Temperature dependence of positron-annihilation lifetime, free volume, conductivity, ionic mobility, and number of charge carriers in a polymer electrolyte polyethylene oxide complexed with NH_4ClO_4

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Various physical properties of the solution-cast films of the proton conducting polymer polyethylene oxide (PEO) complexed with ammonium perchlorate (NH_4ClO_4) have been studied in the temperature range 300–370 K. These properties studied by us include free volume by positron lifetime spectroscopy, ionic conductivity by impedance spectroscopy, ionic mobility by transient ionic current technique, number of charge carriers, dielectric constant, etc. The hole volume and conductivity show a steep rise at $T \simeq T_m$ (~333 K). It appears that the increase in free volume arises out of the increase in the size of the holes rather than an increase in their number. Although the free volume shows an increase around T_m, the measured ionic mobility does not show similar behavior. The increase in the conductivity at T_m is, therefore, ascribed to an increase in the number of charge carriers at $\sim T_m$. A suitable dissociation model involving the dielectric constant is proposed to explain this increase. The value of the dissociation energy for PEO:NH_4ClO_4 has been determined to be 2.4 eV. [S0163-1829(96)07533-9]

I. INTRODUCTION

Study of ion-conducting polymer electrolytes is an active area of recent theoretical and experimental interest because of their possible applications in modern electrochemical devices.[1–7] One of the important classes of polymer electrolytes developed recently are the ''polymer-salt complexes'' which show high ionic conductivity of about 10^{-3}–10^{-5} S cm^{-1} at room temperature. These ''polymer-salt complexes'' can be prepared by doping polar polymers [like polyethylene oxide (PEO), polypropylene oxide (PPO), polyvinyl alcohol (PVA), etc.] with alkali-metal salts, ammonium salts, silver salts, acids, etc. As a part of the systematic program of developing proton-conducting polymer electrolytes in our laboratory, different polymers like PEO,[8] PESc,[9] etc., have been doped with different ammonium salts, viz, NH_4ClO_4, NH_4HSO_4, $(NH_4)_2SO_4$, NH_4I, etc. The mechanism of conductivity (σ) in polymeric electrolytes is not yet clearly understood because σ is governed by various factors[1] like degree of crystallization, relative values of T_g (glass transition temperature), T_m (melting temperature), intrinsic motion of elastomeric phase, degree of dissociation of salts in the complex which controls the number of charge carriers, interfacial effects, ion pair formation, etc. It is well known that most of the viscoelastic transport properties of polymers depend strongly on temperature. Further the concept of free volume[10] has been widely used over the last three decades for explaining some of the observed results in polymeric materials.[11] The observed temperature dependence of the electrical conductivity of ion-conducting polymers has also been explained[1] in terms of the free-volume theory. The study of thermally induced microstructural changes leading to free-volume changes in polyacrylonitrile[12] (PAN) or free-

volume change associated with the amorphicity of polymer salt complexes,[13] have been reported using a positron annihilation technique. In spite of all these studies the theoretical explanation of the measured ion transport properties is far from satisfactory.

The electrical conductivity σ in the conducting polymers can be expressed in terms of the mobility μ by the relationship

$$\sigma = \sum n_i q_i \mu_i, \qquad (1)$$

where n_i and μ_i are, respectively, the number density and mobility of the ith type of charge carriers and q_i the charge of ith species. Both cations and anions have been found to be mobile. Further, n_i and μ_i are temperature (T) dependent. In order to understand the behavior of σ with $1/T$ we have to know (a) variation of n with T, (b) mechanism of generation of mobile carriers, (c) variation of μ with T, (d) mechanism of temperature dependence of μ, and (e) whether the variation of n or μ is the controlling factor?

In the literature[1] an explanation for the behavior of σ with $1/T$ has been accepted in terms of the somewhat vague statement that the amorphicity (and hence the free volume) increases with temperature and that this leads to an increase in the mobility and hence in the conductivity. It may be pointed out that such an explanation has been accepted in the absence of any reported (in literature) direct measurement of n and μ over a wide temperature range on any *specific* materials for which the measurement of free volume (usually a difficult measurement) has also been carried out. In the present work we have tried to address ourselves to some of these vital questions by choosing the polymer electrolyte polyethylene oxide complexed with NH_4ClO_4 (or

PEO:NH_4ClO_4) on which systematic studies could be performed. In our earlier report[14] the ion transport in the proton conducting polymer electrolyte PEO:NH_4ClO_4 has been characterized using optical spectroscopy, X-ray diffraction (XRD), differential thermal analysis (DTA), IR, Coulometry, transient ionic current, and electrical conductivity studies. In the present paper we report the results of the following systematic studies on PEO:NH_4ClO_4 and analyze them to obtain partial answers to some of the vital questions raised above: (i) temperature dependence of the bulk electrical conductivity using impedance spectroscopy technique, (ii) temperature dependence of mobilities using transient ionic current technique, (iii) temperature dependence of the number of mobile charge carriers from the knowledge of the respective values of σ and μ, (iv) temperature dependence of the mean free volume and of their probability density function by the positron annihilation technique.

