

Preferential solvation and free volume as interrelated features governing ion conduction in plasticised polyether electrolytes

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Abstract

This work concerns the relationship between the T_g depression and the conductivity elevation produced by various dipolar diluents in $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ rubbery electrolytes based on high molecular weight poly(ethylene oxide) (PEO). Some of these diluents are tetraalkylsulfamides, $(\text{R}_1\text{R}_2\text{NSO}_2\text{NR}_3\text{R}_4)$, which are known to be stable toward strong reducing agents, but which lead to associated ionic species in the absence of PEO. The other diluents are propylene carbonate and γ -butyrolactone, which are known to yield high conductivities under the same conditions. For a fixed salt content (1.2 mol kg^{-1}), plots of T_g as a function of the diluent content show two distinct regions. One in which the T_g depression does not depend markedly on the physical properties of the diluents, and one in which these properties become dominant. At low diluent contents in the first region (0–20 wt.% with respect to PEO), the conductivity elevation essentially depends on the T_g depression. In agreement with other works, this feature indicates that the lithium ions are preferentially coordinated to PEO. An analysis made in terms of the conductivity at $T = T_g + 70^\circ\text{C}$ shows sudden changes above this range that suggest an initial regime in which the diluent molecules have a low diffusivity. This feature should make these electrolytes (particularly those plasticised by small amounts of sulfamides) less aggressive toward lithium and insertion electrodes than their gelled, diluent-rich counterparts. A second study performed on poly(propylene oxide) electrolytes shows that the microphase separation phenomenon characteristic of these electrolytes persists upon diluent addition. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Plasticisers; Lithium imide; Polyether electrolytes

1. Introduction

Large scale secondary batteries, particularly those intended for electric vehicles, must sustain high power demands. This requirement, as well as cyclability and safety, is already fulfilled by lithium batteries based on rubbery polyether electrolytes [1,2]. Yet, these all-solid devices must operate above a certain temperature, otherwise electrolyte conductivity and electrode activity become limiting factors under high power demands. The conductivity constraint is mainly due to the high T_g (glass transition temperature) of the polyether electrolyte. Although non-volatile, low molecular weight dipolar diluents can be used to depress T_g and to increase permittivity (ϵ) [3–8], their nature and their amount must be optimised to preserve electrode stability and safety. Previous tests reported on $\text{Li-V}_6\text{O}_{13}$, Li-TiS_2 and $\text{Li-Mn}_2\text{O}_4$ cells based on plasticised polyether electrolytes [3] or gelled polyacrylonitrile

electrolytes [8] show that usual aprotic dipolar solvents such as propylene carbonate (PC, $T_g = -110^\circ\text{C}$, $\epsilon = 65$) and γ -butyrolactone (BL, $T_g \cong -140^\circ\text{C}$, $\epsilon = 42$) are much too aggressive toward lithium metal to provide long cycling life to such devices.

Ten years ago, Armand et al. [9] discovered that tetraalkylsulfamides, $(\text{R}_1\text{R}_2\text{NSO}_2\text{NR}_3\text{R}_4)$, which are non-volatile dipolar solvents stable toward strong reducing agents [10], can act as plasticisers in polyether–salt systems. They reported that 10 wt.% tetraethylsulfamide (TES, $T_g = -111^\circ\text{C}$, $\epsilon = 29$), in $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ rubbery electrolytes based on a copolyether rich in ethylene oxide (EO) units, provide good discharge performance to Li-TiS_2 cells down to 0°C . More recently, such cells involving another sulfamide were shown to exhibit long cycling lives with good discharge performance at 25°C [11]. In view of these findings, a study was meant to examine the relationship between the T_g depression and the conductivity elevation produced by small amounts of various dipolar diluents, including some sulfamides, in $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ rubbery electrolytes based on high molecular weight poly(ethylene oxide) (PEO).

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In a former study dealing with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ [12], we reported that over the range 0–30 wt.% diluent with respect to PEO the T_g depression produced by TES is about half that produced by PC. This feature, which concerns supercooled mixtures with a fixed salt concentration (1.2 mol kg^{-1}), was interpreted as an indication that TES is not as competitive as PC for displacing PEO from the coordination shells of the lithium ions. According to recent studies by Clericuzio et al. [13] and Forsyth et al. [14], PC itself is not very competitive for lithium ion coordination in the presence of EO-rich crosslinked copolyethers. IR data show that the carbonyl stretching band of PC (1790 cm^{-1}), which is shifted to a lower wave number (1780 cm^{-1}) in PC– LiBF_4 binary mixtures, remains unchanged in copolyether–PC– LiBF_4 ternary mixtures [13]. In agreement with this finding, ^{13}C NMR spin-lattice relaxation time (T_1) data show that more and more EO units are coordinated to the cations when PC content is increased under a fixed LiClO_4 concentration [14].

