Ionic Interactions and Transport Mechanism in Polyurethane Electrolytes

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ABSTRACT: Alternating current (AC) impedance, Fourier transform (FT)–Raman, and Fourier transform infrared (FTIR) have been conducted on solutions of poly(ethylene oxide)$_{(MW=1000)}$–urethane electrolytes commingled with $LiCF_3SO_3$ as the function of temperature and salt concentration. From the analysis of the $Vs(SO_3)$ vibration, the ionic concentration of salt in various chemical environments can be calculated approximately. The spectroscopic evidence was found for the redissociated ion pairs, and ionic congeries increased with increasing temperature. AC impedance measurements is used to calculate the ionic diffusion coefficient (D_i). Investigated the various concentrations (from O/Li = 4 ~ 20) at the different temperature (40 ~ 120°C), We found that the calculated values (D_i) with the Nernst–Einstein equation are higher than the direct measurement. The discrepancy increases with the increase of temperature. A good correlation between the conductivity and the ionic redissociation is determined from the $Vs(SO_3)$ vibration band. The fraction of the "free" ion significantly corresponds to the revised Nernst–Einstein equation by using the Nernst–Einstein relation and compared with those direct measurement. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 785–790, 2002

Key words: polyurethane; ionic conductivity; solid state electrolyte

INTRODUCTION

Lithium trifluoromethane suphone has become the representation of a new family of bulky of lithium salts combining great charge localization favorable to ionic dissociation in a solvating polymer such as poly(ethylene oxide) (PEO).[1] Good chemical electrochemical and thermal stability, and also a plasticizing effectivity, which decreases the crystallinity of the host polymer, make the ionic mobility easier.[2,3] The conductivity of the PEO/LiCF$_3$SO$_3$ has been extensively investigated for mechanical capability and conductivity.[4] In these investigations it was found, due to the specific cation–polymer interaction, the mechanisms governing ionic transport through a macromoleculer polar solvent are considerably different from liquid organic or aqueous electrolytes. In polymer electrolytes, most of polymer solvents' dielectric constants are low and give a rise to extensive ion–ion interactions and engender several different types of ionic species, which can be present in the polymer–salt complexes, e.g., "free" anions, ion pairs, and triple ions. The concentration dependence of molar conductivity (Λ, ionic conductivity normalized by the total salt concentration) in liquid electrolytes has been thoroughly studied by several authors,[5–7] and an observed increase from a low salt concentration with increasing concentration has been explained

in terms of changes in the relative number of charge carriers. These authors explained the increase of molar conductivity (Λ) had two different effects: either through redissociation of ion pairs, or through the formation of charged triplets from ion pairs—free ion interactions or the combination of both.

Infrared (IR) and Raman spectroscopics are powerful tools for probing the local chemical environments of certain polymer electrolytes, e.g., $LiCF_3SO_3$ and $LiClO_4$ systems.[8–10] The shifts of the $Vs(SO_3)$ mode at $1030 \sim 1050$ cm^{-1} anions have indifferent configurations in varied fettle, such as ion pairs, triple ions, and "free" anions. However, it is now not clear whether ionic species effects depending salt concentrations have a direct bearing on ionic transport properties such as diffusion and ionic conductivity.

In order to investigate the influence of ion–ion interaction on transport mechanism, the $LiCF_3SO_3$ was doped into the poly(ethylene-oxide)$_{(MW=1000)}$–urethane (PEU) system, and the interaction between cation or anion and solvating sites has been particularly investigated by employing AC impedance, and vibrational spectroscopic (Raman and IR) measurements on complexes of PEU/$LiCF_3SO_3$ salt.[11,12] We further elucidate the interionic interactions by Fourier transform (FT) Raman, Fourier transform infrared (FTIR) spectroscopy, and conductivity measurement as a function temperature and salt concentration. Comparisons are made between experimental molar conductivity (Λ_{exp}) and calculated molar conductivity (Λ_{n-e}) from the Nernst–Einstein (N-E) equation. The results indicated that FT–Raman and IR spectra both show that extent of ionic aggregation in the system increases with temperature. The observed discrepancy between calculated results and experimental results can be revised by the "free" ion fraction from the Raman and IR spectra analysis. We suggest that these findings may be very useful evidence that ion–ion interaction strongly influence the charge transport in polymer complexes.

