Thermal analysis and NMR study of a poly(ethylene oxide) complex electrolyte : PEO(LiCF3SO3)x

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Thermal analysis and NMR study of a poly(ethylene oxide) complex electrolyte : PEO(LiCF₃SO₃)ₓ

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Résumé. — Nous avons établi le diagramme d'équilibre entre les différentes phases qui coexistent dans les complexes formés entre le poly(oxyde d'éthylène) et LiCF₃SO₃, en combinant les techniques de calorimétrie différentielle à balayage et Résonance Magnétique Nucléaire et nous avons mesuré la variation de la température de la transition vitreuse en fonction de la concentration en sel $dT_g/dx = 280$ K/(mole de sel) (mole d'unités monomères)$^{-1}$. Nous montrons que dans la plage de température 340-420 K, seule la phase amorphe participe à la conduction ionique $\sigma(T)$. La variation de σ avec la température, interprétée à tort en terme de loi d'Arrhenius, résulte en fait de la variation de trois facteurs : la concentration en sel de la phase amorphe (nombre de porteurs), la dynamique locale des mouvements de chaînes (coefficients de diffusion) et les proportions relatives de phases amorphes et cristallines. La dépendance en température de chacun de ces paramètres a été évaluée expérimentalement, dans le composé $x^{-1} = 8$ et leur combinaison permet une bonne description des variations de $\sigma(T)$. Un résultat intéressant est la faible dépendance en température de la somme des coefficients de diffusion anionique et cationique qui est évaluée à $D_\sigma = 6 \times 10^{-8}$ cm² s^{-1} à 375 K.

L'ensemble des paramètres considérés fournit également une interprétation satisfaisante des différents comportements de la conductivité ionique observés dans la plupart des complexes formés entre PEO et les sels de métaux alcalins.

Abstract. — We have determined the equilibrium diagram between the different phases which coexist in the complexes between the poly(ethylene oxide) PEO and the salt LiCF₃SO₃, by using DSC and NMR techniques. We have also measured the variation of the glass transition temperature as a function of the salt concentration $dT_g/dx = 280$ K/(mole of salt per mole of monomer unit). We show that in the temperature range 340-420 K the ionic conduction σ only takes place in the amorphous phase. The thermal dependence of σ, previously interpreted in term of Arrhenius law, indeed results from that of three terms : the salt concentration in the amorphous phase (number of carriers), the local dynamics of the polymer chains (diffusion coefficient) and the respective amounts of crystalline and amorphous phases. The temperature dependence of each of these parameters has been estimated from experiments in the sample $x^{-1} = 8$ and they combine to give a fair description of $\sigma(T)$. A striking result is the small temperature dependence of the diffusion coefficient ($D_\sigma \cong 6 \times 10^{-8}$ cm² s^{-1} at 375 K).

Taking into account these parameters also provides a satisfactory interpretation of the ionic conductivity behaviour in most of complexes formed between PEO and the alkali metals salts.

1. Introduction.

Since M. Armand *et al.* [1] suggested that complexes between poly(ethylene oxide) and various alkali metal salts could be used as « solid electrolytes » in high specific energy batteries, these compounds have raised a widespread interest [2]. According to the nature and the concentration of the salt, the tem-perature dependence of the conductivity exhibits 3 types of behaviour [3] :

— type I compounds obey a Fulcher law in the whole experimental temperature range,

— type II compounds change from an Arrhenius law at low temperature to a Fulcher behaviour, while type III change from a high activation energy to a low activation energy Arrhenius law.

These sytems have been shown to consist of several phases depending on the temperature [4-7] but the

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thermal behaviour of the ionic conductivity is not clearly understood yet. Recently, we have shown [8] that several factors affect the conductivity and that in most cases, the thermal behaviour could not be simply described by a single Fulcher or Arrhenius law.