Recent studies have established the usefulness of the positron annihilation technique for the measurement of (iv) above. The basic process of positron annihilation and the application of this technique for the study of free volume in polymers has been reviewed in the literature.[15-17] Upon entering a polymer, the positron can form a positron-electron (e^+-e^-) bound state (called a positronium or Ps atom). Once inside the polymer such Ps atoms are localized (or trapped) preferentially in the free-volume holes having an atomic scale of volume. What is further interesting is that these Ps atoms are unstable and they annihilate within the free-volume region with characteristic parameters (e.g., lifetime τ, intensity I, etc.) carrying information about the free-volume region without any significant interference from the other bulk properties. The usefulness of the positron lifetime technique has been further enhanced by the development of the Laplace inversion technique,[18] translated into a computer program CONTIN,[18,19] to analyze the measured positron spectra in terms of continuous lifetime distribution functions $\alpha(\lambda)$ where λ is the annihilation rate. Further these positron lifetime distributions $\alpha(\lambda)$ can be converted into free-volume hole radius distribution functions $f(R)$ and hole volume distribution functions $g(V)$. Such positron lifetime studies of the free-volume properties in polymers, specifically measuring the variations in the free volume with temperature,[20] pressure,[21,22] physical aging, and structural relaxation,[23] stress-induced structural deformation,[24] etc., have been reported in the literature. Theoretical treatment using molecular dynamics and kinetic theory[25,26] has predicted that the radii and the hole volumes of the free volume in a polymer obey a distribution function $f(R)$ and $g(V)$, respectively. Experimentally the dependence of these distribution functions on pressure[21,22] and temperature[20] have been estimated with the positron lifetime technique, combined with the CONTIN program for data analysis.[19,27]

Coming back to the measurements (i)–(iv) listed above, we have carried all these both above ($T>T_m$) and below ($T<T_m$) the melting temperature T_m because most of the properties are expected to change significantly at T_m. Second, the choice of the material to be studied had to be guided by the criteria that significantly large changes in the physical properties like σ, n or μ, free volume, etc., should be observed. A survey of the observed behavior of σ *vs* $1/T$ reported by various workers[1,14,28-30] for some H^+ and Li^+ ion-

conducting PEO-based polymers showed that these materials exhibit three different types of behavior, some of which are partly explained by the so-called Vogel-Tamman-Fulcher[31] (VTF) and Williams-Landel-Ferry[32] (WLF) equations. Since our aim was to study the mechanism of the ionic conductivity in the polymer electrolytes and its correlation with the number of charge carriers (n), mobility (μ), free-volume, etc., we found it important to choose a system in which distinct and large change in σ with temperature (especially around T_m) is observed. The results reported in the literature[1,14,28-30] indicated that the system PEO:NH_4ClO_4 fulfills this criterion best and hence this material has been chosen for the present study. Further, this polymer electrolyte has been previously studied in detail by us.[14] Our studies of the composition dependence of conductivity[14] have shown that the 80:20 weight percentage composition of PEO:NH_4ClO_4 has the highest conductivity at room temperature and hence this composition was chosen for the present work.

The results of the present work are described below. The most significant result obtained by us for the present material is that both σ and free volume show rapid increase at $T \approx T_m$. However the increase in the free volume is not associated with an increase in the ionic mobility. In view of this, the changes in mobility cannot be the main cause for the variation of σ. On the other hand, the number density n is found to change rapidly at T_m and a suitable dissociation model has been proposed by us to account for this increase in n at T_m. The positron lifetime data have been analyzed to provide a detailed discussion of the free volume and its distribution, hole size, etc.

II. EXPERIMENT

The polyethylene oxide (PEO) was procured from Aldrich (MW$\sim 6 \times 10^5$) while ammonium perchlorate (NH_4ClO_4) was obtained from VEB Laborchemie Apolda, Germany. Films (~ 300 μm thick) of polymer-salt complexes were prepared by a solution-cast technique using dehydrated methanol as solvent. The solution of polymer-salt was poured into polypropylene dishes for casting the films by slow evaporation. Finally, the films were dried under vacuum to eliminate all traces of the solvent.

The electrical conductivity of the PEO:NH_4ClO_4 sample was measured in the temperature range 300–400 K using vacuum-coated silver electrodes. The complex impedance-admittance plots were obtained using computer-controlled Schlumberger Solartron (1250) frequency response analyzer coupled with a Solartron (1286) electrochemical interface. The temperature dependence of the electrical conductivity was evaluated using complex impedance-admittance plots.[33,34]

The transient ionic current (TIC) measurement technique was used to detect the number of different types of mobile ionic species in the bulk and to evaluate their respective mobilities. In this method, the sample was first polarized across a dc voltage using Ag electrodes. The transient ionic current was monitored as a function of time after reversing the polarity of the polarizing voltage. Details of the experimental technique have been reported elsewhere.[35] The mobility, μ, of mobile ionic species was calculated using the formula[36]

$$\mu = \frac{d^2}{tV}, \qquad (2)$$

where d is the thickness of the sample, V is the voltage applied, and t is time of flight corresponding to the current maxima.