EXPERIMENTAL

Purification of Solvents and Reagents

PEO with molecular weight of 1000 from the Aldrich Chemical Co. was dried under a vacuum at 60°C. 4,4′-Methy-enebis(phenyl isocyanate) (MDI) was distilled under a vacuum and used immediately. N,N-Dimethylacetamide (DMA) and 1,4-butanediol (BDOL) were dried by refluxing over CaH for 4 h to exclude trace water and then distilled under a vacuum.

Synthesis of PEU

PEU was prepared by mixing PEO and MDI under a nitrogen atmosphere at 40°C for 3 h. Subsequently, the DMA solution containing BDOL was added dropwise over a period of 30 min and continually reacted for 1.5 h. The polymer was carefully dried under high vacuum at 70°C for 24 h.

Preparation of Polymer Electrolytes

$LiCF_3SO_3$ were dried under high vacuum at 80°C for 24 h and at 120°C for another 24 h prior to use. Polymer electrolytes were prepared by a blend PEU and $LiCF_3SO_3$ (Aldrich Chemical Company) for concentrations in the range of O/Li = $4 \sim 20$ (the molar ratio of C—O—C and lithium salt in polymer electrolyte). Polymer and salt complexes were prepared in a dry nitrogen atmosphere where the salt was dissolved into the polymer using magnetic stirrer.

FTIR and Raman Spectroscopy

FTIR spectra were recorded at different temperatures from 295 to 393 K using a Bruker IFS 66 with the IR module. FT–Raman spectra were recorded at the temperature of 295 K using a Bruker IFS 66 with a Raman module FRA106 and a near-infrared YAG laser with wavelength 1064 nm.

The Raman spectra's resolution is 3.0 cm^{-1}. The IR spectra's resolution is 1.0 cm^{-1}. To analyze the band shape of the $Vs(SO_3)$ mode of the triflate anion, the spectrum of the pure polymer was subtracted from the spectra of the polymer–salt complexes. The $Vs(SO_3)$ spectral region $\sim 1030 \sim 1055$ cm^{-1} was analyzed using a three-component model (Gassian and Voigt function). The relative error in the determined area of the various peaks was estimated for each set of experimental data to be less than 10% by varying the fitting parameters. The band shape analysis was performed using Bruker's IR software.

AC Impedance

Ionic conductivities were measured for temperatures ranging from 295 to 393 K using a Solartron
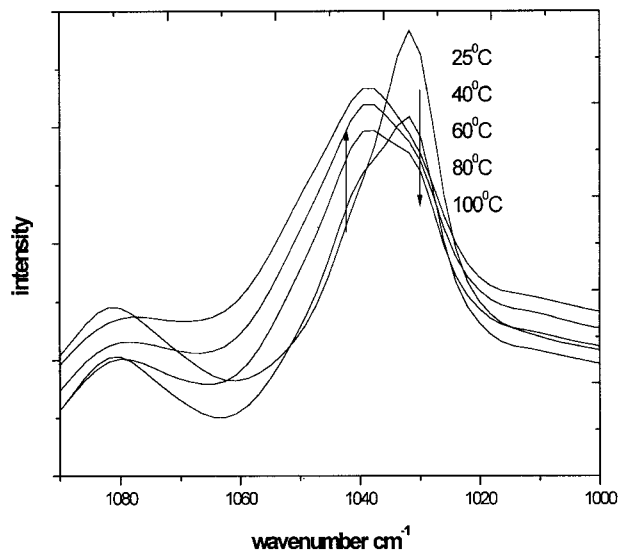
Figure 1   FTIR spectra of $Vs(SO_3)$ in $PEU/LiCF_3SO_3$ (O/Li = 4).