In this paper, we present Differential Scanning Calorimetry (D.S.C.) and NMR measurements in the type III complexes $PEO(LiCF_3SO_3)_x$ for several x values (x is the number of cations per monomer unit). The phase diagram of the system $PEO(LiCF_3SO_3)_x$ is discussed in the light of the results of both experimental techniques and compared with that proposed by Sorensen et al. [9]. We also analyse the various parameters which govern the ionic conductivity and give an estimate of the overall ionic mobility, as well as its temperature dependence.

2. Experimental.

2.1 SAMPLES. — PEO with molecular weight 900 000 was supplied by Aldrich. $LiCF_3SO_3$ was prepared by stoichiometric reaction between HCF_3SO_3 (Merk) and Li_2CO_3 Merk (suprapure) recrystallized in acetone and vacuum dried at 120 °C.

The polymer and salt were weighted in an argon dry box (less than 1 ppm H_2O and O_2) to the desired O/M ratio, and dissolved in acetonitrile (Merk anhydrous) to $\cong 5\%$ weight. The solution was outgased under partial vacuum and cast in the dry box on to a polished PTFE plate. A closed circuit apparatus was used to remove excess solvent by circulating argon (50 l/h) through a column of 10 X molecular sieve. Dried membrane was cut into pieces to fill the NMR sample tube (heat treated Pyrex) and the DTA aluminium capsule. The samples were then annealed at 480 K, cooled down to room temperature and left for several days at this temperature before any measurements.

2.2 NMR. — Pulsed NMR measurements were performed at 15 and 22 MHz. The vacuum sealed sample tube was placed in a furnace operated under helium atmosphere. The fractions of protons ^1C and fluorine nuclei ^{19}C belonging to a crystalline or vitreous phase were determined at several temperatures by analysing the shape of the free induction decay signal since the signal due to nuclei in an amorphous phase decreases much more slowly than that due to nuclei in a crystalline phase [8]. The determination of the fraction of lithium nuclei ^7C belonging to a crystalline phase is more difficult since the quadrupolar interactions may reduce the amplitude of the F.I.D. in the solid state (if the r.f. field is not large enough) or broaden the line in the elastomeric phase by reducing T_1. Nevertheless, ^7C measurements were performed in some cases and give $^7C = ^{19}C$. The salt concentration of the various phases occurring in the system was determined from the values of ^1C, ^7C and ^{19}C.

The shape of the decay of the transverse magnetization related to the protons in the amorphous phase has also been measured using the spin echo technique.

2.3 DIFFERENTIAL SCANNING CALORIMETRY. — Differential scanning calorimetry traces were obtained using a Perkin Elmer DSC II instrument between 160 K and 480 K. The rate of heating was 5, 10 or 20 K/min without noticeable differences in the thermograms.

3. Experimental results.

3.1 DSC. — The DSC spectrum for $x^{-1} = 4, 4.5, 6, 8, 10$ and 16 between 200 K and 400 K are shown in figure 1. As for $PEO(LiCF_3SO_3)_{1/8}$ [7, 8], the endothermic peak at about 325 K corresponds to the melting of pure PEO crystalline phase, while the endothermic event which extends from the end of the PEO melting peak up to 390/440 K corresponds to the progressive dissolution of a salt rich crystalline phase in the elastomeric phase. From NMR results, Berthier et al. [8] have deduced that the concentration of this crystalline phase corresponds to $x^{-1} = 3.5$ in $PEO(LiCF_3SO_3)_{1/8}$. One also observes that the relative intensity of the PEO melting peak increases with x^{-1}, while the temperature of the upper peak decreases and its shape is modified. The cooling rate was varied between 0.31 K/min and 320 K/min in order to investigate the kinetics of recrystallization. After cooling, the thermograms of the compounds $x^{-1} = 4$ to $x^{-1} = 8$ are similar to those obtained initially, whatever the cooling rate, except that the area of the peaks is slightly smaller (particularly, the melting peak of pure PEO in the $x^{-1} = 4$ compound).

