polymer papers

Infra-red and X-ray diffraction study of the hydration process in the polymer electrolyte system $M(CF_3SO_3)_2PEO_n$ for $M=$ Pb, Zn and Ni

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(Received 10 September 1992)

Water uptake in the system $M(CF_3SO_3)_2PEO_n$, where $M=$ Ni, Zn and Pb, and $n=6$–24, has been investigated at room temperature using i.r. spectroscopy and X-ray diffraction. It has been found that the ion-pairing/clustering involving M^{2+} and $CF_3SO_3^-$ is highly affected by hydration, with water replacing $CF_3SO_3^-$ at the cation. At intermediate degrees of hydration, the $CF_3SO_3^-$ ions are hydrogen bonded to metal–ion coordinating water molecules. In conditions of water excess, features typical of $CF_3SO_3^-$ ions in aqueous solution are observed. The interaction between PEO and M^{2+} is also affected by hydration for $M=$ Ni and Zn. The $\nu(COC)_a$ stretching band is shifted to higher wave numbers, indicating a weakening in the interaction between PEO and a hydrated cation. X-ray diffraction has shown that any crystalline component present in the anhydrous form is destroyed by water uptake.

(Keywords: hydration process; polymer electrolytes, poly(ethylene oxide); triflate ion; x-ray diffraction; i.r. spectroscopy)

INTRODUCTION

It has been found that poly(ethylene oxide) (PEO) can dissolve a wide variety of ionic salts to form solid polymer electrolytes[1]. PEO systems containing rare-earth metals also have potentially interesting optical applications[2]. The ionic conductivities of these systems will vary strongly depending on cation and anion type, salt concentration and temperature. Unfortunately, many of these salts are hygroscopic. It is therefore important to eliminate the presence of water, since it has been shown that water changes the conductivity drastically and uncontrollably. This could lead, for example, to the destruction of the Li anode in a lithium battery system. Chandra *et al.*[3] report an increase of up to three orders of magnitude in the ionic conductivity of the NH_4ClO_4-PEO system at ~30°C as a function of humidity; similarly, Huq *et al.*[4] observe an increase of roughly four orders of magnitude in the conductivity for $PbCl_2$ dissolved in PEO (3.4×10^{-10} to 5.0×10^{-6} $(\Omega\,cm)^{-1}$ at 22°C) on exposure to humid air for 10 h, with the conductivity returning to its original value after dehydration. A reversible hydration/dehydration process has also been observed for $CoBr_2$ dissolved in PEO, where the conductivity increases by several orders of magnitude on hydration[4]. Studies of $NiBr_2$ in PEO have shown that two types of water are present: tightly bound, corresponding to water in a hexaaquo complex, $Ni(II)\cdot6H_2O$, and more loosely bound[5,6]. In total, a fully hydrated sample can incorporate up to about 30 water molecules per cation. The conductivity again increases upon hydration, here by a remarkable ten orders of magnitude at RT. What is different in this system is that fresh, dry films are almost solely anion conductors, while films expressly hydrated and then dehydrated show considerable Ni^{2+} mobility. From these examples, we see that the hydration/dehydration process is highly dependent on the type of salt dissolved into PEO.

The degree of crystallinity at RT for these polymer electrolytes is also highly affected by hydration. Since water is a better solvent than PEO for many salts (due to its higher dielectric constant), it is not surprising that a crystalline complex formed between the salt and PEO should be destroyed on hydration of the cations. In the study of zinc halides in PEO, Glasse *et al.*[7] have found that water impedes the formation of a high-melting crystalline complex, and studies of $ZnCl_2PEO_4$ and $NiBr_2PEO_8$, which are crystalline in these anhydrous forms, show that water uptake clearly destroys crystallinity[8]. This has also been reported for several lithium salts. Exceptions are the $LiCF_3CO_2$-PEO and $LiCF_3SO_3$-PEO complexes, which retain their crystallinity on hydration[9]. Twomey and Chen[2] have reported reversible water uptake for the $NdCl_3$–PEO system, where results from i.r. studies suggest that water displaces the ethylene oxide unit from its complexation with Nd^{3+}.

In this work, we focus on the hydration process for some divalent cations in the system $M(CF_3SO_3)_2PEO_n$, where $M=$ Ni, Zn and Pb, and $n=6$–24, using *FT*i.r. spectroscopy and X-ray powder diffraction. Our aim is to arrive at some understanding of how water uptake influences the ion-pairing/clustering reported previously for these systems in their anhydrous forms[10,11]. We use

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the $CF_3SO_3^-$ ion (the triflate ion) as a probe of ion-pairing, since its internal vibrational modes can be readily observed using *FT*i.r. spectroscopy. Model studies have been made of salt solutions in CH_3CN (acetonitrile), where controlled amounts of water have been added, and of $Pb(CF_3SO_3)_2PEO_9$ containing 1 H_2O per Pb^{2+}, to provide reference spectra. The influence of hydration on the degree of crystallinity has also been investigated.

EXPERIMENTAL

Sample preparation

The triflate salts were prepared by dissolving $NiCO_3 \cdot 2Ni(OH)_2 \cdot xH_2O$ ($x \sim 4$) (Merck, extra pure), ZnO (Baker, pro analysis) and $PbCO_3$ (Schering, purissimum) in a slight excess to aqueous HCF_3SO_3 solution, followed by a filtering and precipitation stage at ~100°C. $Ni(CF_3SO_3)_2$ (s) (yellow) and $Zn(CF_3SO_3)_2$ (s) (white) precipitates were dried in vacuum at 240°C; $Pb(CF_3SO_3)_2$ (s) (white) at 140°C. *FT*i.r. spectra of the anhydrous salts were checked for O–H stretching bands from water prior to use.

