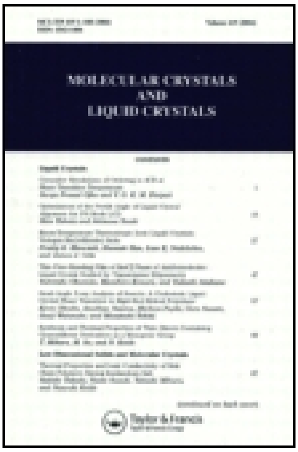

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Coulomb Trapping Effects in Polymer Solid Electrolytes: A Simulation Study of Stoichiometry Dependence

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The effects of interionic attractive interactions on the diffusion of a tracer ion in polyelectrolytes are studied using a one-dimensional hopping model. In this model the tracer cation is assumed to interact with anions placed at regular distances apart, but all inter-cation repulsions are ignored. The effects of both anion density and temperature on the diffusion of the tracer were evaluated through simulation. The tracer is found no longer to undergo simple diffusion, but to display two different diffusion rates, one for local diffusion near an anion, and another slower rate for long-range diffusion. The local diffusion rate varies little with either stoichiometry or temperature, whereas the long-range diffusion is highly correlated to these variables. These behaviors are relevant to ion-pair trapping in polymer electrolytes.

INTRODUCTION

One-dimensional hopping models have been useful in understanding diffusion and conduction in a wide variety of systems, including organic conductors, fast-ion conductors and excitons in molecular crystals.[1] Among the systems studied using such one-dimensional hopping models have been the solvent-free polymer electrolytes.

The microscopic models employed previously to study ion motion in polymer electrolytes have been based upon dynamic percolation theory. These studies[2–5] have focused on how polymer backbone fluctuations affect the ion conduction in these systems. They, like the more macroscopically based free-volume discussions of the polymer electrolytes,[6–10] largely ignore the effects of ion–ion interactions on conductivity. However, the polymer electrolytes show an interesting concentration dependence in their conductivity behavior. The constant temperature conductivity generally goes through a maximum as the concentration of salt increases.[11] For example, in the polyphosphazene systems studied by Blonsky and Shriver, the complex with highest room temperature conductivity corresponded to a stoichiometry of four phosphazene monomer units to one formula unit for lithium triflate. Further addition of salt resulted in a lower conductivity at room temperature. One possible explanation for the decrease in ionic conductivity at higher salt concentrations is an increase in interionic interactions, since the concentration of salt in these solutions is considerably greater than one molar.

Relatively few experimental studies[10,12–17] have been done to determine directly the extent of ion association in polymer electrolytes; the studies which have been done have been largely restricted to spectroscopic probes which give the average environment for the cation or the anion in these systems, but are unable to quantify the exact nature of the species in the complex. For example,[12] by observing a loss in the degeneracy of the anion deformation modes in the IR, Papke was able to determine that in $NaBH_4$ complexes with PEO there is tight ion-pairing between the cation and the anion. He suggested that the low conductivity of these complexes is due to these interactions. However, there have been no direct determinations of whether ions exist in polymer electrolytes as solvent-separated ion pairs, and how this would affect the ionic conductivity.

The objective of this study was to modify the simple hopping model to include attractive interactions between a mobile tracer ion and immobile ions of opposite charge and to study the effects of such interactions on the diffusion characteristics of the tracer ion in a one-dimensional example. This can be regarded as a model for understanding ion conduction in polyelectrolyte systems with only one mobile ion such as those studied by Hardy,[18] LeNest,[19] and others.[20] An understanding of ionic conduction processes and the effects of interionic interactions in these systems should provide insight into ion conduction in the more complex systems where both the anion and cation are mobile.

At low concentrations of the trapping ions and at low temperatures, the tracer ion would be trapped completely in a deep coulomb trap and could not diffuse. As the temperature is raised, one expects that the tracer should (in its thermally-averaged motion) diffuse further from the trapping ion until a temperature with k_BT greater than the maximum barrier height is reached. Above this temperature the tracer ion should become a quasi-free hopper and diffuse as if there were no interactions between it and the trapping ions; further increase in the temperature would affect the diffusion characteristics only weakly. It would also be expected that as the trapping concentration becomes larger, the tracer ion would diffuse more freely until the typical distance between the trapping ions became so small that the local potential for the tracer showed barrier heights generally below k_BT; at this point the tracer would also become quasi-free.

