperature scale of the diluent-free materials. Up to this composition, plasticization (T_g lowering) appears to be the main factor that governs the conductivity magnitude. With further dilution, however, conductivity becomes seriously affected by the nature of the diluents.

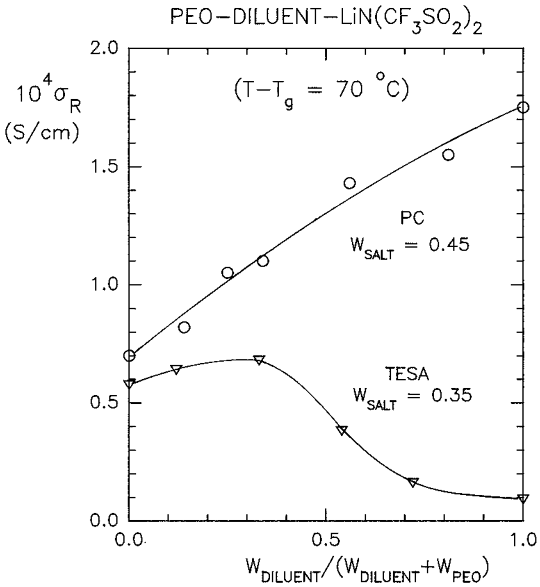

Figure 9. Reduced conductivity ($\sigma_R = \sigma$ at $T - T_g = 70$ °C) for the PEO–PC–salt system with $W_{salt} = 0.45$ and the PEO–TESA–salt system with $W_{salt} = 0.35$. Same remarks as in Figure 8.

A large amount of TESA is not favorable to a high conductivity. It may be seen that above a certain temperature (60 °C), the 100% TESA mixture ($T_g = -84$ °C) is less conductive than the corresponding 100% PEO mixture ($T_g = -43$ °C). This contrasts with the 100% PC mixture ($T_g = -74$ °C), whose the conductivity at 60 °C is 1 order of magnitude greater than that of the corresponding 100% PEO mixture ($T_g = -34$ °C).

This particular behavior of TESA cannot be explained on the sole basis of its physical properties. Although the viscosity of this diluent ($\eta = 4.2$ cP) is greater than that of PC ($\eta = 2.5$ cP), its permittivity ($\epsilon = 29$) is intermediate between those of PEO ($\epsilon = 5$) and PC ($\epsilon = 65$). Therefore, one must consider that TESA forms either a neutral complex or a charged complex of very low mobility with the salt. This feature is confirmed by Figure 9, in which a comparison is made of the conductivity data of the two systems at the same reduced temperature ($T - T_g$) of 70 °C. The resulting reduced conductivity (σ_R), which corresponds to conditions of local isoviscosity, allows a clear separation of this effect specific to TESA from that related to T_g. Although σ_R increases gradually with increasing PC content, it exhibits a complex change with increasing TESA content. It first passes through a maximum of small amplitude near 33% TESA to decrease markedly toward an asymptotic value, which is 6 times lower than that of the diluent-free material. In comparison, the value of σ_R for 100% PC is 2.5 times greater than that of the diluent-free material.

The maximum of σ_R at 33% TESA corresponds to a molar ratio EO/Li = 8 (EO/TESA = 10), which is close to the composition (EO/Li = 6) above which an abrupt decrease in σ_R was also reported for the PEO–LiN(CF_3SO_2)$_2$ system.[20] Since the latter feature was attributed to the depletion in free EO units in the diluent-free materials (full complexation of PEO was estimated to correspond to EO/Li = 3.5),[20] the present data seem to confirm that LiN(CF_3SO_2)$_2$ is preferentially solvated by PEO in the mixtures containing TESA. Such a preferential solvation was already proposed to explain that TESA produces a smaller T_g depression than PC over the range from zero to 60% diluent (EO/Li = 5, EO/

TESA = 3). Therefore, the maximum of σ_R for TESA is probably due to the increase in local permittivity with increasing TESA content, on the one hand, and to the decline in free EO units that forces the displacement of the solvation equilibrium in favor of TESA, on the other hand.

The continuous rise in σ_R for the PEO−PC−salt system suggests that the ions in the complex formed with PC are not as associated as in the complex formed with either TESA or PEO. However, since σ_R is only 2.5 times greater in 100% PC than in 100% PEO, the difference with respect to PEO is not spectacular. Measurements performed at the same salt content as for the PEO−TESA−salt system (1.2 mol/kg instead of 1.6 mol/kg) yielded a greater difference between 100% PC and 100% PEO (a factor of 6.4 instead of 2.5). This indicates that ion−ion interactions play a substantial part in the σ_R data of Figure 9. These latter measurements also show that σ_R is 40 times greater in 100% PC than in 100% TESA for $W_{\text{salt}} = 0.35$ (1.2 mol/kg). Since these two PEO-free electrolytes have essentially the same T_g (upper plot in Figure 5), this difference also applies to their absolute conductivities (σ).

