Compound Formation and Ionic Association in the Poly(ethylene oxide)−Potassium Triflate System

Sangamithra Chintapalli,[†] Christine Quinton,[‡] Roger Frech,[*,†] and Colin A. Vincent[§]

Department of Chemistry and Biochemistry, The University of Oklahoma, Norman, Oklahoma 73019, Ecole Nationale Superieure de Chimie de Clermont-Ferrand, BP 187 63174 Aubiere Cedex, France, and School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife KY16 9ST, Scotland

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ABSTRACT: Results of a spectroscopic study in the high molecular weight PEO−potassium triflate system indicates the presence of a crystalline compound with a 1:1 stoichiometry, (PEO)KCF_3SO_3, which has also been confirmed with X-ray diffraction and DSC studies. The presence of the compound leads to a decrease in ionic conductivity at very high salt concentrations. Ionic association of potassium triflate in glymes and glycols as a function of salt concentration was also studied using infrared spectroscopy, with particular attention to the effect of chain length and end group on the ionic association.

1. Introduction

Polymer electrolytes have become increasingly important due to their wide range of electrochemical applications.[1−6] Thus, much attention has been paid to the role of ionic association, ion−polymer interactions, and polymer segmental motion, all of which play a major role in the mechanism of ion transport in polymer−salt systems. These factors have been well-studied in the PEO−$LiCF_3SO_3$ systems[7−12] and are being extended to other triflate salts in PEO.[7,13−17] Based on conductivity studies of PEO−alkali metal triflates at a 10:1 O:M (ether oxygen:metal cation) ratio, Rietman et al.[15] reported that conductivity increased with ionic radius in the sequence from Li^+ to Cs^+. That study also showed that the interaction between the cation and anion in the polymer matrix is an important consideration in the mechanism of ionic conductivity, a conclusion with which most workers in this field would probably agree.

The PEO−KCF_3SO_3 system has received relatively little attention, perhaps because of the assumption that its ionic association and ion−polymer interactions are similar to those in the PEO−$LiCF_3SO_3$ system. However, the phase diagram of the PEO−KCF_3SO_3 system[18] indicates a compound with a 1.2:1 stoichiometry, which differs from the 3:1 compound found in the PEO−$LiCF_3SO_3$ system.[18] This carries the implication that the cation−anion and cation−polymer interactions might be significantly different in the two systems, with the further implication that these interactions should be carefully examined over a wide range of salt concentrations in PEO−KCF_3SO_3. That is the goal of this paper.

Here, a systematic study of the high molecular weight PEO−KCF_3SO_3 system using infrared spectroscopy, X-ray diffraction, DSC and impedance spectroscopy is reported. In addition, infrared spectroscopic measurements of solutions of glymes and glycols with potassium triflate are also described, since the low molecular weight oligomer−salt systems are useful in interpreting the spectra of high molecular weight PEO−salt systems.

2. Experimental Section

The glymes, glycols (Aldrich), and PEO ($\langle MW \rangle = 4 \times 10^6$, Aldrich) were used as received. Potassium triflate (Johnson Matthey Electronics) was dried at ~100 °C in vacuum. The oligomer solutions were prepared by dissolving the salt directly in the oligomer. The high molecular weight PEO−salt systems were prepared by the dissolution of PEO and KCF_3SO_3 in a sufficient amount of acetonitrile. In both cases, the solutions were stirred overnight at room temperature.

For infrared studies of the oligomer−salt solutions, the liquid was spread between two CsI windows of dimensions 38 mm × 19 mm × 4 mm, while for the high molecular weight PEO−salt systems, thin films were cast on CsI windows and dried at ~80 °C under vacuum for 20 min. The IR spectra were recorded with a Bruker IFS66V FT-IR spectrometer in the absorbance mode in the region 4000−400 cm^{-1} and at a resolution of 2 cm^{-1}. The IR spectra in the ionic association region were curve-fitted to a straight base line and one Gaussian−Lorentzian product function for each band using a nonlinear least-squares method with a commercial program, Grams 386 (Galactic Industries). In a given spectral region such as the SO_3 symmetric stretching mode or the CF_3 symmetric deformation mode of the triflate anion, the relative intensities of the bands due to various triflate ion species (i.e., “free” ions, contact ion pairs, etc.) can be shown to be directly proportional to the relative concentrations of those species.[19]