Schlumenberger SI 1286 electrochemical interface and 1254 four-channel frequency response analyzer. A potential difference of 10 mV was applied to the sample at frequencies ranging from 10^6 to 1 Hz. The ionic conductivity was obtained from AC impedance data, plotted in the formation of a complex-plane plot (Nyquist).

The salt ionic diffusion coefficient was determined for each sample from the Cole–Cole plot.

RESULTS AND DISCUSSION

Figure 1 shows the typical IR spectra of the $Vs(SO_3)$ spectra region of triple ions, and the spectra of pure polymer has first been subtracted from that of polymer electrolytes. The component observed at 1032 cm^{-1} has been assigned to free anions not interacting directing with lithium cations. In polymer electrolytes, the fraction component of the free anion decreases monotonically with an increase of temperature from 295 to 393 K for the O/Li = 4. The free anion components decrease with an increase of aggregated ions components. This is in agreement with previous findings in relating systems.[7,13] Figure 2 shows a typical Raman spectrum of the $Vs(SO_3)$ spectra region of $CF_3SO_3^-$, along with a three component curve fit. The spectra of pure polymer has first been subtracted from that of the electrolyte. According to the literature,[14–16] the $Vs(SO_3)$ band's ascription is 1032 cm^{-1} for the free triflate anion, 1043 cm^{-1} for ion pairs, and 1053 cm^{-1} for aggregate ions like $CF_3SO_3Li_2^+$. Figure 2 indicated that there are extensive cation–anion interactions
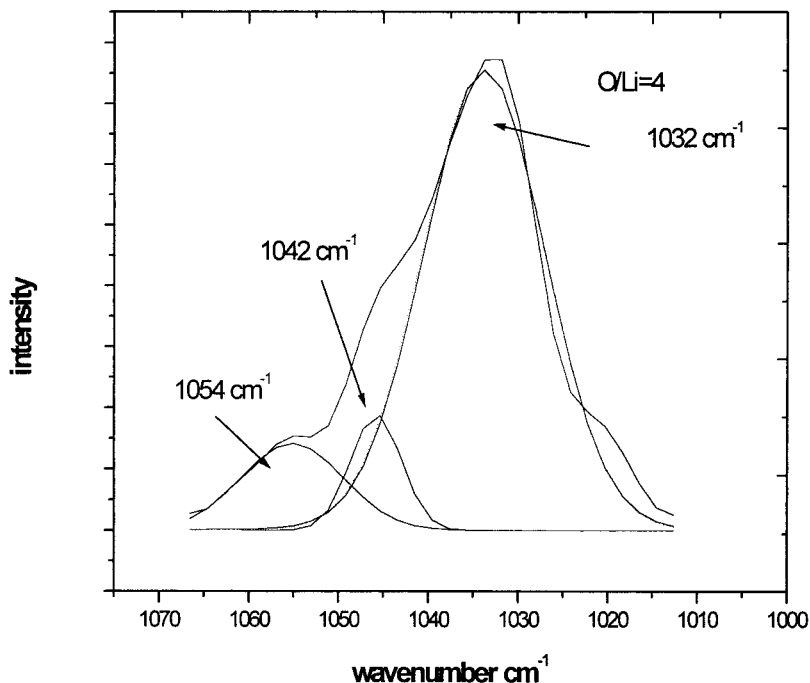