Polymer films were prepared by dissolving stoichiometric amounts of the appropriate salt and PEO (BDH: $M_w = 4 \times 10^6$) separately in anhydrous acetonitrile, CH_3CN (Merck, for spectroscopy) with ether oxygen:cation ratios (n) of 9, 16 and 24 for $M = Zn$; 9, 12, 16 and 24 for $M = Ni$; and 6, 9, 12, 16 and 24 for $M = Pb$. The solutions were cast onto a Teflon plate or polyethylene paper, prior to X-ray diffraction studies. The films obtained were normally 50–100 μm thick and stored, as cast, at room temperature. The films intended for the *FT*i.r. studies were made by applying a thin layer of the solution to BaF_2 or KRS-5 windows. These were checked for water content and, when necessary, heat treated under vacuum at 100°C for one hour prior to the i.r. spectroscopy experiment. All preparations were performed in dry air (r. h. 3%) at room temperature, and the samples stored in a dry-box. We were unable to prepare $Zn(CF_3SO_3)_2PEO_9$ under anhydrous conditions for X-ray diffraction analysis. Therefore, only the *FT*i.r. results are presented in this case.

The films used for the *FT*i.r. measurements were too thin to allow direct gravimetric determination of the water uptake. Instead, a setup was used whereby a constant relative humidity was maintained inside the hood of an analytical balance. The thin film for the *FT*i.r. analysis was conditioned at the same time as the thicker sample used in the gravimetric analysis. A water content corresponding to 1 H_2O per Pb^{2+} ion was obtained for a sample of $Pb(CF_3SO_3)_2PEO_9$ for a r. h. of 20% at 23°C. This result was used to calibrate the *FT*i.r. bands in the OH and CH stretching regions, as described below. Model studies of the hydration process for lead and zinc triflate were made by dissolving the salts in anhydrous acetonitrile at ~23°C at concentration 0.26 molal. Appropriate amounts of water were added gravimetrically, corresponding to H_2O/M^{2+} ratios of 0.0, 1.0, 2.6, 6.0, 16.0 and 30.0 for $M = Zn$; and 0.0, 3.0 and 15.0 for $M = Pb$.

X-ray powder diffraction studies

The X-ray powder diffraction studies were made using a STOE powder diffractometer fitted with a stationary curved-wire position-sensitive detector (PSD) covering a 2θ range of ~45°. The minimum attainable full-width at half-height (FWHH) is ~0.15°. All experiments used Ge monochromatized $CuK\alpha_1$ radiation. Exposure times were typically 20 min. The sample was supported by an acetate foil on one side of the sample holder, which was rotated about the normal to its plane. The experimental arrangement could be enclosed in a chamber with a dry-air flush (r. h. 2% at 25°C) to prevent hydration. The entire chamber could be detached from the diffractometer for transfer to and from the dry-box. Hydration processes were followed by exposing the films to a 100% r. h. atmosphere for periods of 0.5–60 min prior to measurement.

FT*i.r.-spectroscopy studies*

*FT*i.r. spectra were recorded on a Digilab FTS-45 *FT*i.r. spectrometer covering a range from 400–4000 cm^{-1}. The spectrometer was equipped with a microscope attachment which could also be used for optical studies under polarized light. BaF_2 or KRS-5 windows were used, since KBr windows were discovered to dissolve in the polymer solution. Two different sample cells were used: for the Pb system, the cell involved two BaF_2 windows and a spacer around the sample, all fixed in place by a rigid frame. This arrangement slowed down the hydration process significantly. The hydration studies were made by exposing the sample to humid air for different times prior to data collection. A second sample cell, enclosed in a chamber which could be evacuated, and equipped with a heating element, was used for the Zn and Ni systems. This ensured completely dry samples. The chamber was also connected to a humid air supply (r. h. = 100%), by means of which small amounts of water could be added during the experiment. The hydrated acetonitrile solutions used in the model measurements were contained in a liquid cell equipped with CaF_2 windows and a Teflon spacer at ~20°C. The path length of 0.017 mm was determined interferometrically. Difference spectra are calculated, where the acetonitrile component has been subtracted from the salt solution spectra. A resolution of 1 cm^{-1} has been chosen for all i.r. measurements.

The area under the OH stretching band was taken as a measure of the water content, and the area under the CH band as a measure of the amount of polymer present. The area under the CH stretching band from the corresponding dry sample was subtracted from the total OH and CH band areas to obtain the OH stretching band area for the hydrated sample. The ratio of these areas and the result for the calibration sample were used to calculate the number of water molecules per Pb^{2+} ion in each polymer film. Since samples containing Ni^{2+} or Zn^{2+} are extremely hygroscopic, the calibration for Pb^{2+} was used for all cation types; the OH and the CH stretching bands have a similar appearance in all the cases.

RESULTS AND DISCUSSION

X-ray diffraction; hydration effects

X-ray diffraction showed the crystal structures of anhydrous $Ni(CF_3SO_3)_2$ (s) and $Zn(CF_3SO_3)_2$ (s) to be isomorphous: this was also true for the corresponding hydrated salts. Diffractograms of the 'as cast' polymer films showed that crystalline PEO was present for concentrations $n = 12$–24 in all cases, and to an ever increasing extent as the salt concentration decreases. Note, however, that no data could be obtained for

$Zn(CF_3SO_3)_2PEO_9$. Higher salt concentrations produced amorphous films. Precipitation of salt could be observed for some of the $Ni(CF_3SO_3)_2PEO_9$ films. This concentration appears to be very close to saturation, and small concentration gradients in the samples during evaporation of solvent may well promote the precipitation process. No crystalline complex is observed.