Thin film samples for the DSC and conductivity experiments were obtained by casting the gelatinous solution on a Teflon support followed by the slow evaporation of solvent. The films were then dried in a vacuum oven at about 100 °C for 24 h. The DSC measurements were carried out with a Mettler DSC 820 calorimeter under a nitrogen atmosphere (flow rate of 87 mL/min) from −25 to +300 °C at a heating rate of 10 °C/min. The conductivity measurements were made using a Hewlett-Packard 4192A LF impedance analyzer in the temperature range 25−95 °C controlled to an accuracy of ±1 °C. The frequency range used for this study was 5 Hz to 13 Mhz. For X-ray diffraction studies, the samples were placed in 7 mm diameter glass capillaries and sealed under argon using a silicone sealant that was allowed to harden for 24 h before data collection. The data were collected using a STOE X-ray diffractometer (STADI-P) using Cu Kα radiation and values of 2θ ranging from 5 to 60°.

3. Results and Discussion

3.1. High Molecular Weight PEO−Potassium Triflate System.

3.1.1. Infrared Spectroscopic Study of Ionic Association. The symmetric deformation mode of CF_3, $\delta_s(CF_3)$, is sensitive to ionic association in polymer−salt systems.[20] Figure 1 shows the spectra

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[†] University of Oklahoma.

[‡] Ecole Nationale Superieure de Chimie de Clermont-Ferrand.

[§] University of St. Andrews.

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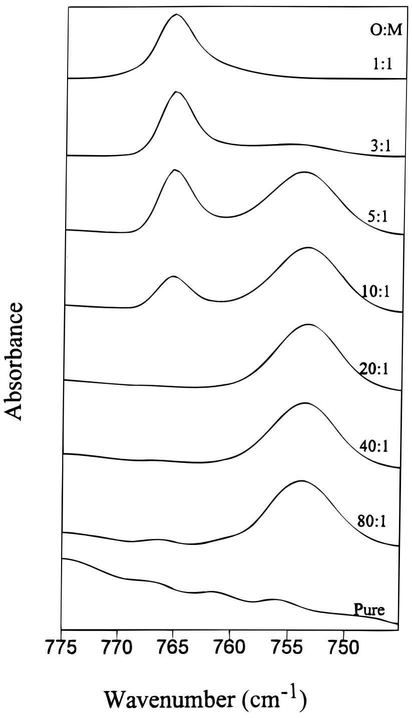

Figure 1. IR spectra of (PEO)$_n$KCF$_3$SO$_3$ as a function of O:M ratio in the δ_s(CF$_3$) region.

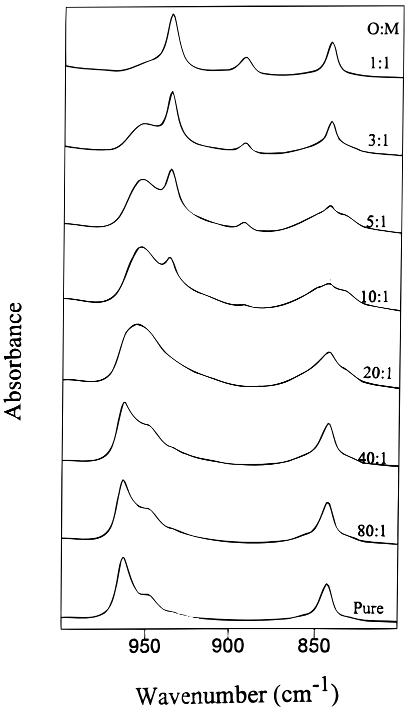

Figure 2. IR spectra of (PEO)$_n$KCF$_3$SO$_3$ as a function of O:M ratio in the 1000−800 cm^{-1} spectral region.