The variation of the dielectric constant of the sample with temperature was also measured. These data were needed for the interpretation of some of the results described later in this paper. The dielectric constant was calculated from the ratio of the measured capacitance with and without dielectric (polymeric film). The capacitance was measured by using a capacitance meter (Boonton Electronics, Model 72B). The frequency of 1 MHz was chosen to avoid relaxation effects of double-layer or electrode-electrolyte interface.

Positron lifetime measurements were carried out at room temperature using a conventional fast-fast coincidence spectrometer and a sandwich geometry for the source (about 15 μCi of ^{22}NaCl) specimen assembly. Polymer electrolyte films were stacked to prepare specimens of about 1 mm thickness. The typical time resolution used in the present work was 0.32 ns (FWHM) while a total of about 5×10^6 counts were recorded under each lifetime spectrum. The lifetime spectra were measured in the temperature range 298–353 K in steps of about 5 K. The measured lifetime spectra were analyzed in two ways. In the first method the lifetime spectra were subjected to a least-squares-fitting procedure using the computer program PATFIT.[37] Our analysis showed that the best $\chi^2 (<1.1)$ and most acceptable standard deviations were obtained when each spectrum is fitted in terms of three lifetime components. In our analysis we have constrained $\tau_1 = 0.13$ ns in order to obtain a consistent result for τ_2, I_1 and I_2.[21] It may be mentioned that we also carried out an analysis by removing the constraint on the values of τ_1. This analysis yielded the values of τ_1 in the range $\tau_1 = 0.10$–0.14 ns while the values of τ_3 (lifetime of present interest) and I_3 showed a typical deviation that was less than 5% from the values obtained by fixing $\tau_1 = 0.13$ ns. The accompanying effect on the free-volume hole radius (see next section) was less than 5%. In view of this, and for obtaining consistent results for τ_2 and τ_3 we constrained $\tau_1 = 0.13$ ns in our final analysis. Our second method of analysis involved determination of the annihilation rate probability distribution function (PDF) $\lambda\alpha(\lambda)$ versus λ (annihilation rate) using the computer program CONTIN.[19] In the present analysis using the CONTIN program we used the annihilation rate $\lambda = 9.1$ ns^{-1} from well-annealed and high-purity (99.99+%) nickel as a reference while a total of 85 grid points over the range $0.25 < \lambda < 13$ ns^{-1} were used.

III. RESULTS AND DISCUSSION

A. Positron lifetime, free volume, and related distribution functions

We shall first present our results obtained from the positron lifetime spectroscopy. The positron lifetime spectra measured for the PEO:NH$_4$ClO$_4$ (80:20 wt. %) at room temperature were first analyzed by the PATFIT (Ref. 37) computer program and it showed that each of the lifetime spectrum measured in the temperature range 298–353 K showed the presence of three lifetimes: $\tau_1 = 0.13$ ns ($I_1 = 39$–44 %),
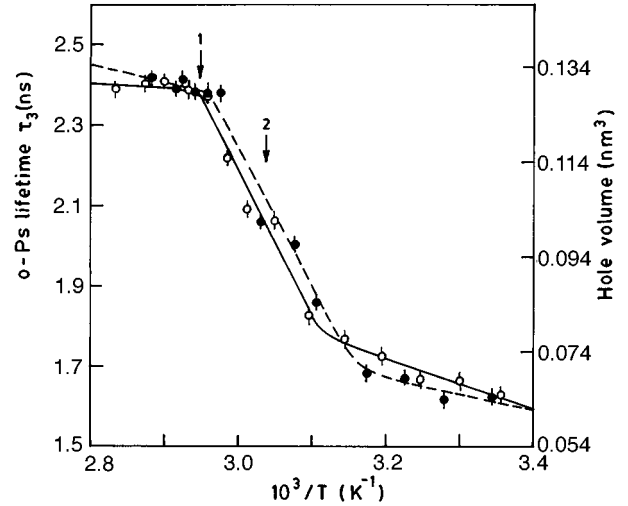

FIG. 1. Temperature dependence of o-Ps lifetime, τ_3, in polyethylene oxide complexed with ammonium perchlorate (PEO:NH$_4$ClO$_4$) (80:20 wt. %). Positions indicated by arrows 1 and 2 correspond to the melting temperatures of uncomplexed PEO ($T_{m_1} \sim 339$ K) and crystalline complexed material ($T_{m_2} \sim 329$ K) (Ref. 36). Open symbols describe the data for increasing temperature, while solid symbols describe the data for decreasing temperature. The continuous and dashed lines indicate the best fit to the observed points.