As water is introduced into the system for $Ni(CF_3SO_3)_2$ PEO_9, peaks belonging to pure salt precipitate disappear as the hydration proceeds, giving place to peaks from a crystalline salt hydrate. After exposure for 1 min to a 100% r. h. atmosphere, this phase had disappeared, and only a broad, amorphous background could be observed. For more dilute samples, crystalline PEO dissolves into the amorphous phase, indicated by the gradual disappearance of the Bragg reflections, as the hydration process proceeds (*Figure 1*).

Microscopy studies

Samples of $Ni(CF_3SO_3)_2PEO_n$, $n=9$, 16 and 24, were investigated under polarized light in the microscope attachment to the *FT*i.r. spectrometer. A totally amorphous film, except for a few small crystallites, could be seen for $n=9$. The crystallites were shown by X-ray diffraction to be anhydrous $Ni(CF_3SO_3)_2$ (s). The $n=16$ case revealed an amorphous film containing scattered spherulites of PEO (again confirmed by X-ray diffraction). In the $n=24$ case, the spherulites extended over the whole film, with amorphous regions lying between the spherulites. The $n=16$ case was selected for a study of hydration/dehydration. On exposure to normal laboratory atmosphere, the disappearance of the crystalline areas could be clearly observed. Similarly, playing a fine dry air-stream onto the film caused the crystalline spherulites to begin to grow within a few seconds. This process appeared to be reversible.

FT*i.r. spectroscopy*

Assignment of PEO vibrational bands. In pure PEO, the C–O–C symmetric stretching mode, $\nu(COC)_s$, at $1116\,cm^{-1}$ has earlier been assigned to E_1 symmetry; the C–O–C antisymmetric stretching mode, $\nu(COC)_a$, at $1103\,cm^{-1}$ to A_2; and the band at $1147\,cm^{-1}$ to a coupled E_1 C–C stretching and C–O–C antisymmetric stretching mode, $\nu(COC)_a+\nu(CC)$[12]. Earlier studies of polycrystalline PEO have shown that only one band at $1106\,cm^{-1}$ and one band at $1148\,cm^{-1}$ are resolvable, both at 25°C and at 70°C, at which temperature PEO has already melted. These two bands shift to $1080\,cm^{-1}$ and $1160\,cm^{-1}$ (overlapping with the CF_3-stretching mode of $CF_3SO_3^-$), respectively, when a salt is dissolved into PEO. This is indicative of a change in the environment of the ether oxygens through their coordination to the cations[10,11].

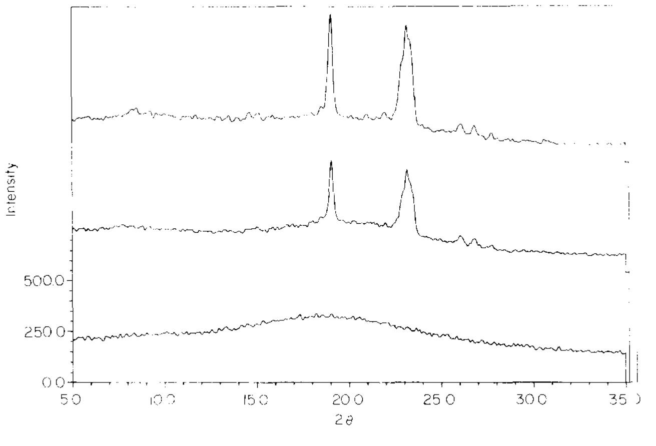

Figure 1 X-ray diffractograms at 23°C for different levels of hydration in $Ni(CF_3SO_3)_2PEO_{16}$ (top: dry sample). The Bragg reflections at 19° and 23° arise from crystalline PEO. As the hydration proceeds, crystalline PEO dissolves into the amorphous phase, indicated by the gradual disappearance of the Bragg reflections

Assignment of the triflate ion vibrational bands. The triflate ion ($CF_3SO_3^-$) was chosen as anion, since its internal vibrational modes can serve as a probe of its local environment. When free, the ion is assumed to have point symmetry C_{3v}. The antisymmetric SO_3-stretching mode, $\nu(SO_3)_a$, with E symmetry is doubly degenerate, while the A_1 symmetric mode, $\nu(SO_3)_s$, is non-degenerate. Both modes are i.r. active. The symmetry of the triflate ion will generally be lowered when coordinated to a cation. This will cause a splitting of the antisymmetric SO_3-stretching mode into two components, while the symmetric SO_3-stretching mode will shift in frequency.

Triflate ion in the anhydrous $M(CF_3SO_3)_2PEO_n$ *system.* Previous studies of the anhydrous systems have shown that the degenerate $\nu(SO_3)_a$ mode corresponding to a non-coordinated $CF_3SO_3^-$ anion is found at $1272\,cm^{-1}$ (refs 10, 11). At high Pb^{2+} salt concentrations, two bands appear at 1303 and $1233\,cm^{-1}$, indicating the presence of triflate ions coordinated to metal ions. This splitting is larger for Zn^{2+} and Ni^{2+} (1325 to $1236\,cm^{-1}$) since their interaction with the triflate ion is stronger. At this stage, it cannot be said whether this splitting is caused by ion pairs or clusters, or both. In the non-degenerate $\nu(SO_3)_s$ region, bands are observed between 1030 and $1020\,cm^{-1}$ for $M=Pb$, suggesting different environments for the anions: reasonably, non-coordinated triflate ions and ion pairs/clusters. The band at $1030\,cm^{-1}$ increases for decreasing salt concentrations. A band appears at higher wave number ($1042\,cm^{-1}$) for $M=Ni$ at high salt concentrations, along with the band at $1030\,cm^{-1}$; while for $M=Zn$ only the band at $1030\,cm^{-1}$ is observed clearly, irrespective of salt concentration. There is therefore no information available from this band as to the possible existence of 'free' ions. At this stage, the different shifts in the frequency of the $\nu(SO_3)_s$ mode for different cation types remain unexplained.