for PEO−KCF$_3$SO$_3$ systems as a function of O:M ratio in the δ_s(CF$_3$) region. With addition of salt to PEO, a peak appears at 753 cm^{-1} in the 80:1 system and increases in intensity with salt concentration. Although the spectra for the electrolytes with O:M from 80:1 to 20:1 have only one intense peak, curve-fitting shows contributions from two peaks at 752 and 754 cm^{-1}, while the 20:1 system has a third contribution at 756 cm^{-1}. The peak at 752 cm^{-1} is due to "free" ions, while the peaks at 754 and 756 cm^{-1}, by analogy to those at 757 and 763 cm^{-1} in the PEO−LiCF$_3$SO$_3$ system,[20] can be attributed to ion pairs and aggregates, respectively. An additional peak appears at 765 cm^{-1} in the 10:1 system and grows in intensity with a further increase in salt concentration, while the intensity of the peak at 753 cm^{-1} decreases. In the 1:1 system, only a single peak at 765 cm^{-1} is present. This peak may be attributed to the presence of a crystalline compound similar to (PEO)$_3$LiCF$_3$SO$_3$ in the PEO−LiCF$_3$SO$_3$ system.[11,21−23] However, these data suggest a 1:1 stoichiometry for the compound in the PEO−KCF$_3$SO$_3$ system.

3.1.2. Infrared Spectroscopic Study of Conformation. The spectral region 1000−800 cm^{-1} shown in Figure 2 consists of a mixture of CH$_2$ rocking and C−O stretching vibrational modes; spectral changes in this region reflect changes occurring in the local structure of the polymer backbone.[24] The peak at 844 cm^{-1} in pure PEO is primarily due to the CH$_2$ rocking mode, while the peaks at 964 and 949 cm^{-1} are mainly due to the C−O stretching modes. No significant changes are seen in the spectra of the dilute samples with O:M ratios of 80:1 and 40:1. However, the peaks broaden considerably in the 20:1 system, signifying that the local structure is considerably disordered. In the 10:1 system, new peaks appear at 936 and 892 cm^{-1}, which increase in intensity with increasing salt concentration. In addition, the peak at 843 cm^{-1} once again becomes the dominant feature at salt concentrations above 5:1. In this spectral region, the 1:1 system exhibits only three peaks at 936, 892, and 843 cm^{-1}, which are attributed to the formation of a new crystalline compound. The peak at 843 cm^{-1} in the 1:1 system suggests that the −O−C−C−O− torsional angle in the compound is similar to that in pure PEO. Supporting evidence for this conclusion comes from the crystal structure of the 1:1 crystalline compound (PEO)NaCF$_3$SO$_3$ recently determined by Andreev et al.[25] The spectra of the PEO−NaCF$_3$SO$_3$ and PEO−KCF$_3$SO$_3$ systems are similar in this region except for the shifting of the peaks at 936 and 892 cm^{-1}. In the crystal structure of the (PEO)NaCF$_3$SO$_3$ compound, the PEO chain is in a stretched zigzag conformation; however, the C−C bonds are either gauche or gauche-minus. This therefore supports our conclusion, inferred from the vibrational spectra, that the torsional angle in the (PEO)KCF$_3$SO$_3$ compound is similar to that in pure PEO.

Figure 3 shows the IR spectra of these systems in the C−O−C stretching region, which is also sensitive to interactions of the polyether oxygen atoms with the cation.[24] The peak at 1112 cm^{-1} in pure PEO broadens slightly with addition of salt up to an O:M ratio of 20:1. In the 10:1 system, the single broad peak is replaced by two distinct peaks at 1104 and 1115 cm^{-1}, which grow in intensity with salt concentration. It may be recalled from the δ_s(CF$_3$) and conformation spectral regions that new peaks which have been assigned to the 1:1 crystalline compound begin to appear in the 10:1 system. Thus the concentration dependence of the spectra in all spectral regions is consistent and indicates the presence of 1:1 crystalline compound.

3.1.3. X-ray Diffraction. Figure 4 shows the X-ray diffractograms in the region $2\theta = 5−35°$ for the systems with O:M ratios 5:1, 3:1, 2:1, and 1:1. In addition, the XRD data for pure PEO and KCF$_3$SO$_3$ are also given for comparison. It can be seen that the 5:1 system consists of a few new peaks in addition to those corresponding to pure PEO. These new peaks do not coincide with those of pure KCF$_3$SO$_3$ (upper curve). The intensities of the new peaks increase, while those due to PEO decrease from the 5:1 to the 3:1 system. The peaks due to pure PEO are faintly visible in the 2:1 system and completely disappear in the 1:1 system. A