Also reported in the former work is that, due to its lower plasticising power, TES does not yield a conductivity elevation as great as PC over the range 0–30 wt.% diluent [12]. Furthermore, just above this range, the conductivity at $T = T_g + 70^\circ\text{C}$ decreases markedly with increasing TES content. Since the opposite trend is observed for PC, this suggests that once a large fraction of EO units are coordinated to lithium ions the equilibrium is displaced toward the formation of a neutral or a charged ionic complex of very low mobility with TES. In the present work, this study is extended to another sulfamide, N,N' -diethyl- N,N' -dimethylsulfamide (DEMS, $T_g = -130^\circ\text{C}$, $\varepsilon = 44$), and to BL, which both have lower T_g 's than TES and PC, and greater permittivities than TES. As in the former work [12], the conductivity data are analysed in terms of a reduced temperature $T = T_g + 70^\circ\text{C}$. This allows the separation of the effect resulting from the T_g depression from those resulting from changes in ion–ion interaction and ion speciation.

Atactic poly(propylene oxide) (PPO), $[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}]_n$, which is non-crystallizable, has often been used as an alternative to PEO, $[\text{CH}_2\text{CH}_2\text{O}]_n$, in basic studies on polyether electrolytes. However, because PPO has a lower solvating power than PEO, diluent-free electrolytes prepared with this polymer do not behave like their PEO amorphous counterparts. Below a certain salt concentration ($\sim 1 \text{ mol kg}^{-1}$), optically clear mixtures exhibit a T_g splitting that suggests a structure consisting of salt-rich microdomains dispersed into salt-depleted PPO [15]. This microphase separation, which yields a percolation threshold for ion conduction [16,17], explains in great part why PPO is not used as polymer host in diluent-free lithium batteries. As reported in this work, contrary to EO-rich copolyethers, high molecular weight PPO is not fully miscible with PC. This was an incitement to further examine the effects of this diluent as plasticiser for PPO– $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ electrolytes.

2. Experimental section

PEO (Aldrich, $M_{\text{GPC}} = 4 \times 10^6$) and PPO (Hercules, Parel-C, $M_{\text{GPC}} = 2 \times 10^5$) were dried under high vacuum at 40°C for 48 h. Oxymethylene-linked PEO, P(OM/PEG200) ($M_{\text{GPC}} = 1 \times 10^5$), was prepared according to the procedure described by Booth et al. [18], by reacting a poly(ethylene glycol) PEG200 oligomer with an excess of dichloromethane in the presence of KOH. The details concerning its synthesis, purification and characterization are reported in a previous paper [19]. Propylene carbonate (Aldrich, 99.7%), γ -butyrolactone (Aldrich 99%), tetraethylsulfamide (Fluka 99%), and N,N' -diethyl- N,N' -dimethylsulfamide (supplied by Hydro-Québec) were dried over aluminum oxide. $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (3 M) was pumped for 24 h at 150°C and for an additional 1 h at 170°C . NaClO_4 (Aldrich, 99%) was pumped for 24 h at 130°C .

Polymer–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 ampoules connected to a vacuum system and the solvent-free mixtures were dried for 24 h at 140°C . Polymer–diluent binary mixtures were prepared by adding weighted quantities of diluent to 2–3 g of polymer in 25-ml Erlenmeyer screw-cap flasks fitted with Teflon liners. The flasks were tightly closed and the mixtures were heated for 48 h at 110°C . A similar procedure was used to prepare the polymer–diluent–salt ternary mixtures. In that case, the diluent was added to polymer–salt mixtures prepared according to the former procedure. For PEO, the salt concentration was fixed to 1.2 mol kg^{-1} (total weight) by using polymer–salt mixtures of various concentrations. For the comparison between PPO and PEO, various amounts of PC were added to polymer–salt mixtures in a molar ratio $\text{O}/\text{Li} = 20$ (or $\text{O}/\text{Na} = 16$).

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. Glass transition features were recorded at $40^\circ\text{C min}^{-1}$, and supercooled specimens (for PEO) were obtained by melt quenching at a cooling rate of $320^\circ\text{C min}^{-1}$. 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. The conductivity cells consisted of two stainless steel solid cylinders encapsulated at both ends of a Teflon ring [20]. The temperature was measured with an accuracy of $\pm 0.2^\circ\text{C}$ 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 analyser. 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%.