Mott[21] suggested a very similar picture to account for stoichiometry-dependent semiconductor/insulator transitions in semiconductors: at low dopant concentrations of, say P in Si, the electrons are coulombically bound to their counterion (P^+) creating an exciton. As the density of dopant increases, the trapping potential is smoothed until its local trap depth is smaller than the bandwidth and the carrier becomes free.

THE MODEL

Two parallel one-dimensional arrays are placed at a characteristic distance r apart. One array is populated with a set of counterions placed at regular distances apart. The effective potential $V(x)$ felt by the mobile ion on the other array is given by

$$V(x) = \sum_i \frac{q_+ q_-}{\epsilon \, |\mathbf{x} - \mathbf{r}_i|} \tag{1}$$

where ϵ is the bulk dielectric constant of the medium, q_+, q_- are the charges of the ions, $\mathbf{r}_i$ is the position of the fixed counterion, and $|\mathbf{x} - \mathbf{r}_i|$ is the distance between the two ions on opposite arrays. The sum is over all the counterions, and V for the mobile ion is assumed to be independent of particles placed on its own array. (That is, no inter-cation repulsions are included.) The attractive interactions between the tracer ion and the counterions result in a periodic potential for the hopping of the tracer ion (Figure 1).

The influence of the potential on the hopping of the tracer ion at site j is given by a Boltzmann distribution

$$\frac{P_j \rightarrow P_{j+1}}{P_j \rightarrow P_{j-1}} = \exp(-2\Delta V/k_BT) \tag{2}$$

where

$$\Delta V = V(j + 1/2) - V(j - 1/2).$$

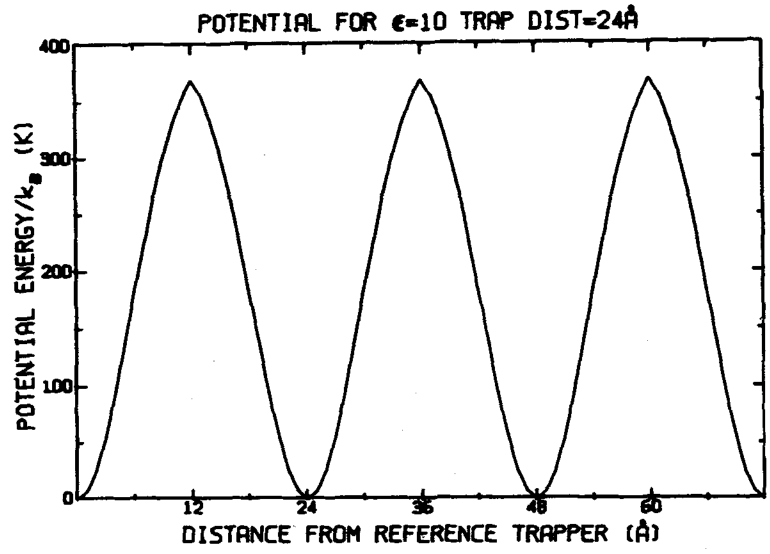

FIGURE 1 Potential profile $V(x)/k_B$ for coulombic attractions between a tracer ion and trappers 24 Å apart, $\epsilon = 10$, $q_+ = e$, $q_- = -e$, $r = 10$ Å. Distance is taken from an arbitrary reference trapper, and r is the distance between hopping and trapping arrays.

The period of the potential and the effective barrier height are both affected when the distances between the counterions are changed. This is because the attractive interactions of the hopper and the nearest two counterions increase when the distances between them is decreased. The dependence of the barrier height on the hopper motion can be evaluated by varying the temperature at constant counterion concentration; because the variables ϵ, T, q_+, q_- enter the equation of motion only in the form $q_+q_-/(\epsilon T)$, varying any one of these is equivalent to varying any. This simplification of the model was checked numerically by varying the parameters with the quotient held fixed, and the results in all cases were identical.

The frequency dependence of the diffusion coefficient was also evaluated using the following relationship†

$$D(\omega) = (i\omega)^2 \int_0^{\infty} e^{-i\omega t} \langle x^2(t) \rangle \, dt \tag{3}$$

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†For notational simplicity, the conventional factor of 1/2 is omitted in defining the D(ω) used here.

where $\langle x^2(t)\rangle$ is the mean-square displacement of the tracer particle after hopping t time steps. For particles undergoing simple diffusion processes $D(\omega)$ is constant for all ω, but for particles not exhibiting simple diffusion more complicated frequency dependencies are seen.