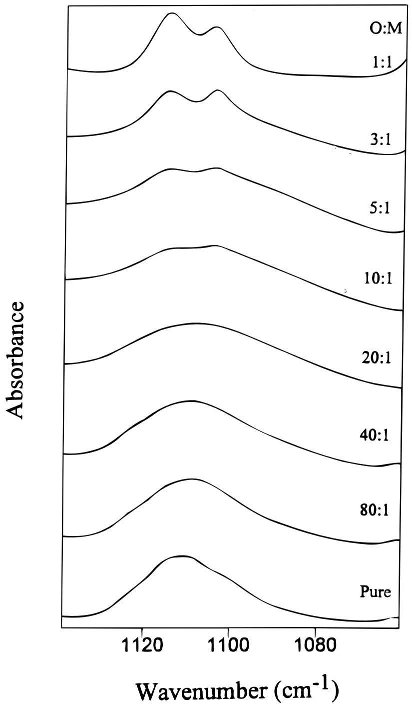

Figure 3. IR spectra of $(PEO)_nKCF_3SO_3$ as a function of O:M ratio in the C−O−C stretching region.

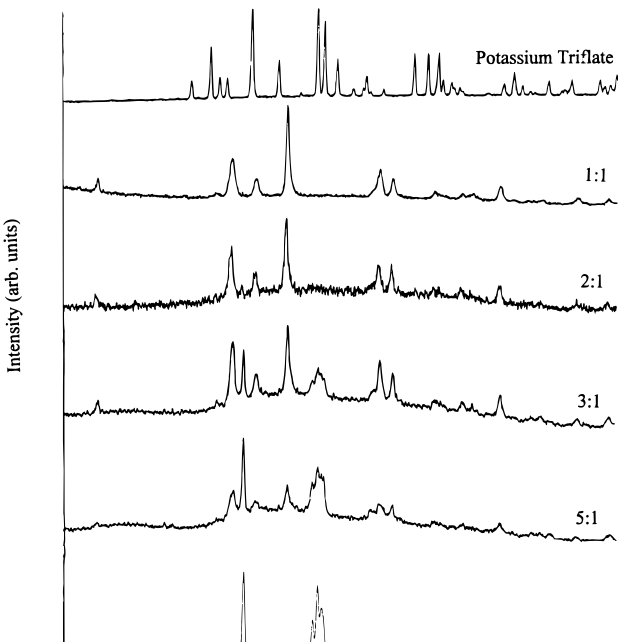

Figure 4. X-ray diffraction data for $(PEO)_nKCF_3SO_3$.

1.5:1 sample formed the 1:1 structure and showed two peaks, which are tentatively assigned to excess PEO (data not shown). The XRD data are also consistent with the spectroscopic data and confirm the formation of a crystalline compound with an O:M ratio of 1:1. Additional X-ray diffraction measurements were made on two samples that were more highly enriched in salt than the 1:1 system. The PEO−KCF_3SO_3 systems at 0.2:1 and 0.5:1 formed what appeared to be a 1:1 structure, with excess pure KCF_3SO_3 making up the rest of the diffractograms. There was no trace of pure PEO in these latter two diffractograms.

3.1.4. Differential Scanning Calorimetry. Figure 5 shows the DSC traces for the 80:1, 20:1, 10:1, 5:1, and 1:1 systems. The endothermic peaks present in the 80:1 and 20:1 systems at 65 and 61 °C, respectively, correspond to the melting of crystalline PEO and are shifted in comparison to a melting temperature of 67 °C observed for pure PEO. This is probably due to the presence of a eutectic mixture consisting of crystalline PEO and crystalline PEO−KCF_3SO_3. This endothermic peak is further shifted to 45 °C in the 10:1 system. In addition to the peak at 45 °C, another endothermic peak appears at 240 °C in the 5:1 system. At an O:M ratio of 1:1, a single sharp peak at 260 °C is seen, while the transition corresponding to the melting of the crystalline PEO phase completely disappears. The peak at 260 °C does not correspond to the melting of pure potassium triflate, which occurs at 221 °C (onset temperature), and is therefore attributed to the melting of the 1:1 compound.

3.1.5. Conductivity Studies. Figure 6 shows a plot of $\ln(\sigma T)$ vs 1000/T for the high molecular weight PEO−KCF_3SO_3 electrolytes. The room temperature conductivity increases with an increase in salt concentration from the 80:1 to the 10:1 system. These curves are characterized by a knee that corresponds to the melting of the PEO crystalline phase. The temperature corresponding to the knee decreases with increasing salt concentration, indicating a reduction in the amount of crystalline PEO. The knee is not observed in the 10:1 system. For electrolytes with higher salt concentrations, i.e., O:M = 5:1 and 3:1, the conductivity decreases. This observation is consistent with the spectroscopic, X-ray diffraction, and DSC results, which argue for the presence of a crystalline compound at high salt concentration. The observed decrease in conductivity at high salt concentrations is therefore due to the presence of the crystalline compound, which does not contribute to the conductivity. Similar behavior has also been observed in the PEO−$LiCF_3SO_3$[23] and PEO−$NH_4CF_3SO_3$[16] systems.