The results obtained for the $x^{-1} = 10$ and $x^{-1} = 16$ complexes are similar to those obtained in $PEO(NaI)_x$ although the kinetics are faster [10] : during a slow cooling the salt rich complex recrystallizes lowering considerably the salt concentration of the amorphous phase. Thus PEO too is able to recrystallize. But on rapid cooling (320 K/min) of
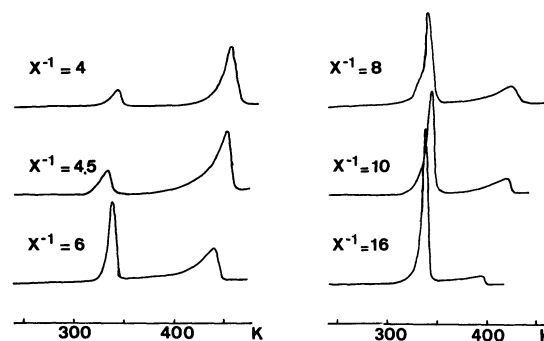

Fig. 1. — DSC traces for $PEO(LiCF_3SO_3)_x$. Heating rate 20 K/min. The curves are normalized for the same weight for all samples.

the $x^{-1} = 10$ or $x^{-1} = 16$ compounds, the amorphous phase is too dilute to allow the recrystallization of PEO(LiCF₃SO₃)$_{1/3.5}$ and too concentrated for a full recrystallization of pure PEO; thus the complex remains mainly amorphous. On heating, the thermograms display successively (Fig. 2) the T_g of the elastomeric phase followed by a cold recrystallization peak of pure PEO (and of the salt rich complex in the $x^{-1} = 16$ compound). The well defined steps at T_g in these two compounds suggest that they must be associated with well quenched parts of the samples. Thus

$$T_g = 228 \text{ K for an elastomeric phase } x^{-1} = 16$$

$$T_g = 238 \text{ K for an elastomeric phase } x^{-1} = 10.$$

If one remembers that $T_g \cong 210$ K for pure PEO [11], the increase in T_g of an elastomeric phase as a function of the salt concentration is linear up to $x = 0.1$ and is given by

$$dT_g/dx = 280 \text{ K/[mole of salt]} \times$$
$$\times \text{ [mole of monomer unit]}^{-1}$$

(to be compared with $dT_g/dx = 450$ K/[mole of salt]. [mole of monomer unit]$^{-1}$ in PEO(NaI)ₓ (10)).

All these results indicate that the kinetics of recrystallization are rather fast and that the mobilities of both Li⁺ and CF₃SO₃⁻ are high in this compound since the formation of pure PEO crystallites (if large enough) requires the migration of both species.

3.2 NMR. — The fraction of nuclei (protons or fluorine) which belong to crystalline phases is plotted as a function of temperature in figures 3 and 4 for $x^{-1} = 4$ (¹C) and $x^{-1} = 8$ (¹C and ¹⁹C). As already shown [8], the sharp drop in ¹C at 326 K is due to the melting of uncomplexed (PEO), while the decrease of ¹C and ¹⁹C above 326 K corresponds to the dissolution in the amorphous phase of the salt rich complex crystallites, the stoichiometry of which is $x_c = x \frac{^{19}C}{^{1}C}$ i.e. 1/3.5 for the PEO(LiCF₃SO₃)$_{1/8}$. The complete dissolution of this complex occurs for ¹C = ¹⁹C = 0, at a temperature in agreement with the determination from the DSC records.

4. Discussion.

4.1 PHASE DIAGRAM. — The comparison between the relative area for the two peaks as a function of x is not straightforward since the second peak does not correspond to the heat of melting of the salt rich complex but to its heat of dissolution in the amorphous phase and since the compounds are only partially crystallized.