$\tau_2 = 0.41$–0.44 ns ($I_2 = 44$–50 %), and $\tau_3 = 1.6$–2.4 ns ($I_3 = 10$–12 %) where the range of values of the intensities (I) is given in brackets. It is generally believed[16] that the lifetime $\tau_1 = 0.13$ ns can be attributed to the annihilation of singlet Ps (or p-Ps) while the second lifetime $\tau_2 = 0.41$–0.44 ns arises from the free (or unbound) annihilation of positrons. The longest or the third lifetime $\tau_3 = 1.6$–2.4 ns is due to triplet Ps (or o-Ps). In the case of present results I_1 is much larger than $I_3/3$ and this suggests that the I_1 component receives contributions from p-Ps as well as other modes of annihilation. Following an earlier approach[38–40] we assume that o-Ps resides in a spherical well of radius R_o having an infinite potential, and make use of the following semiempirical relationship[38–40] between the values of τ_3 and the free-volume radius R:

$$\tau_3 = \frac{1}{\lambda_3} = \frac{1}{2}\left[1 - \frac{R}{R_o} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_o}\right)\right]^{-1}, \qquad (3)$$

where we have used, $R_o = R + \Delta R$ and $\Delta R = 1.66$ Å (an empirical value obtained[17] by fitting the measured annihilation lifetime for cavities of known sizes). The values of τ_3 evaluated by the PATFIT program were thus used to determine the values of R with the help of Eq. (3). The temperature dependence of τ_3 and I_3 are shown in Figs. 1 and 2, respectively, where the variation with $1/T$ is plotted because other physical properties of polymer electrolytes are usually described as a function of $(1/T)$. The values of R calculated from τ_3 using Eq. (3) are used to obtain the hole volume $V_f = 4\pi R^3/3$, and the variation in the values of V_f (see the right axis) is also shown in Fig. 1. Our results (Fig. 1) show an increase in τ_3 with temperature leading to an increase in the radius of the free-volume hole (in which o-Ps is annihi-
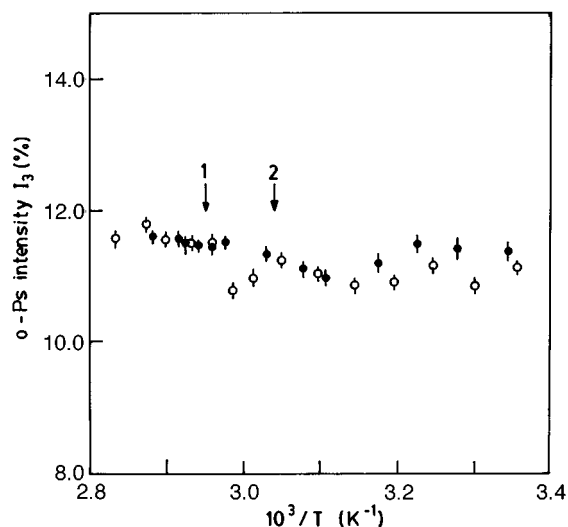
FIG. 2. Same as Fig. 1, but for the temperature dependence of o-Ps lifetime intensity, I_3.

lating) with temperature. This observed behavior conforms to the known behavior of free volume in polymers.[41]

It is observed from Fig. 1 that as temperature is increased from 298 K, the hole volume steadily increases up to 318 K after which it shows a steeper rise until 338 K and then reaches a plateau. This sharp increase in τ_3 in the region $T=318$–338 K in our sample PEO:NH$_4$ClO$_4$ (80:20 wt. %) is due to the phase transition (i.e., semicrystalline to amorphous) taking place around $T=T_m$ (~ 333 K) which results in the softening of the material.

The total free volume available in a polymer is determined by the hole volume as well as the density (number of free-volume sites) of the holes although the dependence of these two factors is not separately understood. According to the Ps-hole theory the probability of o-Ps formation is related to the fraction of free-volume hole space, F_v, in a polymer.[42–45] A simple semiempirical equation has been proposed[42–45] for F_v,

$$F_v = A I_3 V_f, \qquad (4)$$

where I_3 is the o-Ps intensity, V_f is the hole volume, and A is a parameter (for the particular material) to be determined. In the present case, I_3 is observed to be basically constant with temperature (Fig. 2) and application of Eq. (4) shows that F_v is almost proportional to V_f and hence should show a temperature dependence similar to that exhibited by V_f in Fig. 1.