Hydration effects

$Pb(CF_3SO_3)_2$–CH_3CN system. Systematic changes are observed in the *FT*i.r. spectra in the regions of the symmetric and the antisymmetric SO_3-stretching bands for the model system 0.26 molal $Pb(CF_3SO_3)_2$ in CH_3CN, as the controlled amount of water is increased. For the anhydrous solution, three bands are seen at 1032, 1026 and $1020\,cm^{-1}$, corresponding to the $\nu(SO_3)_s$ vibrations (*Figure 2a*). The band at $1032\,cm^{-1}$ has earlier been identified as arising from non-coordinated triflate ions[10,11]. A reasonable interpretation of the other two bands is that the one at $1026\,cm^{-1}$ corresponds to a 1:1 complex of Pb^{2+} and $CF_3SO_3^-$ ions, and the one at $1020\,cm^{-1}$ to a corresponding 1:2 complex. The addition of water up to a concentration of ~ 3 H_2O per Pb^{2+} causes the band at $1020\,cm^{-1}$ to diminish, whereas the other two increase. This is the expected behaviour as a

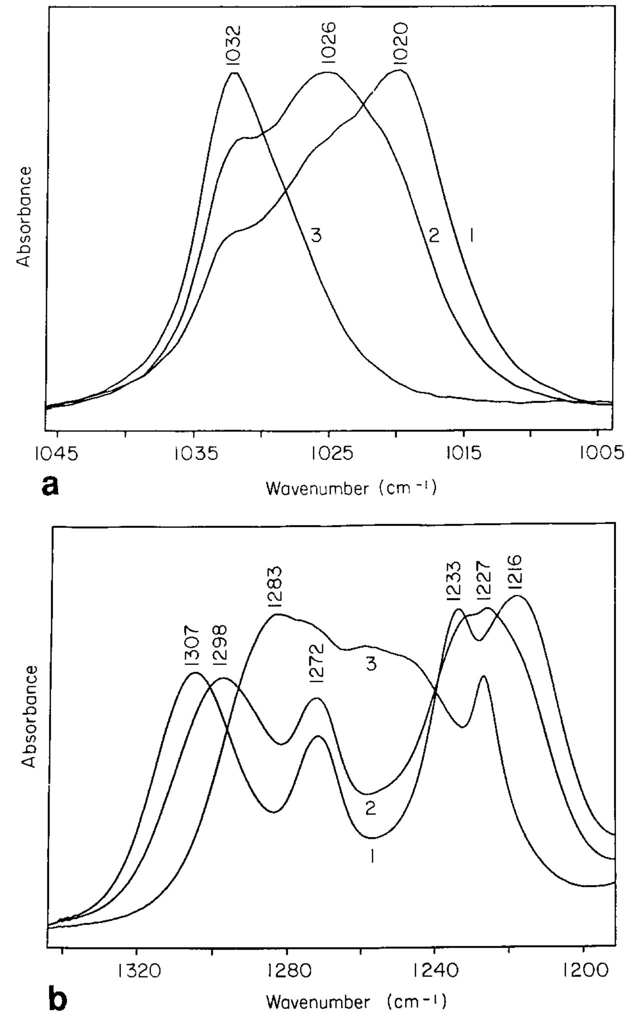

Figure 2 *FT*i.r. absorption spectra in (a) the $\nu(SO_3)_s$ region, and (b) the $\nu(SO_3)_a$ region of 0.26 molal $Pb(CF_3SO_3)_2$ in CH_3CN at 23°C, with H_2O/Pb^{2+} ratios of 0, 3 and 15 (marked 1, 2 and 3)

water molecule replaces one $CF_3SO_3^-$ ion in a 1:2 complex to create a 1:1 complex and a non-coordinated $CF_3SO_3^-$ ion. On the addition of ~15 H_2O per Pb^{2+} ion, almost all triflate ions are replaced and non-coordinating triflate ions (absorbing at 1032 cm^{-1}) dominate in the solution.

In the dry sample, the $\nu(SO_3)_a$ region contains a degenerate band at 1272 cm^{-1} together with a split band with components at 1307 and 1233 cm^{-1}. These correspond to the non-coordinated and coordinated triflate ion, respectively (*Figure 2b*). The band at 1216 cm^{-1} arises from a CF_3-stretching mode. On adding 3 H_2O per Pb^{2+}, a band appears at 1298 cm^{-1}. The addition of ~15 H_2O per Pb^{2+} causes the spectrum to resemble that of a 'free' triflate ion dissolved in water, with a band at ~1283 cm^{-1} (ref. 13). It is difficult to say whether the bound triflate-ion band at 1307 cm^{-1} shifts towards lower wave numbers, or whether the band at 1298 cm^{-1} is an overlap of 1307 and 1283 cm^{-1} bands. However, a possible explanation for a band at 1298 cm^{-1} would be a weaker interaction between a hydrated cation and a triflate ion.