In a recent study performed on PC−LiN(CF_3SO_2)$_2$ and TESA−LiN(CF_3SO_2)$_2$ liquid electrolytes at 25 °C, Perron *et al.*[29] have observed a conductivity maximum near 0.6 mol/kg for PC and near 0.3 mol/kg for TESA. These maxima (5×10^{-3} S/cm for PC and 9×10^{-4} S/cm for TESA) are in agreement with a greater ion association in TESA. These workers have also investigated another tetraalkylsulfamide, $(CH_3)_2NSO_2N(CH_2CH_3)_2$, in which two of the four ethyl groups of TESA are asymmetrically substituted by methyl groups. In this solvent, which has a higher permittivity ($\epsilon = 41$) than TESA, conductivity of LiN(CF_3SO_2)$_2$ at 0.3 mol/kg (1.7×10^{-3} S/cm) is greater than in TESA. We noted that this sulfamide and its symmetrically substituted isomer ($\epsilon = 44$) are glass-forming liquids with T_g's of −122 and −130 °C, respectively. Preliminary results obtained for PEO electrolytes containing these diluents are more encouraging than those related to TESA. Over the range 10−20% diluent, their conductivities are higher than those obtained with PC. The study of these new diluents is in progress.

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References and Notes

(1) Armand, M.; Sanchez, J. Y.; Gauthier, M.; Choquette, Y. In *Electrochemistry of Novel Materials*; Lipkowski, J., Ross, P. N., Eds.; VCH Publishers: New York, 1994; p 65.

(2) Gray, F. M. *Solid Polymer Electrolytes*; VCH Publishers: New York, 1991.

(3) Kelly, I.; Owen, J. R.; Steele, B. C. H. *J. Power Sources* **1985**, *14*, 13.

(4) Munshi, M. Z. A.; Owens, B. B. *Solid State Ionics* **1988**, *26*, 41.

(5) Cameron, G. G.; Ingram, M. D.; Sarmouk, K. *Eur. Polym. J.* **1990**, *26*, 1097.

(6) Ballard, D. G. H.; Cheshire, P.; Mann, T. S.; Przeworski, J. E. *Macromolecules* **1990**, *23*, 1256.

(7) Huq, R.; Farrington, G. C.; Koksbang, R.; Tonder, P. E. *Solid State Ionics* **1992**, *57*, 277.

(8) Croce, F.; Panero, S.; Passerini, S.; Scrosati, B. *Electrochim. Acta* **1994**, *39*, 255.

(9) Morita, M.; Fukumasa, T.; Motoda, M.; Tsutsumi, H.; Matsuda, Y.; Takahashi, T.; Ashitaka, H. *J. Electrochem. Soc.* **1990**, *137*, 3401.

(10) Wang, C.; Liu, Q.; Cao, Q.; Meng, Q.; Yang, L. *Solid State Ionics* **1992**, *53−56*, 1106.

(11) MacFarlane, D. R.; Sun, J.; Meakin, P.; Fasoulopoulos, P. Hey, J.; Forsyth, M. *Electrochim. Acta* **1995**, *40*, 2131.

(12) Nagasubramanian, G.; Di Stefano, S. *J. Electrochem. Soc.* **1990**, *137*, 3830.

(13) Walker, C. W., Jr.; Salomon, M. *J. Electrochem. Soc.* **1993**, *140*, 3409.

(14) Lee, S. H.; Yang, X. Q.; McBreen, J.; Xu, Z. S.; Skotheim, T. A.; Okamoto, Y. *J. Electrochem. Soc.* **1994**, *141*, 886.

(15) Armand, M.; Gauthier, M.; Muller, D. European Patent No. 87402441.7, 1987.

(16) Richey, H. G., Jr.; Farkas, J., Jr. *J. Org. Chem.* **1987**, *52*, 479.

(17) Robitaille, C. D.; Fauteux, D. *J. Electrochem. Soc.* **1986**, *133*, 315.

(18) Vallée, A.; Besner, S.; Prud'homme, J. *Electrochim. Acta* **1992**, *37*, 1579.

(19) Clericuzio, M.; Parker, W. O., Jr.; Soprani, M.; Andrei, M. *Solid State Ionics* **1995**, *82*, 179.

(20) Lascaud, S.; Perrier, M.; Vallée, A.; Besner, S.; Prud'homme, J.; Armand, M. *Macromolecules* **1994**, *27*, 7469.

(21) Fauteux, D.; McCabe, P. *Polym. Adv. Technol.* **1995**, *6*, 83.

(22) Armand, M.; Gorecki, W.; Andréani, R. In *Second International Symposium on Polymer Electrolytes*; Scrosati, B., Ed.; Elsevier Applied Science: New York, 1990; p 91.

(23) Gorecki, W.; Jeannin, M.; Belorizky, E.; Roux, C.; Armand, M. *J. Phys. Condens. Matter* **1995**, *7*, 6823.

(24) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1980; Vol. 3, p 67.

(25) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 574.

(26) Riande, E.; Markovitz, H.; Plazek, D. J.; Raghupathi, N. *J. Polym. Sci., Polym. Symp.* **1975**, *50*, 405.

(27) Scandola, M.; Ceccorulli, G.; Pizzoli, M. *Polymer* **1987**, *28*, 2081.

(28) Cauley, B. J.; Cipriani, C.; Ellis, K.; Roy, A. K.; Jones, A. A.; Inglefield, P. T.; McKinley, B. J.; Kambour, R. P. *Macromolecules* **1991**, *24*, 403.

(29) Perron, G.; Brouillette, D.; Pesant, M.; Desnoyers, J. E. Unpublished results.

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