3. Results and discussion

3.1. PEO–Diluent–LiN(CF₃SO₂)₂ electrolytes

In the absence of diluent, LiN(CF₃SO₂)₂ forms a 6/1 (EO/Li) intermediate compound of low melting point (55°C) that partakes in a eutectic equilibrium at 42°C with high molecular weight PEO ($T_m = 69^\circ\text{C}$) [12]. However, near the eutectic composition (EO/Li = 11, $c = 1.3 \text{ mol kg}^{-1}$), even small amounts of a dipolar diluent impede the eutectic crystallization. With PC, TES, DEMS and BL, this effect is severe enough to allow conductivity measurements down to 0°C under supercooling conditions. Though the aim of this study was to investigate the effects produced by small amounts of diluent (10–30 wt.% with respect to PEO), a more extensive investigation (up to 100 wt.% diluent) was performed to get a broader perspective on the features specific to each diluent. Fig. 1 depicts conductivity isotherms constructed at 60°C over a range of concentrations (from 0.1 to 1.6 mol kg⁻¹) for different PC contents. It shows that the concentration selected for this investigation (1.2 mol kg⁻¹) is slightly above the conductivity maxima, which remain close to 0.9 mol kg⁻¹ for all compositions including 100 wt.% PC. It also shows that

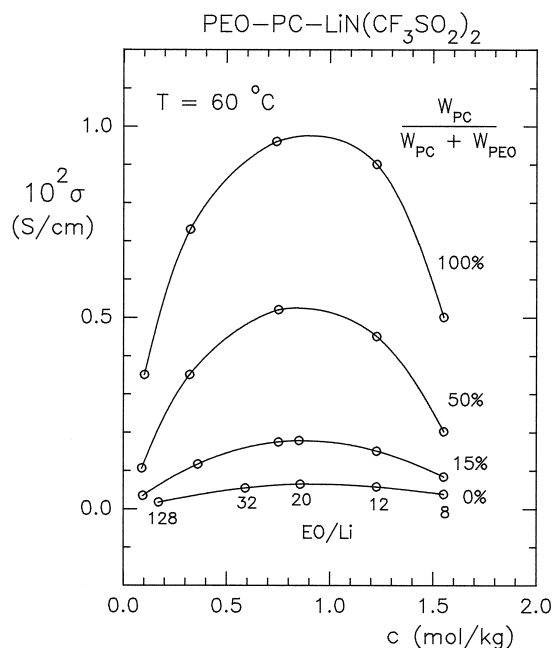


Fig. 1. Conductivity isotherms of the PEO–PC–LiN(CF₃SO₂)₂ system at 60°C. As a function of salt concentration for various PC contents.