SIMULATIONS AND DISCUSSION

The characteristic hopping distance for the tracer ion was taken as 2 Å. The tracer ion was first placed on the array using a Boltzmann distribution for its initial-location probability and then the tracer was allowed to move over the lattice, with the relative hopping probabilities P_r/P_l computed before each jump where P_l and P_r are hop probabilities to the left and right respectively. The hopping sequence was repeated over 300 time steps, and the behavior of 5000 independent particles was averaged after each time step. The distance between the arrays was r = 10 Å, and the bulk dielectric constant was set at 10. For simulations where the temperature was varied, the distance between the counterions was set at 20 Å. When the distance between the counterions was varied between 20 and 200 Å, the temperature was set at 300 K.

For systems in which the counterions were less than 20 Å apart, the tracer ion behaved as an essentially free tracer with no important spatial variations in the interactions between it and the counterions. When the distance between the counterions is greater than or equal to 20 Å, $\langle x^2\rangle$ exhibits different behavior in the two different time regimes. The plot of $\langle x^2\rangle$ versus t (Figure 2) is essentially linear at both long and short times, but the short time diffusion coefficient is much larger than the diffusion coefficient in the long time regime.

The time t_t at which the turnover from the short time behavior to the long time behavior occurs can be estimated by drawing tangents to the curve in each region and estimating the point of intersection. From the value of $\langle x^2(t_t)\rangle$ the root mean square distance from the original position of the tracer to the turnover position can be estimated. The average potential energy at this point for both the variable temperature simulations and spatially varied simulations is close to k_BT (see Tables I and II).

The tracer ion thus diffuses rapidly among sites where the potential energy is below k_BT, but moves more slowly to surmount barriers in the potential that exceed k_BT. The tracer ion no longer undergoes simple diffusion, since $\langle x^2(t)\rangle$ is no longer linear in t. Rather, there are two characteristic diffusion rates, one for local diffusion within

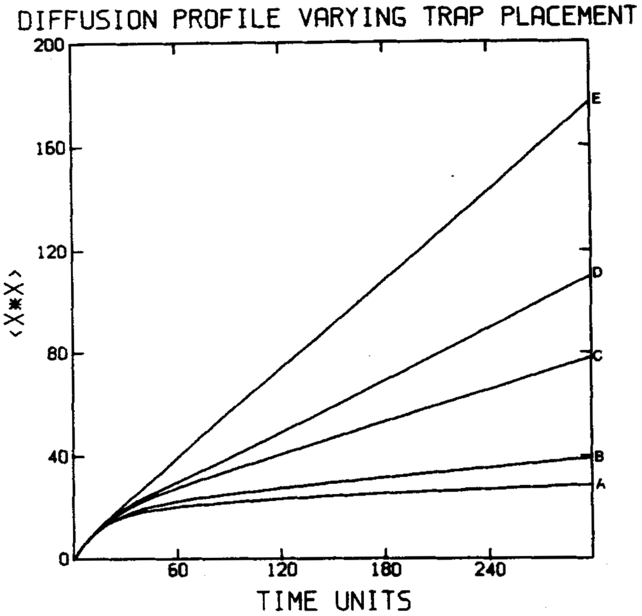

FIGURE 2 Variation of $\langle x^2(t)\rangle$ in one-dimension with varying trap placement. Trappers are placed (A) 200 Å, (B) 50 Å, (C) 40 Å, (D) 32 Å, (E) 24 Å apart, $\epsilon = 10$, $q_+ = e$, $q_- = -e$, $T = 300$ K, and $r = 10$ Å.

the local potential minimum, the other a slower behavior for long-time hopping.

The frequency dependence of the diffusion coefficient was also evaluated. A typical curve for the frequency dependence of the diffusion coefficient is shown in Figure 3. This was obtained by fitting the $\langle x^2(t)\rangle$ versus t curves to the following general expression

$$\langle x^2(t)\rangle = e^{-\alpha t}(at + bt^2) + (1 - e^{-\alpha t})(ct + d) \qquad (4)$$

TABLE I

Turnover Characteristics for Trap Distance Variations

Trap-trap distance (Å)	Turnover time (t_t)	$\langle x^2(t_t)\rangle^{1/2}$(Å)	$\frac{\langle V(t_t)\rangle}{k_B t}$
200	17(3)	7.2(.3)	1.01(.06)
50	22(3)	7.8(.3)	.91(.06)
40	18(3)	7.0(.3)	.91(.06)
30	13(3)	5.0(.9)	.99(.18)
24	7(3)	4.4(1.0)	.79(.19)