$Pb(CF_3SO_3)_2$–PEO system. A study of $Pb(CF_3SO_3)_2$-PEO_9 was made since this system is completely amorphous. The effective salt concentration in the amorphous phase will thus correspond to the nominal value (n) while for more dilute samples, the PEO excess will crystallize to produce a higher than nominal (and unknown) salt concentration in the amorphous regions which remain. A broad band ranging from 1030 to 1018 cm^{-1} can be observed in the $\nu(SO_3)_s$ region (*Figure 3a*). No clear resolution into three components is observed here, as was observed in the model study. However, on the addition of water, the absorption on the low-frequency side of the band diminishes. One band, centred at 1030 cm^{-1}, is finally obtained on the addition of 4.5 H_2O per Pb^+, as observed in the model study. In the $\nu(SO_3)_a$ region (*Figure 3b*), the degenerate band from non-coordinating $CF_3SO_3^-$ is found at 1273 cm^{-1}, while the split band components from coordinating $CF_3SO_3^-$ are found at 1298 and 1234 cm^{-1}. When water is added through exposure to humid air (r.h. = 24–100%), the coordinated triflate-ion bands diminish, while the non-coordinated triflate-ion band does not increase. This behaviour is also observed in the model study, and can be explained by the growth of two bands at 1283 and 1254 cm^{-1}. These bands probably correspond to triflate ions which are hydrogen bonded to H_2O, while the band at 1273 cm^{-1} corresponds to triflate ions dissolved in PEO. The disappearance of the two bands at 1298 and 1234 cm^{-1} is complete on the addition of 1.0 H_2O/Pb^{2+}. This indicates that one water molecule replaces one triflate ion at each cation.

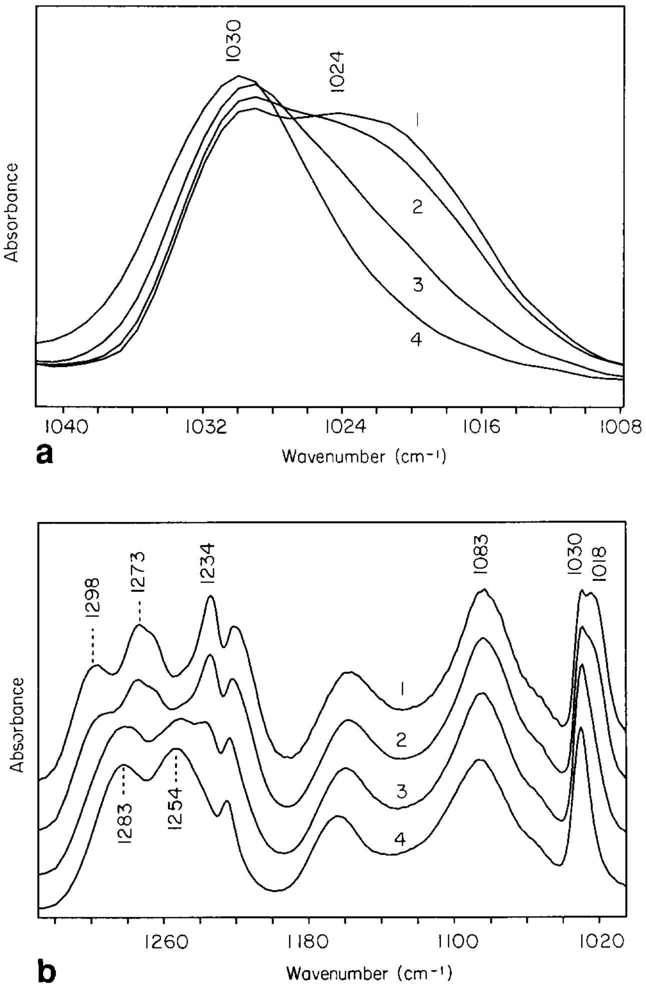

Figure 3 *FT*i.r. absorption spectra in (a) $\nu(SO_3)_s$ region, and (b) the $\nu(SO_3)_a$ and $\nu(COC)$ region for $Pb(CF_3SO_3)_2PEO_9$ at 23°C, with H_2O/Pb^{2+} ratios of 0.0, 0.3, 1.0 and 4.5. (marked 1, 2, 3, and 4)

In spite of the many changes observed in the SO_3-regions, no changes are observed in the (COC)-stretching region; the band at 1083 cm^{-1} remains practically unchanged, implying that the metal-ion coordination to the ether oxygens is unaffected by hydration. In other words, Pb^{2+} is able to maintain a sufficiently large coordination number to keep all nine ether oxygens per cation coordinated, regardless of whether a triflate ion or a water molecule also coordinates to the cation.

$Zn(CF_3SO_3)_2$–CH_3CN system. Only one band at 1032 cm^{-1} is found in the $\nu(SO_3)_s$ region for the model system 0.26 molal $Zn(CF_3SO_3)_2$ in CH_3CN (*Figure 4*). In the $\nu(SO_3)_a$ region, the band corresponding to non-coordinating $CF_3SO_3^-$ is found at 1272 cm^{-1}, while the split band components arising from the coordinated anion are observed at 1312 and 1241 cm^{-1}. The bands in the region 1230–1150 cm^{-1} are the CF_3-stretching modes. As 1 H_2O per Zn^{2+} is introduced into the system, no changes are observed in the $\nu(SO_3)_s$ region, while in the antisymmetric region, the bands at 1312 and 1241 cm^{-1} diminish, and two bands appear at 1289 and 1251 cm^{-1}. This can be related to one H_2O molecule replacing one $CF_3SO_3^-$ ion, with the H_2O now forming hydrogen bonds to the $CF_3SO_3^-$ ion. This has the effect that the triflate ion experiences a weaker interaction than it does when directly coordinated to the cation. Since there are already a considerable number of free triflate ions present, only slightly more than one water per cation is needed to replace the remaining coordinated anions. On the addition of 2.6 H_2O per Zn^{2+}, the bands corresponding to the metal-ion coordinated triflate ion in CH_3CN disappear, indicating the absence of ion pairs/clusters, but the 'free' triflate band in CH_3CN can still be observed at 1272 cm^{-1}. As the amount of water is successively increased to 30 H_2O per Zn^{2+}, the bands at 1289 and 1251 cm^{-1} move closer together (to 1281 and 1259 cm^{-1}, respectively), approaching the situation for the 'free' triflate ions in aqueous solution[13]. The $\nu(SO_3)_s$ mode is not affected in any way, however. No evidence of ion pairing/clustering is therefore provided by this region for the zinc system.