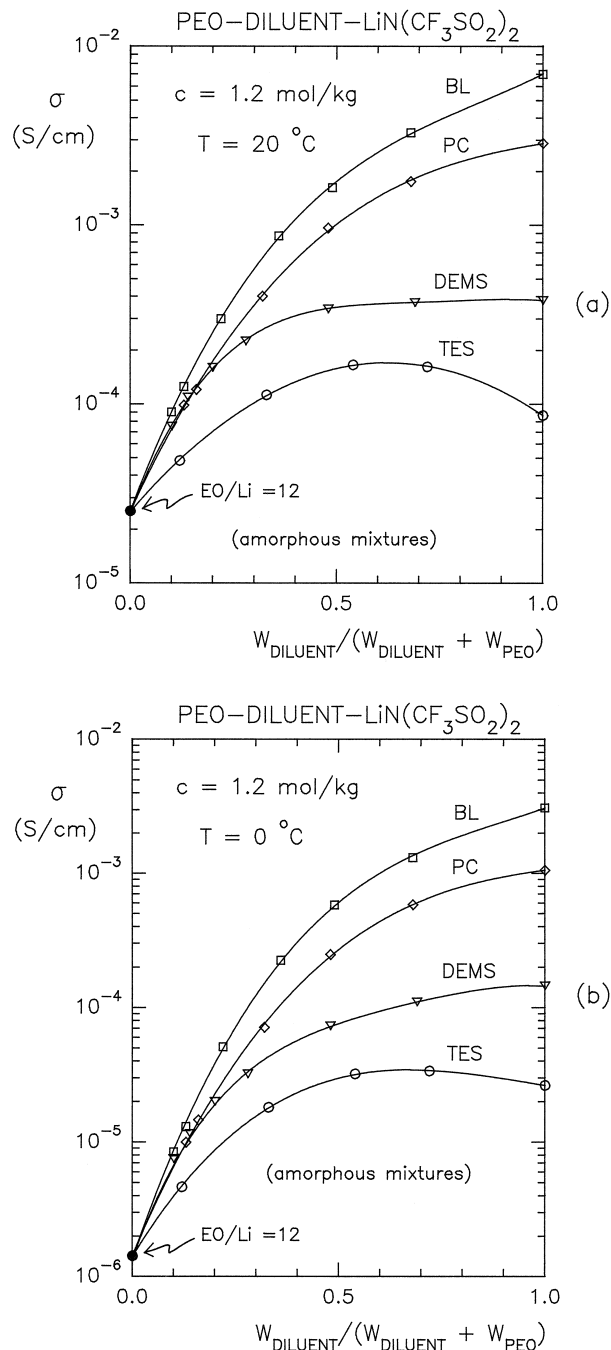


Fig. 2. Conductivity isotherms at 20°C (a) and 0°C (b) of the four PEO–diluent–LiN(CF₃SO₂)₂ systems studied in this work. As a function of diluent content for a fixed salt concentration (1.2 mol kg⁻¹).

the conductivity elevation produced by 15 wt.% PC is a modest threefold at 60°C.

Since the conductivity of glass forming electrolytes decreases exponentially with decreasing temperature toward T_g , a greater effect takes place at lower temperatures. This is illustrated in Fig. 2, which depicts conductivity isotherms constructed at 20°C and 0°C for $c = 1.2 \text{ mol kg}^{-1}$ electrolytes containing PC, BL, TES and DEMS. Fig. 2 also shows that the conductivity elevation produced

by DEMS is comparable to that produced by PC over the range 0–20 wt.% diluent. With further dilution, however, the conductivity data related to this sulfamide exhibit an increasing departure from those related to either PC or BL. This suggests that the same type of association as that reported for TES takes place with increasing DEMS content. Note that viscosity of DEMS (3.4 cP) is lower than that of TES (4.2 cP) but greater than those of PC (2.5 cP) and BL (1.8 cP). The latter diluent (BL), which has the lowest viscosity and the lowest T_g among the present plasticisers, is the one that yields the greatest conductivity over the whole range of compositions.

Fig. 3 presents the T_g -composition relationships of the four systems depicted in Fig. 2. It shows that BL and DEMS essentially produce the same T_g depression as PC over the range 0–25 wt.%. It also shows that the relationships related to these three diluents exhibit a sudden fall above a certain composition (30 wt.% BL, 55 wt.% DEMS and 63 wt.% PC). This feature, as well as the change in curvature near 60 wt.% TES, was accompanied by a T_g broadening. As quoted in the former work, similar features have been reported for many polymer–diluent systems [21,22]. The T_g broadening suggests that local fluctuations in composition of large amplitude take place over a range of compositions. For optically clear mixtures of some other systems [e.g., polystyrene ($T_g = 103^\circ\text{C}$)-tricresyl phosphate ($T_g = -68^\circ\text{C}$), or poly(vinyl chloride) ($T_g = 85^\circ\text{C}$)-butyl acetate ($T_g = -118^\circ\text{C}$)], these fluctuations lead to heterogeneities large enough to yield separate T_g features on the DSC curves [21,23].

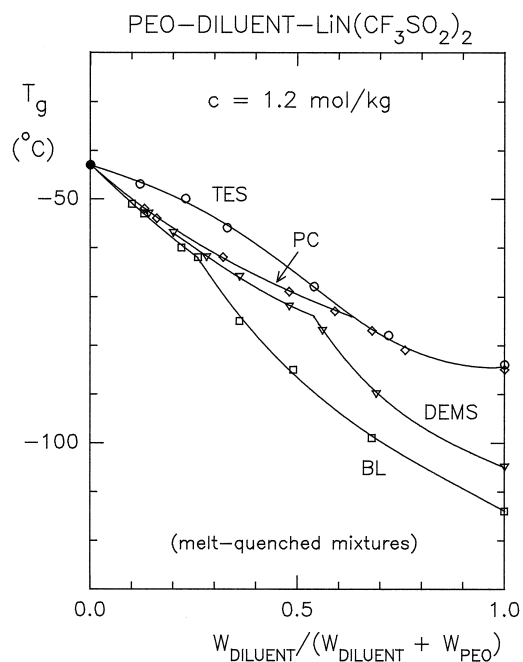


Fig. 3. T_g -composition relationships of the four PEO–diluent– $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ systems depicted in Fig. 2.