3.2. Spectroscopic Study of Glyme and Glycol Solutions with Potassium Triflate. 3.2.1. Conformation. In the spectral region of PEO oligomers assigned to the CH_2 rocking motion mixed with a small contribution from C−O stretching motion,[26,27] there are striking spectral changes which occur upon the addition of KCF_3SO_3. Figure 7 compares the IR spectra of the diglyme, triglyme, and tetraglyme solutions of KCF_3SO_3 at an ether oxygen to metal ratio (O:M) of 20:1. In these spectra a new peak appears at 862 cm^{-1} upon addition of the salt. This peak is assigned to the CH_2 rocking vibration of a new oligomer conformation that is not observed in the pure liquid, but is adopted by the oligomer in coordinating the potassium ion upon formation of the complex. The presence of such a new conformation has been previously reported in the PEO oligomer−salt systems of MCF_3SO_3 (M = Li, Na, K).[28]

3.2.2. Dependence of Ionic Association on Chain Length. Figure 8 shows the spectra for the systems (O:M = 40:1) as a function of the chain length. The spectra appear to show broad, single peaks that are centered at 756, 754, 753, and 754 cm^{-1} in the monoglyme, diglyme, triglyme, and tetraglyme solutions, respectively. However, each of the apparent single peaks have been curve-fitted to reveal contributions from three distinct bands at 752, 754, and 756 cm^{-1}, which are attributed to “free” triflate ($CF_3SO_3^-$) ion, the ion pair ($K^+CF_3SO_3^-$), and an aggregate species, respectively. The results of the curve-fitting analysis are summarized in Table 1. It is evident from Table 1 that the monoglyme solution has a higher concentration of aggregate species, which decreases in the diglyme and triglyme

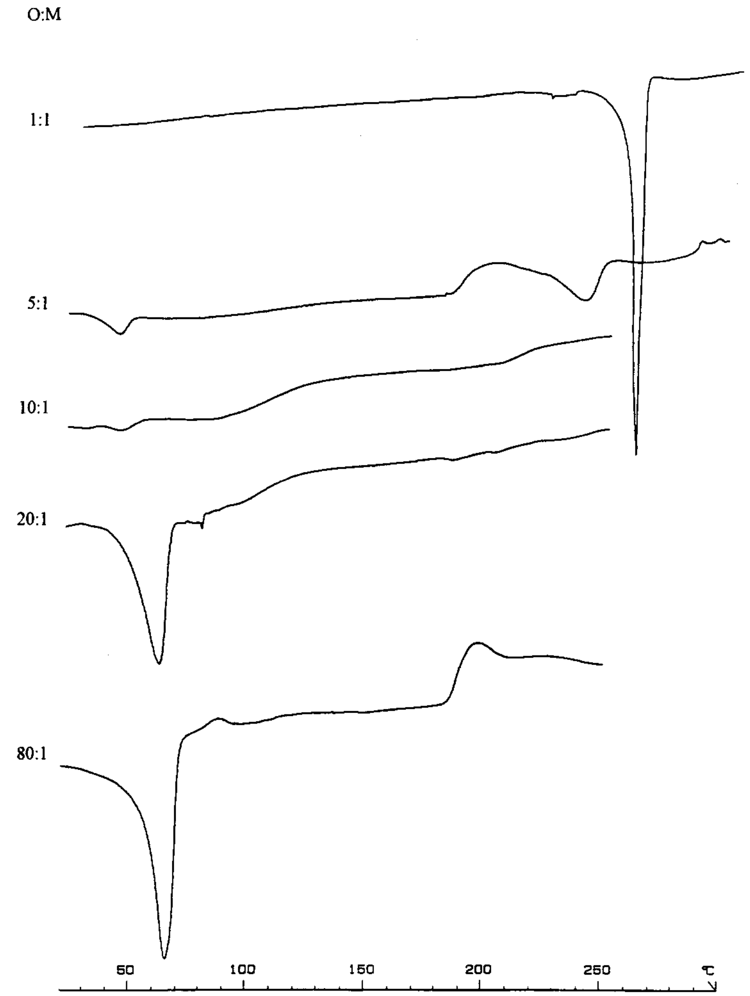

Figure 5. DSC data of $(PEO)_nKCF_3SO_3$ as a function of O:M ratio.