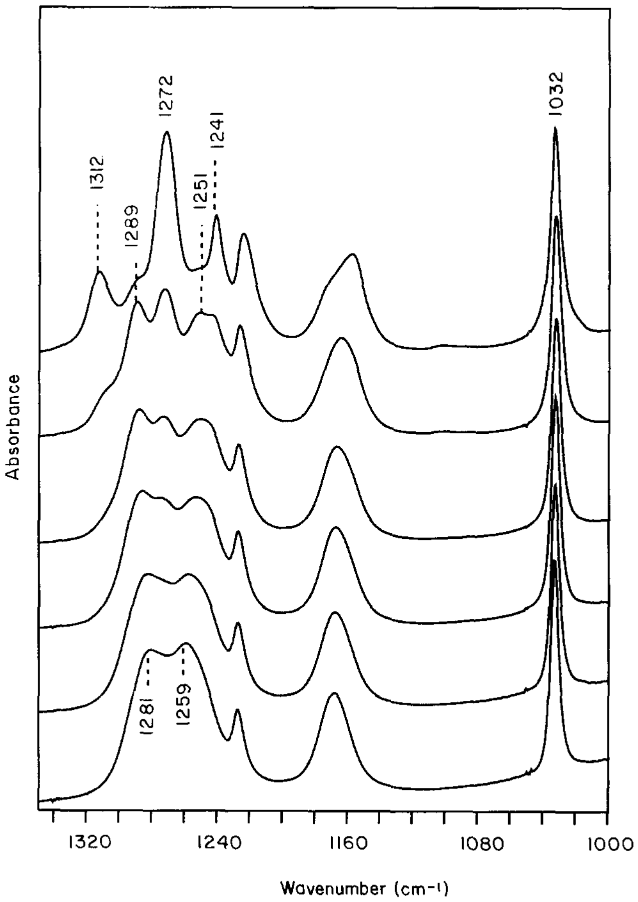

Figure 4 *FT*i.r. absorption spectra of 0.26 molal $Zn(CF_3SO_3)_2$ in CH_3CN at 23°C, with H_2O/Zn^{2+} ratios of 0.0 (top), 1.0, 2.6, 6.0, 16.0 and 30.0 (bottom)

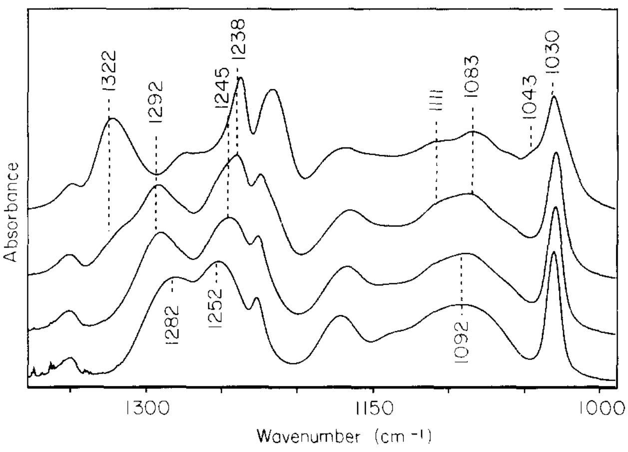

Figure 5 *FT*i.r. absorption spectra of $Zn(CF_3SO_3)_2PEO_9$ at 23°C with H_2O/Zn^{2+} ratios of 0.0 (top), 1.7, 3.8 and 7.0 (bottom)

$Zn(CF_3SO_3)_2$–PEO system. Infra-red spectroscopy and polarized optical microscopy show the anhydrous $Zn(CF_3SO_3)_2PEO_9$ system to be completely amorphous; neither sharp bands nor spherulites characteristic of crystalline regions are observed. This means that the salt concentration in the amorphous phase is again given by the nominal concentration (*n*). Here, one band at 1030 cm^{-1} and a shoulder at 1043 cm^{-1} are observed in the $\nu(SO_3)_s$ region, while the bands for coordinated $CF_3SO_3^-$ (at 1322 and 1238 cm^{-1}) dominate in the $\nu(SO_3)_a$ region (*Figure 5*). On average, this corresponds to one Zn^{2+} ion coordinating two $CF_3SO_3^-$ ions, since no 'free' triflate band is observed at 1272 cm^{-1} (ref. 11). As the sample is exposed to humid air (r. h. = 100%) for a few seconds, each Zn^{2+} ion takes up 1.7 H_2O molecules. The $\nu(SO_3)_a$ bands diminish, but do not disappear, while two new bands appear at 1292 and 1245 cm^{-1}. These latter bands remain on further hydration. On longer exposure to humid air (~2 min), 7 H_2O molecules are taken up per Zn^{2+} ion, and two bands (at 1282 and 1252 cm^{-1}) now dominate. These observations are consistent with a situation in which water molecules coordinate to the cations and, in doing so, replace the $CF_3SO_3^-$ ions, which can then only coordinate to the cations via the water molecules. This, in turn, causes a reduction in the splitting of the $\nu(SO_3)_a$ bands. Bands corresponding to 'free' triflate ions in an aqueous solution appear for an excess of water. These observations thus correspond closely to those made on the model system. The bands at 1322 and 1238 cm^{-1} disappear on the addition of 3.8 H_2O per Zn^{2+}, again indicating that initially one water molecule replaces one triflate ion at each cation.