TABLE II

Temperature dependent turnover characteristics

Temperature (K)	t_t	$\langle x^2(t_t)\rangle^{1/2}$(Å)	$\frac{\langle V(t_t)\rangle}{k_B T}$
200	12(3)	5.0(.6)	.83(.18)
210	13(3)	5.8(.3)	1.0(.09)
250	15(3)	6.6(.2)	1.0(.05)
300	18(3)	7.0(.3)	.91(.06)
350	28(3)	9.2(.3)	1.1(.05)
400	29(3)	9.6(.3)	1.1(.05)
450	31(3)	9.2(.4)	.99(.05)

and then evaluating the Fourier integral for this expression. This gives a frequency dependence of the form

$$\mathrm{Re}(D(\omega)) = \frac{(c-a)(\alpha^2-\omega^2)\omega^2}{(\alpha^2+\omega^2)^2} - \frac{2b\omega^2(\alpha^3-3\omega^2\alpha)}{(\alpha^2+\omega^2)^3} + \frac{d\omega^2\alpha}{\alpha^2+\omega^2} + c \qquad (5)$$

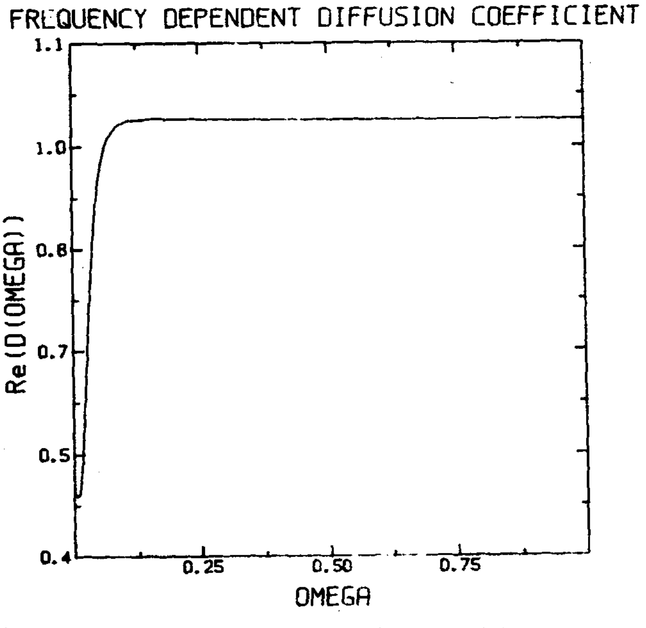

FIGURE 3 Frequency dependence of the diffusion coefficient. For a system with trappers 100 Å apart, $\epsilon = 10$, $T = 450$ K, $q_+ = 1$, $q_- = -1$.

The diffusion coefficient rises from its initial value of c to approach asymptotically a constant value of $d\alpha + a$ at higher frequency, where $d\alpha$ is much larger than a. The dependence at the high frequency end of the spectrum reflects short-time motion, and the long time diffusion behavior should be seen at low frequency. This is indeed seen: since the long time diffusion coefficient is small in comparison to the short time diffusion coefficient, the frequency behavior of the diffusion coefficient should be initially low and then rise to a value characteristic for diffusion in the short time regime, as occurs in Figure 3. In general for these systems the low frequency diffusion coefficient obtained rises with temperature, and with increasing trapper concentration. The high frequency diffusion coefficient is generally found invariant with respect to change of model parameters. It appears that the local diffusion characteristic of the short time regime is not strongly correlated to the steepness of the potential well, whereas the long time behavior, and therefore the low frequency diffusion, is strongly correlated to the potential well steepness. Inertial effects, which are absent in any hopping picture, would yield additional structure at low frequency, as well as asymptotic decay (i.e., $\lim D(\omega \rightarrow \infty) = 0$) at high frequency.

Simulations with a random placement of traps have also been performed. Disorder in the trapping array gives rise to deep coulombic traps similar to those seen in the low density regular trap placement. The tracer ion is still trapped completely at average trapper densities where in the regularly placed systems the tracer is quasi-free.

REMARKS

This study would indicate that for polyelectrolytes with varying concentrations of ionized groups on the backbone, the diffusion coefficient characteristic of the mobile ion would increase as the concentration increases, and therefore, the constant temperature DC conductivity would also increase. At higher frequencies the conductivity would in general be invariant in the different systems. However, this model fails to include interactions between the mobile ions themselves, and ignores the important fact that an increase in the concentration of ionized groups would also tend to increase the rigidity of the system and decrease the polymer backbone fluctuations, which are the dominant mechanism for ionic conduction in polymer electrolytes. Just such weak-crosslinking effects are probably responsible for the observed decrease in ionic conductivity in polymer-electrolytes at high salt concentrations.[11-14]

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