On the other hand, Ito $et\ al.$[44] have argued that both the chemical factor (e.g., electron affinities) and the physical factor (e.g., hole size distribution) determine the o-Ps intensity or I_3 values in polymers. In the present sample the chemical factor does not change and I_3 is observed to remain almost constant with temperature. The physical factor can control I_3 through the hole volume size and the hole density. The present results (Fig. 1) already indicate a variation of the hole volume size with temperature but no corresponding variation in I_3 with temperature. Unless the effects of hole volume size and hole density on I_3 cancel out, we can interpret the constancy of I_3 as well as the low Ps yield to mean that I_3 values in the present case are determined by the
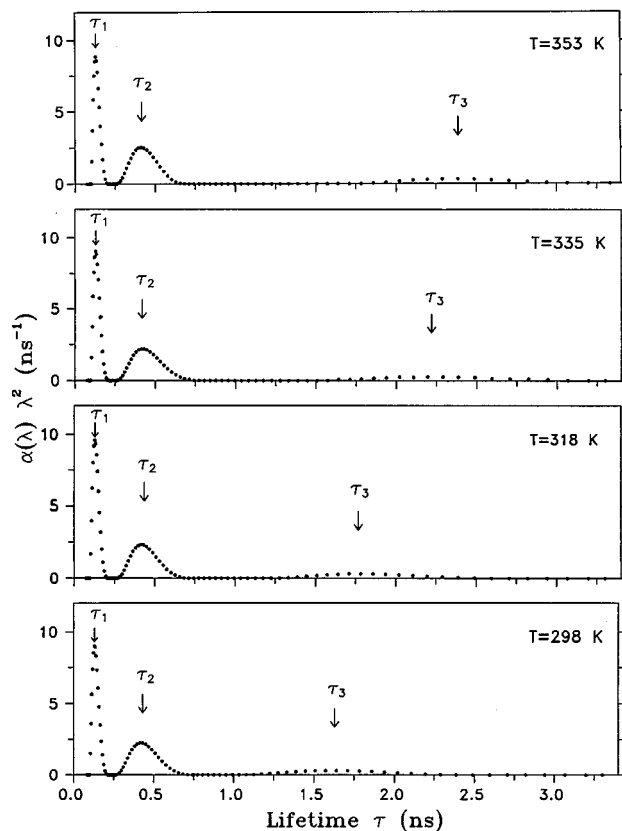

FIG. 3. Positron lifetime distribution functions in PEO:NH$_4$ClO$_4$ (80:20 wt. %) at some representative temperatures obtained from CONTIN (Ref. 19) analysis. The positions corresponding to the lifetime values τ_1, τ_2, and τ_3 obtained from PATFIT (Ref. 37) analysis are shown by arrows.

chemical factor. If this is true then the present results for I_3 may not offer much information about the hole density. If it is assumed that hole density does not change with temperature, we can conclude that the observed increase in the hole size with temperature (Fig. 1) will lead to proportional increase in total free volume. A similar conclusion based on the interpretation of Eq. (4) was arrived at in the last paragraph. It is interesting to note that Peng $et\ al.$[13] have interpreted their positron lifetime results for PEU-LiClO$_4$ above T_g by proposing that the increase in total free volume with temperature arises out of the growth in hole size rather than an increase in number of holes. Recently Jean[45] has reviewed our present understanding of the applications of positron annihilation spectroscopy to the study of hole size, content, distribution, and anisotropic structure in polymers and has posed several questions that need to be answered before a more comprehensive understanding is reached.

By analyzing the measured positron lifetime spectra with the CONTIN program we have been able to determine the positron lifetime probability function, $\alpha(\lambda)\lambda^2$, and our results for some representative temperatures are shown in Fig. 3. Using the CONTIN results the mean positron lifetimes and intensities ($\bar{\tau}_i$, and $\bar{I}_j$, $i=1$–3) have been obtained with the help of the formulas[21]

$$\bar{\tau}_i = \int_{\tau_a}^{\tau_b} \alpha_i \lambda_i^2 \tau_i d\tau_i \bigg/ \int_{\tau_a}^{\tau_b} \alpha_i \lambda_i^2 d\tau_i \qquad (5)$$
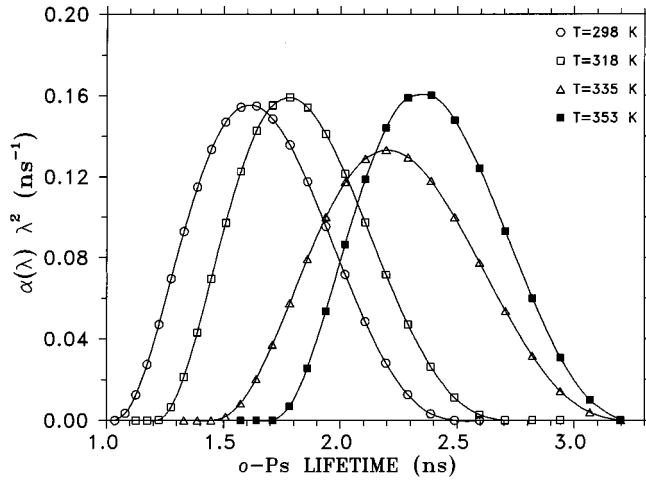
FIG. 4. o-Ps lifetime distribution functions in PEO:NH$_4$ClO$_4$ (80:20 wt. %) at different temperatures. These functions are the expanded profiles of the extreme right peaks (marked as τ_3) of Fig. 3. The continuous lines are drawn through the data points for visual guidance.