The only change observed in the $\nu(SO_3)_s$ region during this hydration process is the disappearance of the shoulder at 1043 cm^{-1}. We still have no explanation for this band, but one possibility is that it has its origin in the presence of ion-clusters.

The (COC)-stretching modes are also affected by water uptake. The band at 1111 cm^{-1} (originating from pure PEO) and at 1083 cm^{-1} (from PEO coordinating to the Zn^{2+} ion) diminish on hydration, at the expense of a broad band which appears at 1092 cm^{-1}. A reasonable explanation is that the ether oxygens experience a weaker interaction with a hydrated cation. This causes a shift in the band at 1083 cm^{-1} to higher wave number. Interestingly, n.m.r. studies have shown an increase in chain mobility on hydration[14]. At the same time, the amount of free PEO decreases, since a hydrated cation can coordinate to a larger amount of PEO. The detailed change in the region 1220–1250 cm^{-1} as a function of hydration is difficult to interpret because of the closeness of the CF-stretching band and the low wave number component of the split $\nu(SO_3)_a$ band.

$Ni(CF_3SO_3)_2$–PEO system. No model studies were performed for the Ni case; it was assumed that the model study made for $M = Zn$ could also apply here. The hydration of $Ni(CF_3SO_3)_2PEO_{12}$ was investigated; the value $n = 12$ was chosen to avoid the complication of salt precipitation. This system, which contained small amounts of crystalline PEO 'as cast', became amorphous after annealing. At this concentration, there thus seems to be a subtle balance between thermal history and crystal formation. Similar behaviour has been observed for $n = 16$. Hydration could be monitored by observation of the O–H-stretching bands of the water molecules (*Figure 6a*). The hydration effects are seen more clearly for Ni than for Zn (*Figure 6b*). For an anhydrous amorphous sample (1 in *Figure 6b*), two bands are readily observed in the $\nu(SO_3)_s$ region (at 1042 and 1030 cm^{-1}), while in the $\nu(SO_3)_a$ region, the bands characteristic of coordinated $CF_3SO_3^-$ are found at 1320 and 1236 cm^{-1}. The shoulder at 1270 cm^{-1} arises from vibrational modes of metal-ion coordinated PEO, probably the CH_2 twisting modes[9,12]. This has been confirmed in a study of $ZnCl_2PEO_4$, a system which consists almost entirely of a crystalline complex formed between PEO and the salt[15]. For this system, the PEO modes can be observed without any overlapping anion bands. At the onset of hydration, the band at 1042 cm^{-1} in the $\nu(SO_3)_s$ region disappears, while in the $\nu(SO_3)_a$ region, bands appear from the weakly coordinated $CF_3SO_3^-$ ions at 1285 and 1252 cm^{-1} (spectra 2–5). This is once again reminiscent of an aqueous solution of triflate ions. The intermediate bands, which correspond to 0.3, 2.7 and 4.4 H_2O per Ni^{2+}, respectively, again probably arise from a hydrogen-bond interaction between $CF_3SO_3^-$ and a hydrated cation, as suggested for the Zn case. After the addition of 2.7 H_2O per Ni^{2+}, all triflate ions have been replaced by water molecules at the cation.

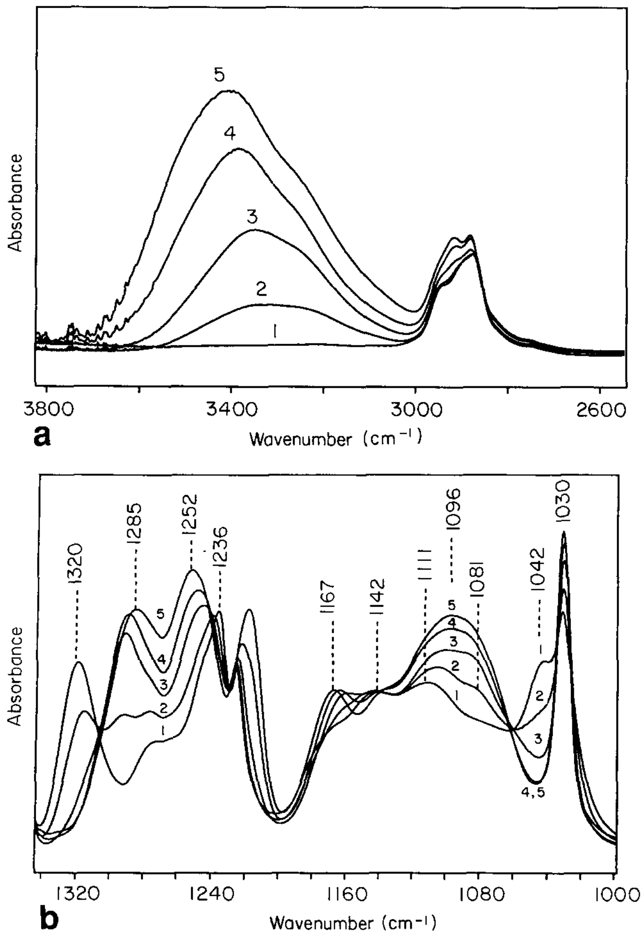

Figure 6 *FT*i.r. absorption spectra of $Ni(CF_3SO_3)_2PEO_{12}$ at 23°C, showing (a) the O–H stretching region, and (b) the 1000–1350 cm^{-1} region, with H_2O/Ni^{2+} ratios of 0.0, 0.3, 2.7, 4.4 and 6.3 (marked as 1 to 5)