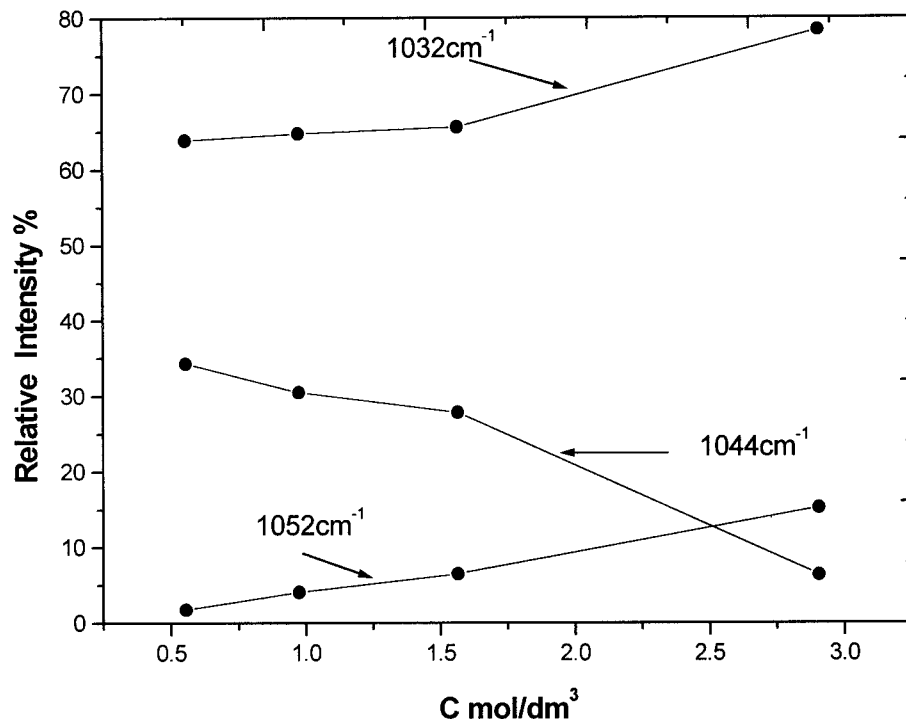**Figure 2**   Raman spectra of $Vs(SO_3)$ in $PEU/LiCF_3SO_3$.

Figure 3   Effect of the salt concentration on three-component analysis of the Vs(SO$_3$) band envelope at 25°C.

present in the system even down to the very low salt concentrations.

Figure 3 shows the variety of relative intensities of a three-component curve fit. The fraction of free ions (1033 cm^{-1}) increase but the fraction of ion pairs (1044 cm^{-1}) decrease with increase of salt concentration. The fraction of triple ions is increasing with increase of salt concentration. From what has been discussed above, there is an obvious evidence for a redissociation of associated ionic species into free ions in higher concentration. The symmetric Vs(SO$_3$) is also active in IR and the analysis of the corresponding band gives similar results with the results of Raman spectra.

Figure 4 shows ionic conductivity as the function of various salt concentration and temperature relationship in a plot. Solid lines show unfit to the Vogel–Tarna–Fulcher.[17,18]

$$\sigma(T) = A_\sigma T^{1/2} \exp[-E_a/k_B(T - T_0)] \qquad (1)$$

In eq. (1), A_σ is a constant related to the number of charge carriers, E_a is the pseudoactivation energy related to polymer segmental motion, and T_0 is a reference temperature related to the glass transition temperature. For dilute homogeneous, binary electrolytes, ionic diffusion coefficients can approximately be related to equivalent ionic conductivity through the Nernst–Einstein relation:

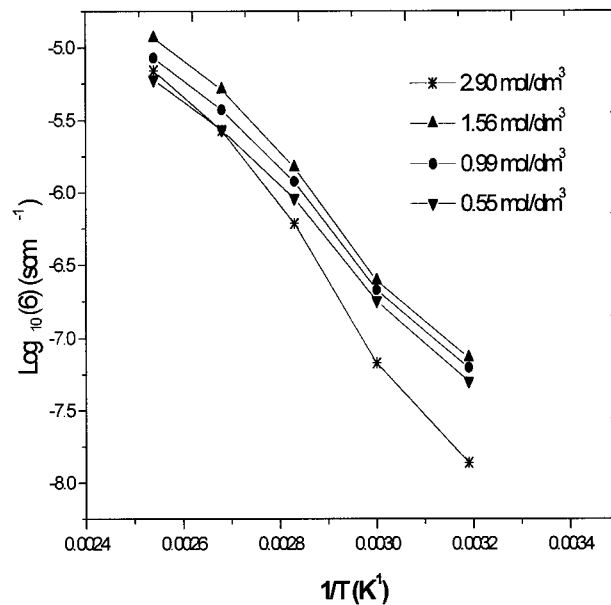$$\Lambda(T) = [(F^2/RT)]D_i \qquad (2)$$