and

$$\overline{I}_i = \int_{\tau_a}^{\tau_b} \alpha_i \lambda_i^2 d\tau_i . \tag{6}$$

Although the values of $\overline{\tau}_i$ and $\overline{I}_i$ ($i=1,2,3$) are not listed here, we have found a good agreement between the peak positions of the three peaks (corresponding to τ_1, τ_2 and τ_3) resolved by the CONTIN program and the values of τ_1, τ_2, and τ_3 obtained by the PATFIT program. The expanded profiles of the extreme right peaks (corresponding to τ_3) of Fig. 3 are shown in Fig. 4 to present the o-Ps lifetime distributions in PEO:NH$_4$ClO$_4$ (80:20 wt. %) at different temperatures.

Following Jean and Deng[22] we have defined the free-volume hole-radius probability density function, $f(R)$, as probed by Ps to be

$$f(R) = -3.32 \left\{ \cos\left[\frac{2\pi R}{(R+1.66)} \right] - 1 \right\} \frac{\alpha(\lambda)}{(R+1.66)^2}, \tag{7}$$

where we have not applied any correction factor for the Ps trapping.[20,22] The quantity, $f(R)dR$, then describes the fraction of free-volume holes having radii between R and $R+dR$. The present results for $f(R)$ are plotted against R in Fig. 5 and they show that as the temperature is changed from 298 to 353 K, the free-volume holes expand in size with their distribution function moving to higher radii while the mean radii changes from 2.5 to 3.20 Å. We further notice that the $f(R)$ functions (Fig. 5) appear fairly symmetric and can be approximately described by a Gaussian-type function whose FWHM changes from 0.8 to 0.6 Å. Jean and Dai[46] have pointed out that two major effects, the counting statistics and the instrument instability, contribute to a dispersion of lifetime distributions when the CONTIN program is used to investigate free-volume hole distributions. In our studies we maintained good counting statistics and instrumental stability. The curves shown in Fig. 5 are raw results, not subjected to any deconvolution for natural broadening. The observed narrowing of the $f(R)$ distributions, if real, needs a suitable
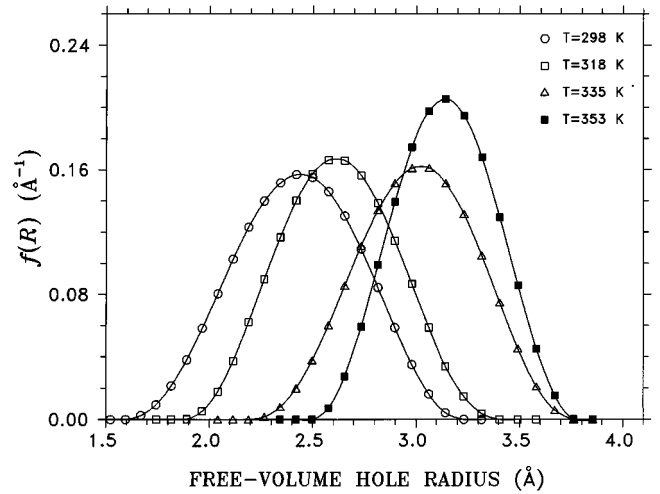

FIG. 5. Free-volume hole radius distribution functions $f(R)$ in PEO:NH$_4$ClO$_4$ (80:20 wt. %) at different temperatures. The continuous lines are drawn through the data points for visual guidance.

explanation. One possible explanation is that ''Ps bubbles'' are formed above the melting temperature and they might have a larger size and a narrower size distribution than the free-volume holes present at lower temperature. A more systematic investigation is necessary to check these possibilities. In view of the uncertainties brought by the experimental factors,[46] the distributions shown in Fig. 5 have to be interpreted qualitatively rather than quantitatively. It is interesting to note that the present results for R lie in the range 2.5–3.0 Å which is consistent with the values obtained from molecular-dynamics simulation.[25]