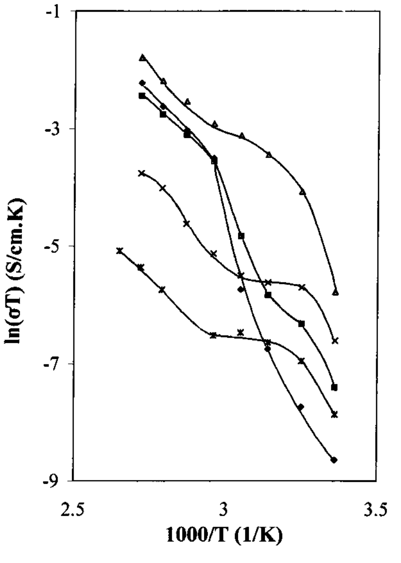

Figure 6. Plot of $\ln(\sigma T)$ vs $1000/T$ for $(PEO)_nKCF_3SO_3$ at O:M ratios (n) of 80:1 (◆), 20:1 (□), 10:1 (△), 5:1 (×), and 3:1 (*).

solutions. The variation in relative concentrations of the various species therefore accounts for the shift in the frequencies of the peaks in Figure 8. There is, however, a slight increase in the concentration of ion pairs and aggregates at the expense of the "free" ion concentration, leading to an upward frequency shift from the triglyme to tetraglyme system. A similar trend has been observed in the $\nu_s(SO_3)$ region [figure not shown]. These data clearly indicate that the degree of ionic association depends upon the chain length of the

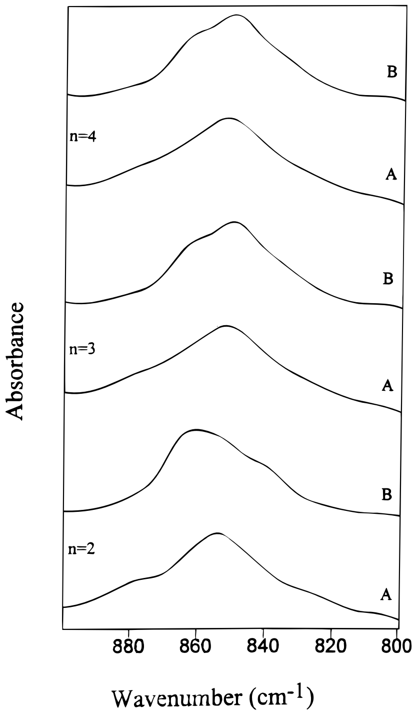

Figure 7. IR spectra of pure $CH_3O(CH_2CH_2O)_nCH_3$ (curves A) and $[CH_3O(CH_2CH_2O)_nCH_3]_{20}KCF_3SO_3$ (curves B) for $n = 2-4$ in the CH_2 rocking region.

oligomers. A similar effect has been observed in the analogous $LiCF_3SO_3$ systems.[20]

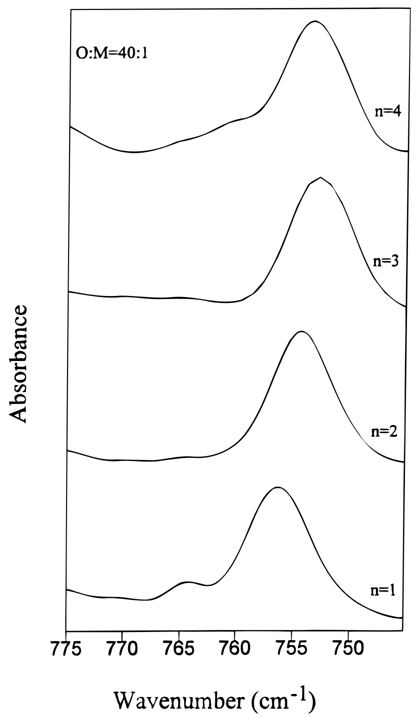

Figure 8. IR spectra of $[CH_3O(CH_2CH_2O)_nCH_3]_{40}KCF_3SO_3$ for $n = 1-4$ in the $\delta_s(CF_3)$ region.