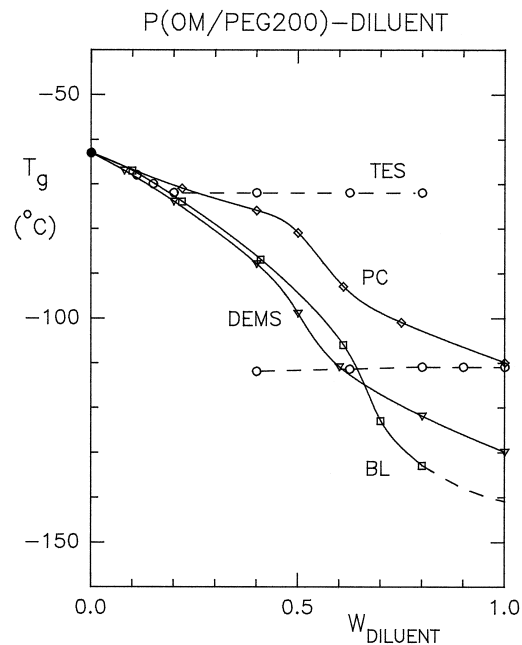


Fig. 4. T_g -composition relationships of P(OM/PEG200)–diluent binary systems based on an oxymethylene-linked PEO prepared with a PEG200 oligomer. For TES, a T_g splitting (dashed lines) shows that a phase separation takes place over the range 20–80 wt.% diluent.

In the absence of salt, polar diluents contribute to enhance the crystallinity of high molecular weight PEO [12]. This effect, which is due to chain disentanglement, precludes any investigation on the T_g behaviour of super-cooled PEO–diluent binary systems. However, such a study could be performed with a high molecular weight oxymethylene-linked PEO, P(OM/PEG200), prepared from a PEG200 poly(ethylene glycol) oligomer. Since this copolymer was shown to rapidly revert to PEG200 in the presence of certain salts suspected to contain traces of Lewis acids [19], it was used as a non-crystallizable alternative to PEO for this study only. As illustrated in Fig. 4, the T_g -composition relationships related to PC, BL and DEMS in this polymer also exhibit a sudden fall above a certain composition (50 wt.% PC or DEMS, and 60 wt.% BL), while its optically clear mixtures with TES exhibit a T_g splitting over the range 20–80 wt.%. Below this range, TES essentially produces the same T_g depression as PC. This confirms that the marked difference between these two diluents in Fig. 3 is due to the presence of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. Fig. 4 also shows that over the range 0–20 wt.% the T_g depression produced by the present diluents is almost insensitive to their physical properties. Since this feature also applies to PC, BL and DEMS in Fig. 3, it may be argued that there is an intrinsic limit to the plasticising power one can expect from any non-volatile diluent over this range.

Fig. 5 depicts the conductivity data of the PEO–diluent– $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ systems at $T = T_g + 70^\circ\text{C}$, that is, under conditions that should correspond to a fixed free

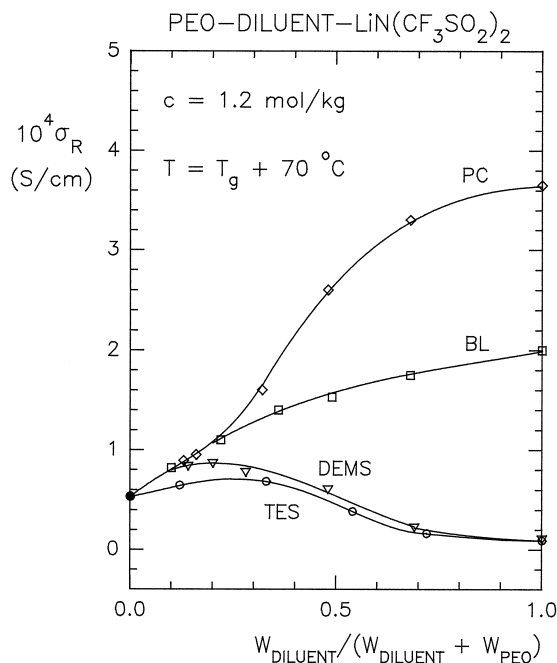


Fig. 5. Reduced conductivity, σ_R , at $T = T_g + 70^\circ\text{C}$ of the four PEO–diluent– $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ systems depicted in Figs. 2 and 3.

volume fraction in homogeneous glass forming materials. These relationships show that all the present diluents including TES produce a small but a finite increase in the reduced conductivity (σ_R) over the range 0–30 wt.%. Above this range, however, PC yields a steeper rise in this quantity than BL, while DEMS and TES yield a marked decline in this quantity. This comparison suggests that at high diluent contents BL ($\epsilon = 42$) is not as effective as PC ($\epsilon = 65$) to either increase charge carrier density or reduce ion–ion interaction. It also confirms that DEMS ($\epsilon = 44$), like TES ($\epsilon = 29$), eventually contributes to the formation of a solvated ionic species that is not favorable to conduction.