B. Conductivity, mobility, number of charge carriers, and free volume

The present results for the temperature dependence of conductivity (σ) and ionic (cationic and anionic) mobilities (μ^+ and μ^-) are shown in Fig. 6. These results show a change of slope in the σ versus $1/T$ plot for PEO:NH$_4$ClO$_4$ (80:20 wt. %) at T_m and similar behavior has been observed by many workers in other polymeric systems. The cationic and the anionic mobilities (Fig. 6), however, do not show significant increase at the melting temperature, T_m. In general, the enhancement in the conductivity at T_m was earlier explained on the basis of an increase in the mobility values occurring during the crystalline-to-amorphous phase change of the material. In the literature,[1,47,48] the approach used to explain the temperature dependence of the conductivity in polymers is based either on the empirical Vogel-Tamman-Fulcher[31] (VTF) relation or the Williams-Landel-Ferry[32] (WLF) empirical relation for polymer relaxation processes. The possible relationships between these empirical relationships and various free-volume models have also been discussed in the literature.[1,49] Proponents of the applicability of the free-volume theory to the ionic transport in polymer electrolytes point out that conductivity as well as free volume increases with temperature and hence suggest that the ionic transport in these materials can be assumed to occur through the carrier ions assisted by the segmental motion of the polymeric chain which will increase
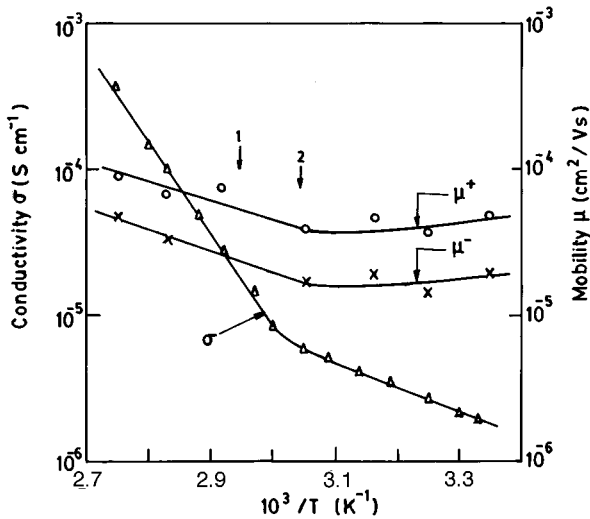
FIG. 6. Temperature dependence of cationic (μ^+) and anionic (μ^-) mobilities along with the conductivity (σ) variation with temperature for PEO:NH$_4$ClO$_4$ (80:20 wt. %). Positions indicated by arrows 1 and 2 correspond to the melting temperatures of uncomplexed PEO ($T_{m_1} \sim 339$ K) and crystalline complexed material ($T_{m_2} \sim 329$ K) (Ref. 36). The continuous lines indicate the best fit to the observed points.
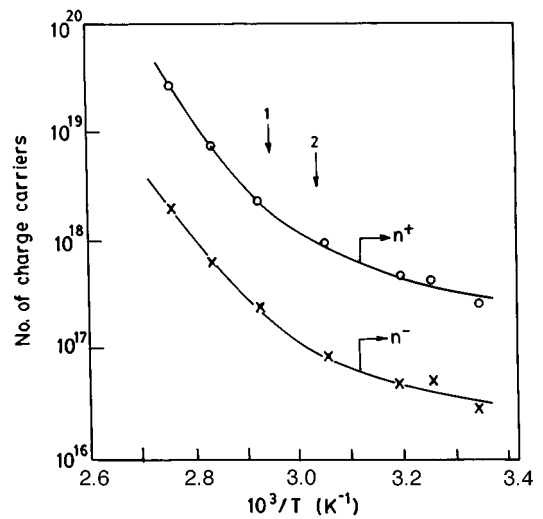

FIG. 7. Variation of number of mobile cations (n^+) and anions (n^-) with temperature for PEO:NH$_4$ClO$_4$ (80:20 wt. %). Positions indicated by arrows 1 and 2 correspond to the melting temperatures of uncomplexed PEO ($T_{m_1} \sim 339$ K) and crystalline complexed material ($T_{m_2} \sim 329$ K) (Ref. 36). The continuous lines are drawn through the data points for visual guidance.

with the increase in the free volume. In this picture one, therefore, expects that with the increase in free volume with temperature the diffusive displacement (and hence mobility) of the carrier ions should also increase. In other words, the pattern of increase in free volume should be reflected in the variation of mobility with temperature. The measurement of the temperature dependence of free volume (Fig. 1) and mobility (Fig. 6) in PEO:NH$_4$ClO$_4$ (80:20 wt. %), however, does not yield such a similar pattern. These results indicate that an alternative explanation has to be sought.

We recall that $\sigma = ne\mu$ and hence the mobility is not the lone controlling factor which could explain the increase in the conductivity at T_m. We may ascribe the conductivity changes to a change in the number of charge carriers. The number of mobile charge carriers (cations and anions) can be calculated using the following equation:

$$\frac{n^+}{n^-} = \left(\frac{t^+}{t^-}\right)\left(\frac{\mu^-}{\mu^+}\right), \tag{8}$$

where t^+ and t^- are the cationic and anionic transference numbers and they have been already determined by us for PEO:NH$_4$ClO$_4$ (80:20 wt. %) from coulometric investigation.[36]

Using Eqs. (1) and (8), and the present experimental data we have calculated the number of mobile cations (n^+) and anions (n^-) and their temperature dependence is shown in Fig. 7. It is interesting to note that the variation in the number of charge carriers is not linear and that it shows a somewhat steeper gradient near T_m as the temperature is raised from room temperature. This indicates that the dissociation of complexed salts is increasing rather rapidly around T_m. On the basis of dissociation theory of electrolytes, the dissociation of ionic salts is determined by the dissociation energy U and the effective dielectric constant (ϵ) of the medium.