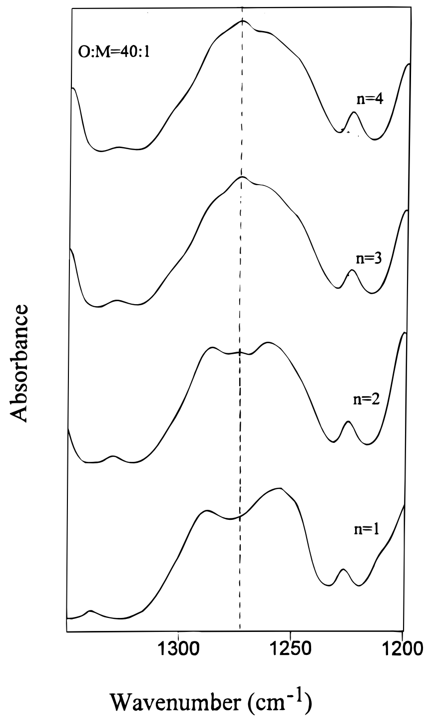

Figure 9. IR spectra of $[CH_3O(CH_2CH_2O)_nCH_3]_{40}KCF_3SO_3$ for $n = 1-4$ in the $\nu_{as}(SO_3)$ region.

Table 1. Relative Intensities of the Various Triflate Species Obtained by Curve-Fitting the 40:1 Glyme–Potassium Triflate Solutions in the $\delta_s(CF_3)$ Region

	relative intensity			
chain length, *n*	752 cm^{-1}	754 cm^{-1}	756 cm^{-1}	764 cm^{-1}
1	4.8	19.4	71.3	4.5
2	35.7	23.6	45.9	
3	70.3	17.3	12.4	
4	63.1	19.2	17.7	

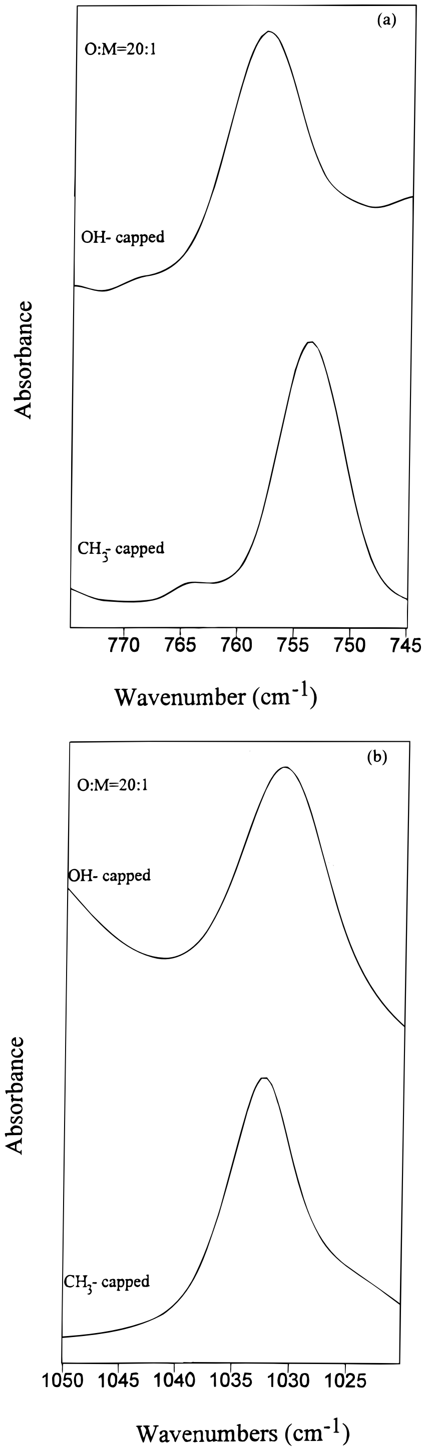

Figure 10. IR spectra of the O:M = 20:1 systems of triglyme and triethylene glycol with KCF_3SO_3 in the (a) $\delta_s(CF_3)$ and (b) $\nu_s(SO_3)$ regions.