Our interpretation is based upon the hypothesis that the stoichiometry of the salt rich crystalline complex is $x_c = 1/3.5$ and is temperature independent. This was determined experimentally by NMR
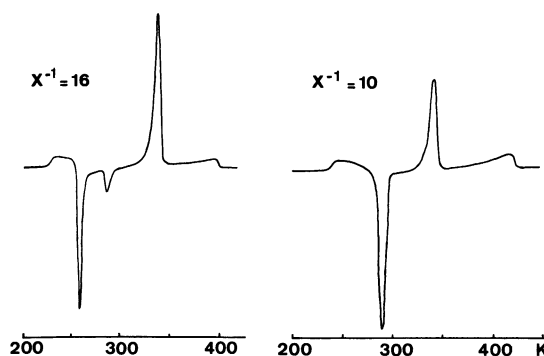

Fig. 2. — DSC traces for PEO(LiCF₃SO₃)$_{1/10}$ and PEO(LiCF₃SO₃)$_{1/16}$ obtained after heating at 450 K and cooling down at 320 K/min.
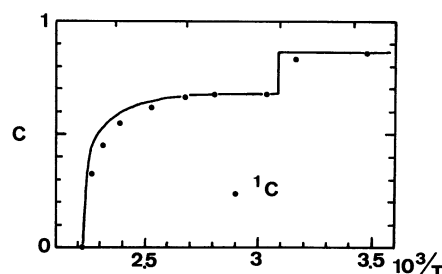
Fig. 3. — Fractions of protons ¹C belonging to the crystalline phase in PEO(LiCF₃SO₃)$_{1/4}$. The line represents ¹C$_{DSC}$ obtained from the phase diagram corrected by the factor α defined in the text.

Fig. 4. — Fractions of protons ¹C (●) and fluorine ¹⁹C (▲) belonging to the crystalline phase in PEO(LiCF₃SO₃)$_{1/8}$. The line represents ¹C$_{DSC}$ obtained from the phase diagram corrected by the factor α defined in the text.

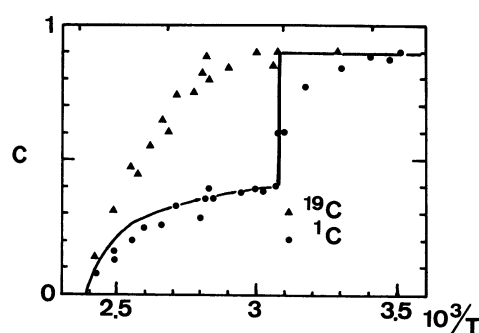in PEO(LiCF₃SO₃)$_{1/8}$ [8] and is extended to all concentrations. This hypothesis is also corroborated by the DSC thermogram of PEO(LiCF₃SO₃)$_{1/4}$ where the PEO melting peak is very small.

Let us denote c the concentration of the complex : $c = 3.5 x$ ($c = 0$ and 1 correspond to pure PEO, and pure PEO(LiCF₃SO₃)$_{1/3.5}$ respectively).

From the NMR and DSC results, one can plot the temperature at which $PEO(LiCF_3SO_3)_{x_c}$ is completely dissolved in the elastomeric phase for $x^{-1} = 4$, 4.5, 6, 8, 10 and 16. One thus obtains the equilibrium diagram (Fig. 5) between crystalline and amorphous phases. This phase diagram differs from that established by Sorensen et al. [9] from ionic conductivity results in two points :

— the stoichiometry of the salt rich crystalline complex that they suppose equal to $x_c = 0.25$ as initially suggested [12],

— the existence of a very dilute eutectic compound $x \cong 0.04$ with a melting temperature $T_m \cong 60$ °C. In fact, there is no definite proof of the existence of such an eutectic and we suggest that the lowering of the melting temperature of pure PEO in these complexes (as compared with pure PEO 900 000) could be due to the « shortering » of pure PEO chains by cation decoration.

From this phase diagram, one can deduce the variations of ^1C and ^{19}C as a function of temperature and compare with NMR results. One can also approximate the shape of the DSC dissolution peak.

i) NMR.