Changes are also observed in the (COC)-stretching region. In spectra 1 and 2 (*Figure 6b*), a band arising from pure, non-coordinating PEO is found at 1111 cm^{-1}, and from nickel-ion coordinated PEO at 1081 cm^{-1}. A band grows at 1096 cm^{-1} as more water is introduced. The same phenomenon has been discussed above for the Zn case, and can again be explained in terms of PEO coordinating to a hydrated cation through hydrogen bonding. This causes a weaker interaction for the hydrated case than for the metal-ion coordinated directly to the ether oxygens, and thus a shift to higher wave number.

Comparison with conductivity measurements

In the Introduction, several examples were cited of large increases occurring in the conductivity on hydration of PEO-salt systems. We can here identify several factors, each of which should imply an increase in conductivity on hydration:

- 'free' ions are produced, giving rise to a larger number of charge carriers
- the number of ion pairs, triplets and higher aggregates which, due to their larger size, are considered less mobile and thus contribute less to the ionic conduction process, decreases
- the hydrated cation has a weaker interaction with PEO, resulting in a higher mobility
- the hydrated cations have a plasticizing effect; the interaction between the cations and the ether oxygens in PEO is weakened on water uptake, causing a higher chain mobility. This is, in turn, closely related to the ion transport mechanism. This result is also found from n.m.r. studies of the increased segmental motion of the polymer backbone for the hydrated $M(CF_3SO_3)_2PEO_n$ systems[14]
- water destroys any crystalline (low conductivity) components present, thus enhancing the amount of amorphous, conducting regions.

We can readily understand, therefore, how just a minute amount of water can affect the conductivity so dramatically. It is thus necessary to work with extreme caution to avoid contamination from water when working with cations which have high water affinity, e.g. Ni^{2+} and Zn^{2+}.

CONCLUSIONS

It has been found by i.r. spectroscopy that ion pairing/clustering between $M = $ Pb, Zn and Ni cations and CF_3SO_3 anions is highly affected by hydration, with water replacing $CF_3SO_3^-$ at the cation. The quantitative measurements show that initially every water molecule which is introduced into the system replaces an anion at the cation. At intermediate levels of hydration, the $CF_3SO_3^-$ ions accept hydrogen bonds from metal-ion coordinating water molecules. For an excess of water, features are observed characteristic of $CF_3SO_3^-$ ions in aqueous solution. The interaction between PEO and M^{2+} for $M = $ Ni and Zn is also affected by hydration. The v(COC) stretching band is shifted to higher wave numbers, indicating a weakening in the interaction between PEO and the hydrated cations. X-ray diffraction has shown that any crystalline component present in the anhydrous form is destroyed by water uptake.

ACKNOWLEDGEMENTS

This work is supported by the Swedish Natural Science Research Council (NFR), the Swedish Technical Science Research Council (TFR), and by a DARPA grant administered through a contract monitored by the United States Office of Naval Research (ONR). Special thanks are due to Dr J. Tegenfeldt for some most valuable discussions.

REFERENCES

1 Ratner, M. A. and Shriver, D. F. *Chem. Rev.* 1988, **88**, 109
2 Twomey, C. J. and Chen, S. H. *J. Polym. Sci., Polym. Phys. Edn* 1991, **29**, 859
3 Chandra, S., Hashmi, S. A. and Prasad, G. *Solid State Ionics*, 1990, **40/41**, 651
4 Huq, R., Chiodelli, G., Ferloni, P. and Magistris, A. *J. Electrochem. Soc.* 1987, **134**, 364
5 Huq, R., Saltzberg, M. A. and Farrington, G. C. *J. Electrochem. Soc.* 1989, **136**, 1260
6 Huq, R. and Farrington, G. C. *J. Electrochem. Soc.* 1988, **135**, 524
7 Glasse, M. D., Linford, R. G. and Schlindwein, W. S. *2nd Int. Symposium Polymer Electrolytes* (Ed. B. Scrosati), Elsevier Applied Science, 1990, p. 203
8 Wendsjö, Å. and Yang, H. *2nd Int. Symposium Polymer Electrolytes* (Ed. B. Scrosati), Elsevier Applied Science, 1990, p. 225
9 Papke, B. L., Ratner, M. A. and Shriver, D. F. *J. Electrochem. Soc.* 1982, **129**, 1434
10 Wendsjö, Å., Lindgren, J. and Paluszkiewicz, C. *Electrochimica Acta* 1992, **37**, 1689
11 Wendsjö, Å, Lindgren, J., Thomas, J. O. and Farrington, G. C. *Solid State Ionics*, 1992, **53–56**, 1077
12 Yoshihara, T., Tadokoro, H. and Murahashi, S. *J. Chem. Phys.* 1964, **41**, 2902
13 Bergström, P.-Å. and Lindgren, J. *J. Mol. Struc.* 1990, **239**, 103
14 Lauenstein, Å and Tegenfeldt, J. unpublished results
15 Yang, H. Thesis, University of Pennsylvania, 1991