In a previous work [20], diluent-free PEO– $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ amorphous electrolytes were examined over the range from 0.05 mol kg^{-1} ($\text{EO}/\text{Li} = 500$) to 2.7 mol kg^{-1} ($\text{EO}/\text{Li} = 2$). Features observed in the reduced molar conductivity (σ_R/c) of this system may help to clarify the behaviour of the present systems. When plotted as a function of c , this quantity rises rapidly to reach a maximum near 0.6 mol kg^{-1} ($\text{EO}/\text{Li} = 30$). Then, it declines slightly (by 30%) over a wide range of concentrations [up to 1.8 mol kg^{-1} ($\text{EO}/\text{Li} = 6$)], to finally exhibit a sudden, tenfold fall above this range. This latter change was attributed to the depletion in the free EO units available for cation jumps. As deduced from the T_g -composition relationship of this system [20], complete saturation of the EO coordination sites should take place near $c = 2.2 \text{ mol kg}^{-1}$ ($\text{EO}/\text{Li} = 3.5$). By assuming a coordination exclusive to PEO, the latter two limits ($\text{EO}/\text{Li} = 6$ and $\text{EO}/\text{Li} = 3.5$) would correspond to 42 and 70 wt.% diluent in the present systems.

Since any coordination to PEO is detrimental to lithium ion mobility, it is tempting to attribute the large increase in σ_R above 30 wt.% PC in Fig. 5 to a greater and greater exchange of coordination sites through this diluent. Furthermore, from this feature and the opposite trend observed above 30 wt.% DEMS and TES, it may be argued that this limit, which corresponds to $\text{EO}/\text{Li} = 8.5$, is a critical point above which ion speciation begins to be particularly sensitive to the diluent bulk properties. The situation appears to be different at lower diluent contents, where most of the diluent molecules (and most of the ions) are probably in close contact with the polymer. In a study dealing with various polymers plasticised by small amounts (15–20 wt.%) of trialkyl phosphates, Cauley et al. [24] reported that a substantial fraction of the diluent molecules (more than 30%) still undergo extensive rotational motion at temperatures well below the single T_g recorded by DSC. This was evidenced by a fast and a slow component in the ^{31}P NMR line shape of the diluents, as well as by a broad peak at temperatures well below T_g in the loss component of the shear modulus of the specimens. If it applies to the present systems (and it should), such a fast rotational motion, not probed through the T_g measured by DSC, could contribute to favor cation jumps at low diluent contents. This effect probably accounts for the maximum of σ_R near 20–30 wt.% DEMS and TES in Fig. 5.

3.2. PPO–PC– $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ electrolytes

Fig. 6 shows T_g data obtained for mixtures of PC with a high molecular weight atactic PPO. Contrary to the

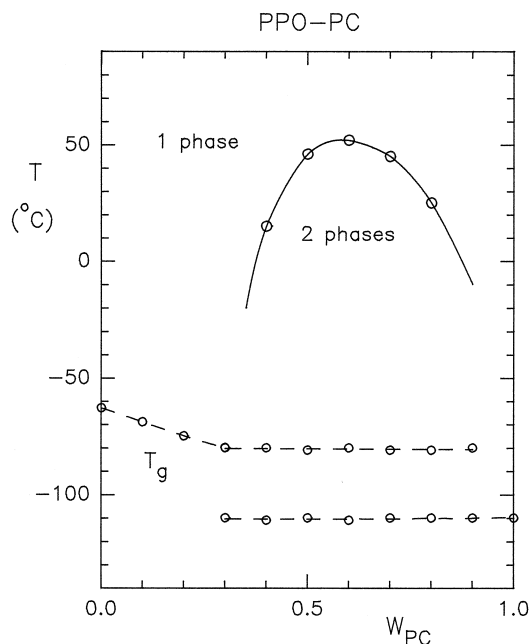


Fig. 6. Phase diagram and T_g data of the PPO–PC binary system. A liquid–liquid macroscopic separation takes place above 30 wt.% PC in this system.