The crystallinity ^1C can be directly deduced from the well known properties of the phase diagram. On figure 5, we have illustrated this property for the complex $x^{-1} = 8$ at $T = 370$ K where the cristallinity ^1C is given by $^1C_{DSC} = \dfrac{l_1}{l_1 + l_2}$. Actually, at all temperatures $^1C_{DSC}$ is larger than $^1C_{NMR}$. This disagreement is not so surprising since the phase diagram does not take into account the residual amorphous phase below 60 °C. If one supposes that this amorphous phase is inhomogeneous and is constituted of a salt rich part ($x^{-1} \cong 3.5$) embedded between the salt rich crystallites in the spherulites and a very dilute part surrounding the pure PEO crystallites, the phase diagram will describe the equilibrium between these two parts. In particular,
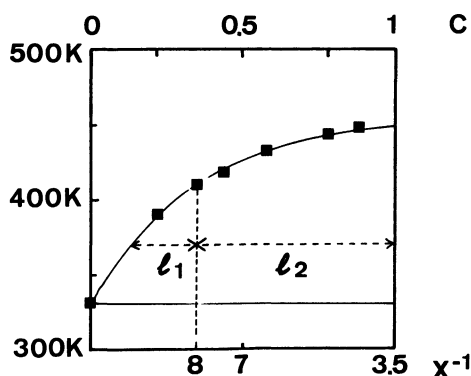
when pure PEO melts, the salt rich amorphous phase does not mix immediately into the « free » amorphous phase but dissolves progressively with the salt rich spherulites. As a consequence, the salt rich complex must be considered as semicrystalline at all temperatures, and $^1C_{DSC}$ has to be corrected by the degree of crystallinity in order to be compared with $^1C_{NMR}$. This correction factor, has been estimated using the following procedure. We assume that, the dilute amorphous part at 20 °C correspond to a degree of crystallinity of approximately 90 % of the uncomplexed PEO. The remaining amorphous part is the salt rich part embedded between the salt riche crystallites. One thus immediately obtains the correction factor α. We have plotted in figures 3 and 4 the crystallinity $^1C = \alpha\,^1C_{DSC}$. The agreement with $^1C_{NMR}$ is fairly good. The small disagreement in the high temperature part of the curve can be qualitatively explained if one supposes that those crystallites of the salt rich complex which melt at the lower temperature are the smallest and do not retain any salt rich amorphous phase.

ii) DSC dissolution peaks.

The equilibrium phase diagram can also be used to determine the shape of the dissolution peak. On the assumption that we are in the low concentration limit (which is certainly a rough approximation as electrostatic interactions in the elastomeric phase are not negligible), the heat of dissolution of Δn moles of $PEO(LiCF_3SO_3)_{1/3.5}$ at temperature T is [13]

$$\Delta Q_p = T^2 \Delta n \frac{\delta \ln c(T)}{\delta T}.$$

The shape of the dissolution peak calculated from this formula is plotted on figure 6 for $x^{-1} = 16$, 8 and 6. The agreement with experimental results is satisfactory.

4.2 T_2 MEASUREMENTS. — In the amorphous phase; a correct treatment of the time dependence of the transverse magnetization $M_x(t)$ should take into account the effect of entanglements. These latter introduce a residual linewidth, the lifetime of which is much longer than the relaxation times τ_p corresponding to the Rouse fluctuations. At least for that reason, $M_x(t, T)$ cannot be expressed as $M_x(t/\tau_{(T)})$

Fig. 5. — Equilibrium phase diagram between uncomplexed PEO, $PEO(LiCF_3SO_3)_{1/3.5}$ and the amorphous phase deduced from DSC experiments. The crystallinity of the complex $x^{-1} = 8$ at 370 K is given by $l_1/l_1 + l_2 = {}^1C_{DSC}$.
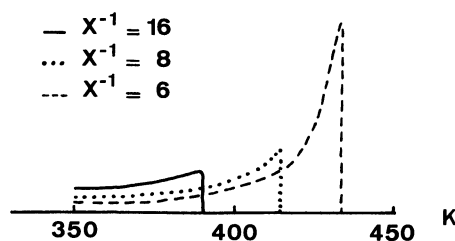
Fig. 6. — Shape of the dissolution peak for $x^{-1} = 16$, 8 and 6 obtained from the phase diagram.