A significant perturbation of the local C_{3v} symmetry of the SO_3 group of the triflate anion will lift the degeneracy of the antisymmetric stretching mode of SO_3, $\nu_{as}(SO_3)$, resulting in two bands. The width of the splitting is a measure of the strength of the perturbation and hence the strength of the cation–anion interactions.[29] Figure 9 shows the spectra for the monoglyme, diglyme, triglyme, and tetraglyme solutions at a 40:1 concentration. In the monoglyme solution, the two components of the $\nu_{as}(SO_3)$ mode are present at 1256 and 1287 cm^{-1}. For the diglyme solution, a contribution of the free ion band at 1273 cm^{-1} can be seen in addition to the two split components at 1262 and 1286 cm^{-1}. The decrease in width of the splitting in the diglyme solution compared to the monoglyme solution argues that the perturbation of the anion is greater in the monoglyme system, indicating a higher degree of ionic association. For the triglyme and tetraglyme solutions, the splitting, although visible, is very weak; but the contribution from the free ion at 1273 cm^{-1} is dominant. Apparently, the cation−anion interactions are less significant in the triglyme and tetraglyme solutions compared to the monoglyme and diglyme solutions. Thus, the results from this spectral region are consistent those from the $\delta_s(CF_3)$ region.

3.2.3. Effect of the End Group. To study the influence of the end group on ionic association, we compare the triethylene glycol and the triglyme solutions at an O:M ratio of 20:1 in the $\delta_s(CF_3)$ and $\nu_s(SO_3)$ regions, Figure 10a,b, respectively. In Figure 10a the peak appears at a higher frequency in the glycol solution (758 cm^{-1}) than in the triglyme solution compared to the glycol solution in the $\nu_s(SO_3)$ region. Curve-fitting [results not given] the spectra in the $\nu_s(SO_3)$ region for the triglyme−KCF_3SO_3 solutions shows three underlying peaks at 1032, 1035, and 1039 cm^{-1}. The peak at 1032 cm^{-1} is undoubtedly due to the "free" ion as its frequency is cation-independent, while the peaks at 1035 and 1039 cm^{-1} are analogous to the peaks at 1041 and 1051 cm^{-1} for the $LiCF_3SO_3$ solutions and may be attributed to ion pairs and aggregates, respectively. Thus, although the $\nu_s(SO_3)$ region indicates "free" ions as the dominant species in the glycol solution, the $\delta_s(CF_3)$ region shows an appreciable degree of ionic association. These differences suggest a complicated interplay between cation−anion interactions, anion−solvent interactions, and possibly cation−solvent interactions in these glycol solutions. Similar results have been reported before in lithium triflate solutions of glymes and glycols.[20] In general, alcoholic solvents are characterized by intermolecular hydrogen bonding, as is clear from inspection of the OH stretching region (data not shown). However, a shifting of the peak from 3462 cm^{-1} in the pure glycol to 3587 cm^{-1} in the 5:1 system indicates a reduction in the degree of intermolecular hydrogen bonding due to the interaction of either the anion or cation (or both) with the OH end of the glycol.

4. Conclusions

IR spectra of high molecular weight PEO−KCF_3SO_3 systems show that the degree of ionic association increases with increasing salt concentration. The spectra in the conformation and ionic association regions suggest the presence of a crystalline compound with an O:M ratio of 1:1. Supporting evidence for compound formation has been obtained from X-ray diffraction and DSC studies, which did not show any trace of either the pure salt or PEO in the 1:1 system. The ionic conductivity of these systems increases with increasing salt concentration from 80:1 to 20:1. However, there is a decrease in conductivity at higher salt concentrations due to the presence of the crystalline compound. A chain length dependence is seen in the $\delta_s(CF_3)$ and $\nu_{as}(SO_3)$ regions for KCF_3SO_3 solutions of glymes, where the degree of ionic association decreases with increase in chain length. The appearance of a new peak at 862 cm^{-1} in the CH_2 rocking region suggests that the conformation of the oligomers change upon addition of salt. A comparison of the hydroxy-capped and methoxy-capped trimer solutions in the $\delta_s(CF_3)$ and $\nu_{as}(SO_3)$ regions showed evidence of cation−solvent interactions via hydrogen bonding with the hydroxy group in the OH-capped system in addition to the cation−anion interaction. The additional possibility of an interaction between the cation and the oxygen atom of the OH group cannot be ruled out at this time. The shifting of the O−H stretching band in the 5:1 system compared to the pure glycol indicates a decrease in the intermolecular hydrogen bonding in the glycols.

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