Barker and Thomas[50] have given the following expression for the number of dissociated ions, n:

$$n = n_0 \exp\left[\frac{-U}{2\epsilon KT}\right] \tag{9a}$$

or

$$\ln n = \ln n_0 + \left[\frac{-U}{2\epsilon KT}\right], \tag{9b}$$

where n_0 is constant. This relation predicts a linear behavior of $\ln n$ versus $1/\epsilon T$. A knowledge of ϵ is necessary if $\ln n$ is to be plotted against $1/\epsilon T$. Hence the dielectric constant of the sample was measured by us at different temperatures and the results are shown in Fig. 8. We note that ϵ increases more rapidly above T_m. The present results show a linear plot when $\ln n$ is plotted against $1/\epsilon T$ (Fig. 9). The value of dissociation energy (U) obtained from the slopes of the straight lines (Fig. 9) is 2.4 eV. Interestingly the value of U for the ammonium salts is nearly same.[36] The dissociation model[50] appears to explain the increase in n observed by us, with the dielectric constant ϵ playing an important role.

IV. CONCLUSIONS

On the basis of positron lifetime, ionic transport and other studies described above, the following important conclusions can be drawn

(i) The total free volume in PEO:NH$_4$ClO$_4$ increases with temperature, and the rate of increase changes its slope at T_m.

(ii) It appears that the increase in total free volume is determined mainly by the enhancement in the hole size rather than the increase in the number of holes.

(iii) The pattern of increase in free volume with temperature is not reflected in the variation of μ with temperature. In particular, there is very little change in the value of mobility
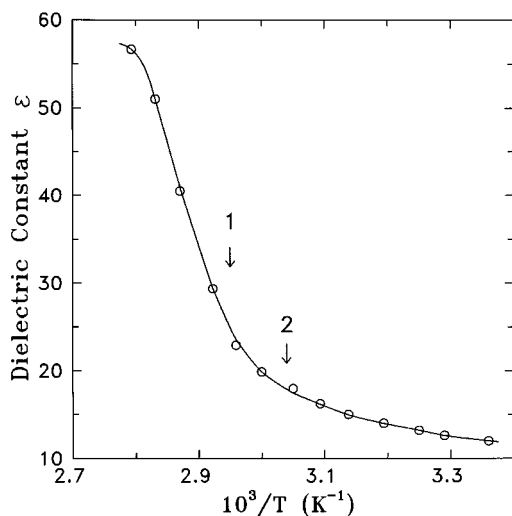
FIG. 8. The dielectric constant, ϵ, at different temperatures for PEO:NH$_4$ClO$_4$ (80:20 wt. %). Positions indicated by arrows 1 and 2 correspond to the melting temperatures of uncomplexed PEO (T_{m_1} ~339 K) and crystalline complexed material (T_{m_2}~329 K) (Ref. 36). The continuous line is drawn through the data points for visual guidance.

at T_m where free volume shows an increase.

(iv) The plot of conductivity σ versus $1/T$ shows a change of slope at T_m.

(v) The increase in conductivity at T_m is influenced more
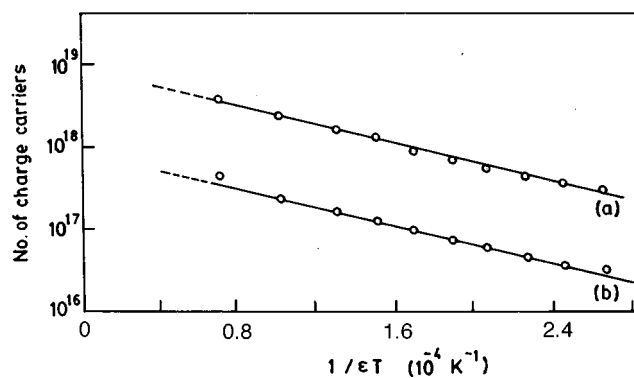

FIG. 9. Variation of number of mobile charge carriers (a) cations (n^+) and (b) anions (n^-) with $1/\epsilon T$ for PEO:NH$_4$ClO$_4$ (80:20 wt. %). The continuous lines indicate the best fit to the observed points.

by the increase in the number of charge carriers (and not so much by the mobility). This behavior may be explained on the basis of a simple dissociation model in which the dielectric constant of the polymer electrolyte plays a role. The value of the dissociation energy has been determined using this model.

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