with $\tau_{(T)}/\tau_{(T_0)} = a_{(T)}$, the WLF factor. Nevertheless, the experimental values of $M_x(t, T)$ can be fairly well superimposed in the temperature range 330 K-410 K (Fig. 7) using a scaling factor $a_{(T)}$ plotted in figure 8; which means that the residual dipolar interactions can be neglected in our case. Thus we identify $a_{(T)}$ with a pseudo-WLF factor in the sense that the glass transition temperature varies continuously with temperature due to the increase of the salt concentration, and since the c_1 and c_2 coefficients of the WLF law are also expected to be salt concentration dependent.

4.3 TEMPERATURE DEPENDENCE OF THE CONDUCTIVITY.

— Berthier et al. [8] have shown that the ionic conductivity is mainly ensured by the elastomeric phase and that as long as a crystalline phase is present, the measured conductivity is different from the conductivity of the elastomeric phase.

They suggest a correction given by Landauer [14] for inhomogeneous media

$$\sigma_{mes} = \tfrac{1}{2}(3\ A(T) - 1)\ \sigma_{elast}$$

where $A(T)$ is the fraction of elastomeric phase which can be deduced from the phase diagram.

Now, $\sigma_{elast} = \dfrac{Ne^2 D}{kT}$, where D is the sum of the diffusion coefficients of cations and anions and N the

Fig. 7. — Time dependence of the transverse magnetization of protons in the amorphous phase in PEO(LiCF₃SO₃)₁/₈. The experimental results at $T = 413$, 392, 355 and 334 K have been corrected by the scaling factor $a(T)$ of figure 8.

Fig. 8. — Scaling factor $a(T)$ used to superimpose the transverse magnetization decays of protons in the amorphous phase at several temperatures. The dotted line has been drawn as a visual aid.

number of carriers, N depends on the temperature as given by the phase diagram. As D is related to viscosity by $D \propto T/\eta$, and as it seems reasonable to assume, in a rough approximation, that $T_2^{-1}(T)$ variations are similar to that of $\eta(T)$, one can suppose that the thermal dependence of D is given by $D \sim a(T)^{-1}$.

The experimental conductivity and the quantity

$$(3\ A(T) - 1)\frac{C(T)}{Ta(T)} \quad \text{for} \quad \text{PEO(LiCF}_3\text{SO}_3)_{1/8} \quad \text{are}$$

plotted in figure 9. It is interesting that this factor has a similar variation to that of σ_{mes} in the range 340 K-400 K : this suggests that the principal parameters have been taken into account and one can deduce the value of D [15]

$$^{375K}D_\sigma = 6 \times 10^{-8}\ \text{cm}^2\ \text{s}^{-1}.$$

The temperature dependence of $D(T)$ is given by $a_{(T)}^{-1}$ and is rather smooth since it changes only by a factor 1.6 between 340 K and 400 K. This small variation is also apparent in the tracor results obtained by Chadwick et al. [16] in PEO(Na SCN)ₓ in which a salt rich crystalline phase is also present above the melting point of PEO.

Below 330 K, pure PEO crystallites appear. The complex is then highly crystalline and other conductivity mechanisms must be considered.

5. Conclusion.

From DSC measurements and NMR studies of ¹H, ⁷Li and ¹⁹F nuclei, we have got a consistent picture of the phase diagram and of the conductivity behaviour of the complexes formed between PEO and LiCF₃SO₃.