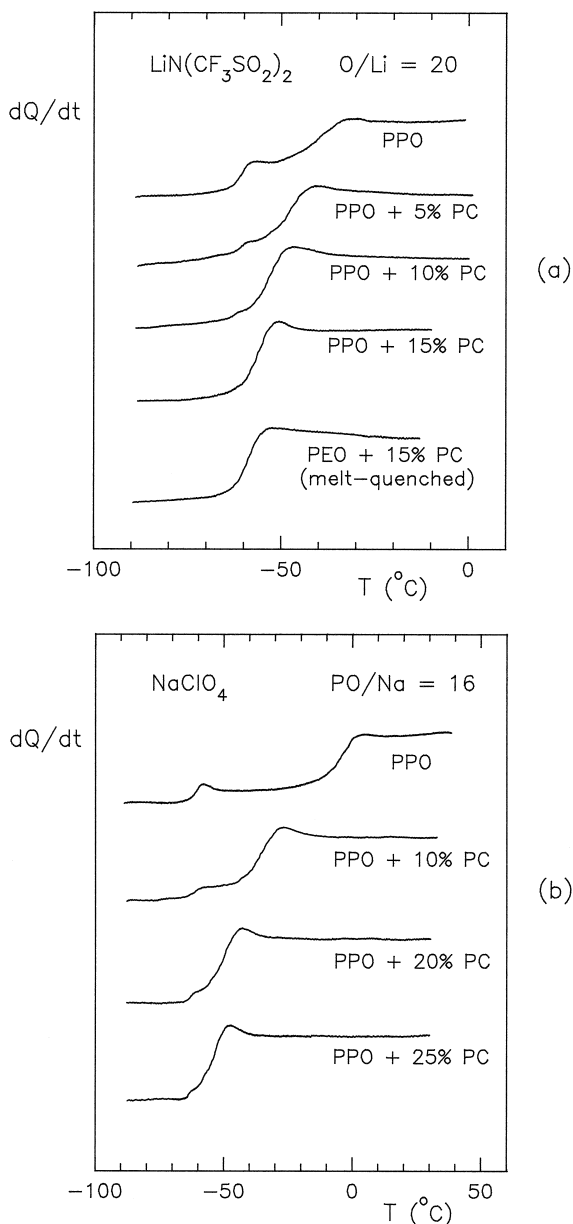


Fig. 7. DSC curves recorded on PPO–LiN(CF₃SO₂)₂ (a) and PPO–NaClO₄ (b) mixtures in a molar ratio PO/Li = 20 ($c = 0.69 \text{ mol kg}^{-1}$) and PO/Na = 16 ($c = 0.95 \text{ mol kg}^{-1}$), before and after dilution by small amounts of PC.

P(OM/PEG200)–PC binary system (Fig. 4), this system exhibits a T_g splitting over a wide range of compositions above 30 wt.% PC. A macroscopic two-phase separation accounts for this behaviour. As estimated from visual inspection made under slow cooling (from 100°C), the upper critical solution temperature of this system is close to 50°C and its critical composition is near 60 wt.% PC. This phase behaviour, which is included in Fig. 6, indicates that PC is a poor solvent for PPO. Above 30 wt.% PC, the high- and the low- T_g features reflect the composition of each phase at -80°C , that is, at the point where the

PPO-rich phase underwent vitrification upon cooling. The second phase was essentially neat PC at this temperature.

As mentioned in Section 1, diluent-free PPO–salt systems yield a microphase separation that strongly affects ion conduction [16,17]. Below a certain concentration ($\sim 1 \text{ mol kg}^{-1}$), a low- T_g feature comparable to that of the neat polymer becomes apparent in the DSC curves and its amplitude increases with further dilution. At the same time, a high- T_g feature characteristic of a salt-rich microphase decreases in amplitude and asymmetrically broadens toward the low- T_g feature to finally disappear at low concentrations ($\sim 0.3 \text{ mol kg}^{-1}$ for high molecular weight PPO) [17]. Such a behaviour suggests that there is a point where salt dilution leads to a critical balance between the cation–oxygen interactions, which favor salt dispersion, and the ion–ion long-range Coulombic interactions, which oppose this dispersion. It also suggests that beyond a certain dilution the salt-rich microdomains decrease in size and eventually transform into more and more labile heterogeneities.