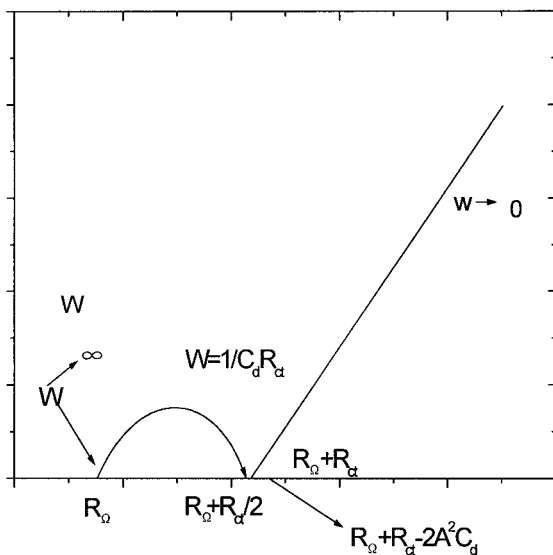**Figure 4**   The conductivity of various salt concentration of polymer electrolyte.

Figure 5 The Cole–Cole plot of PEU/LiCF$_3$SO$_3$.

Figure 6 Effect of temperature on D_i of PEU/LiCF$_3$SO$_3$ (O/Li = 4).

In eq. (2), F is Faraday's constant; D_i is the ion diffusion coefficient.

The D_i can be measured by AC impedance by supposing the electrode reaction dominated by charge transport of the interface and matter's diffusion. The swing of AC polarized voltage is less than 10 mV when the sample is measured; then the relation of polarized voltage and current is eqs. (3) and (4).[19,20]

$$dE/dt = (R_{ct} + A/w^{1/2})Iw \cos wt + IAw^{1/2}\sin wt \tag{3}$$

$$A = RT/2^{1/2}n^2F^{2*}(D_i^{-1/2}C_0^{-1/2} + D_i^{-1/2}C_R^{-1/2}) \tag{4}$$

The impedance $Z(R - JX)$'s real number and imaginary number is used to draw a plural impedance graph (Cole–Cole plot), such as Figure 5. R_e, R_{ct}, C_d and A can be known through the plural impedance graph; then one can proceed to next step to get D_i. For example, Figure 6 is the D_i plot of sample (O/Li = 4) in the different temperature.