First of all, NMR data demonstrate that the concentration of the salt rich crystalline complexe corresponds to $x_c^{-1} = 3.5$ (instead of 4 as initially suggested).
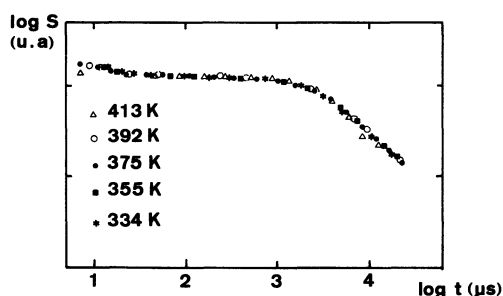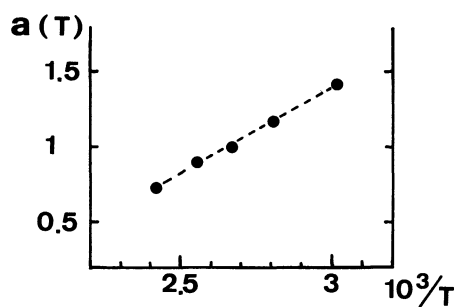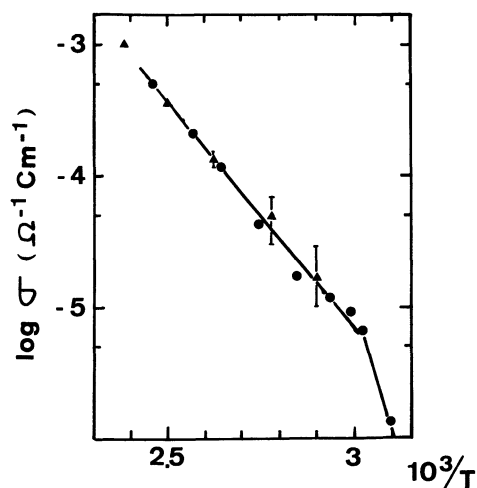

Fig. 9. — Experimental conductivity results (●) in PEO(LiCF₃SO₃)₁/₈ compared with

$$\sigma = \frac{1}{2}(3\ A(T) - 1)\frac{N(T)\ e^2\ D_\sigma^{375K}}{k(T)\ a(T)}$$

(factors defined in the text) (▲). The large error bar in the calculation at lower temperature is a consequence of the uncertainty on the salt concentration of the amorphous phase.

We have followed the temperature of dissolution of this complexe in the compounds $PEO(LiCF_3SO_3)_x$ for various x values and thus established the phase diagram between PEO, the salt rich complexe and the amorphous phase. A consistent interpretation of both NMR and DSC data implies the existence of a salt rich amorphous phase, presumably trapped in between the complexe crystallites. Thus, above the melting temperature of uncomplexed PEO, the phase diagram describes the equilibrium between a semi-crystalline salt rich phase and a dilute amorphous phase responsible for the ionic conductivity.

The ionic conductivity has been previously described by an Arrhenius law in the temperature range 340 K-420 K. This apparent variation is indeed fully explained when account is taken of the temperature dependence of the salt concentration in the dilute amorphous phase (number of carriers), as well as the Landauer correction for inhomogeneous conducting media. The striking result is the fairly small variation of D_σ in the considered temperature range which agrees with the temperature dependence of the chain dynamics deduced from our NMR measurements. Such a correlation between D_σ and the chain motions has already been observed in polyurethane networks [17].

In conclusion, the various behaviours of the ionic conductivity in the poly(ethylene oxide) alkali salts adducts can be understood as follows : for most of the alkali salts, a salt rich complex is formed, the melting temperature of which T_c is higher than that of pure PEO. Above the melting point of pure PEO, and below T_c; the system in principle possesses two phases and the ionic conductivity is ensured by the dilute amorphous phase, the concentration, the T_g and the amount of this phase are temperature dependent. Thus the temperature dependence of the conductivity cannot be described by a simple Arrhenius or Fulcher law, even though they give a correct account of the experimental data.

Nevertheless, for reasons of kinetics, metastable situations leading to an homogeneous amorphous phase below T_c can be encountered, such as in $PEO(NaI)_{0.1}$ for example [10]. Only under these homogeneous conditions is the description by a single Fulcher behaviour valid. Below the melting point of PEO, the overall degree of crystallinity of the system becomes very large and the conductivity paths are considerably lengthed. Thus other transport mechanisms must be considered, probably involving exchange between crystalline and amorphous phases.

Acknowledgments.

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