Fig. 7 shows DSC curves recorded on PPO–LiN(CF₃SO₂)₂ and PPO–NaClO₄ mixtures plasticized by increasing amounts of PC. In each case, the composition of the diluent-free mixture (PO/Li = 20 or PO/Na = 16) was selected to allow a clear view on the effect produced by small amounts of PC. It is 30% below the critical concentration for microphase separation of each of these systems (1.0 mol kg^{-1} or PO/Li = 13 for the PPO–LiN(CF₃SO₂)₂ system, and 1.3 mol kg^{-1} or PO/Li = 11 for the PPO–NaClO₄ system [17]). In either case, though PC addition yields a substantial change in the T_g of the salt-rich microphase, a smaller but a finite amount of a

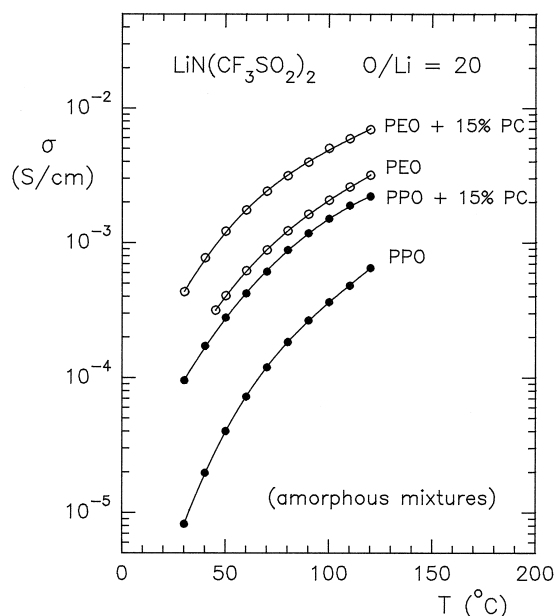


Fig. 8. Comparison of conductivity data obtained for PPO–LiN(CF₃SO₂)₂ and PEO–LiN(CF₃SO₂)₂ mixtures in a molar ratio O/Li = 20, before and after dilution by 15 wt.% PC with respect to the polymer.

salt-depleted, diluent-free PPO microphase remains present in the mixtures. Due to the overlapping of the T_g features associated with these two microphases, the presentation is limited to 15 wt.% PC for $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 25 wt.% PC for NaClO_4 .

In Fig. 8, a comparison is made of conductivity data obtained for $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in a molar ratio $\text{O}/\text{Li} = 20$ with PPO and PEO. Included are data obtained for each of these electrolytes plasticised by 15 wt.% PC with respect to the polymer. In agreement with the foregoing changes in the relative amount and in the T_g of the salt-rich microphase, such a small dilution produces a much greater conductivity elevation in PPO than in PEO. However, in spite of these changes, the conductivity magnitude at 30°C is still four times lower in PPO than in PEO. Measurements (not shown) made on the same electrolytes diluted by 50 wt.% PC led to a conductivity departure of 33% only. Since both these latter mixtures exhibited a single T_g at -95°C , it is likely that the much greater departure between the PPO and PEO electrolytes containing 15 wt.% PC is due to the microphase separation in the former polymer.

According to Fig. 6, over the range 0–30 wt.% PC, the PPO–PC system yields mixtures that are fully homogeneous down to their vitrification. On this basis, there is no special reason why PC should be confined to the salt-rich microphase in the PPO–PC–salt systems, except that the ion–ion long-range Coulombic interactions still oppose to a complete dispersion of the salt in these systems, and that PC has a greater affinity for the salt than for PPO. This suggests a situation in which the diluent molecules are in close contact with the polymer through their own interaction with the salt as in the case of the corresponding homogeneous electrolytes with PEO. In either case, the diffusivity of these molecules is probably much lower than above 30 wt.% PC where a sudden rise occurs in the reduced conductivity of the latter electrolytes.

4. Conclusion

The main features of this study are twofold. First, over the range 0–20 wt.% with respect to PEO, the conductivity elevation produced by dipolar diluents of different permittivities ($29 \leq \varepsilon \leq 65$) mostly depends on the T_g depression. Although the diluent molecules appear to favor cation jumps within the polymer, no marked effects can be attributed to changes in either ion–ion interaction or ion speciation. Such changes become noticeable above 30 wt.% diluent only. Second, over the same range of compositions (0–20 wt.%), there is an intrinsic limit to the T_g depression produced by non-volatile diluents of lower and lower T_g . This feature applies to PEO–diluent and PEO–diluent–salt systems. It indicates that over this range the diluent dynamics mainly consists of rotational motions not probed by T_g . This feature, which suggests a low diluent

diffusivity, should make these polyether electrolytes, particularly those containing small amounts of sulfamides, less aggressive toward lithium and insertion electrodes than their gelled, diluent-rich counterparts.

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