In Figure 7, obviously, a large deviation between this Λ_{exp} and Λ_{N-E} can be found. The former decreases from O/Li = 20 to 4, but the latter is significantly higher over the entire range, and the discrepancy increases with the decrease of salt concentration. This agrees with the ion pair's redissociation. In Figure 8, the larger deviation between Λ_{exp} and Λ_{N-E} appeared with the increase of temperature. This agrees with the Raman and
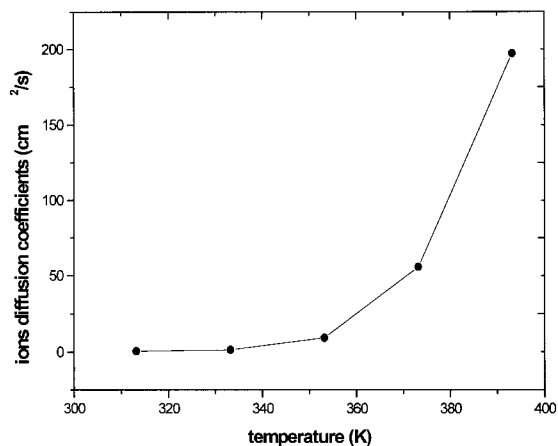
IR analysis results about the free ions's decreasing with temperature. In fact, according the dilute solution electrolyte theory, the principal requirement for the Nernst–Einstein relation to hold is that ionic entities involved in diffusion motion are the same as those responsible ions for conduction. The real conduction is the free ion. Noting that the calculated value Λ_{N-E} refers to an "ideal" situation where all diffusers contributed to charge transfer, the ratio $\Lambda_{exp}/\Lambda_{N-E}$ may show the true ions involved in the conductivity.[8,9] We found that the $\Lambda_{exp}/\Lambda_{N-E}$ was very similar to the fraction of free ions in the Figure 7 and Figure 8 shows. By using the free ion fraction of relative intensity of Vs(SO$_3$) Raman spectra (1032 cm^{-1}) to amend the
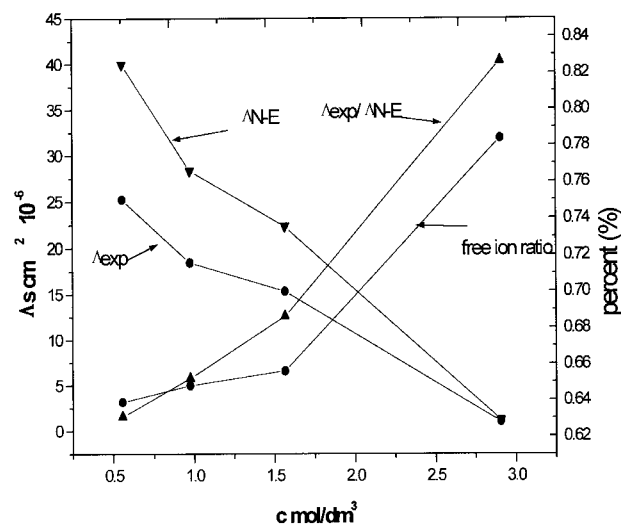

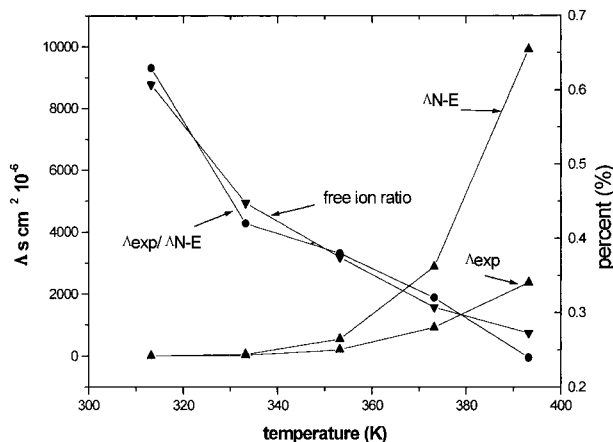**Figure 7** The trend of $\Lambda_{exp}/\Lambda_{N-E}$ with the various ionic concentrations (25°C).

Figure 8 The trend of $\Lambda_{exp}/\Lambda_{N-E}$ with various temperature.

equation of the N-E relation, the discrepancy between Λ_{exp} and Λ_{N-E} becomes very small.

Clearly, the N-E relation will fail in polymer electrolytes because of the strong interaction of ions. The true ion concentration is joined in ionic conductivity to correct the Eq. (2), such as

$$\Lambda(T) = A[F^2/RT]D_i \qquad (5)$$

The A is the fraction of free ions that gained from the relative intensity of $Vs(SO_3)$ Raman spectra $(1032 \ cm^{-1})$ (Fig. 3).

CONCLUSIONS

FTIR and Raman spectra of PEU/LiCF$_3$SO$_3$ show that the free ion components decrease and aggregated ion components increase with the increase of temperature. Through analysis of the $Vs(SO_3)$ in Raman and IR spectra $(1032 \sim 1055 \ cm^{-1})$, extensive cation–anion interactions exist in this system. The ion pairs' redissociation was found in the higher concentration. Through comparing experimental and calculated molar conductivity, however, we find that the observed deviation from the Nernst–Einstein relation increases with the decrease of salt concentration or the increase of temperature. In fact, the free ions in the polymer electrolytes are really involved in conductivity. For the N-E equation applied in polymer electrolytes, a good revision must be established by using the fraction of free ions. Through the revision, the Λ_{exp} and Λ_{N-E} are very similar.

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