This is the published version (version of record) of:


Available from Deakin Research Online:
http://hdl.handle.net/10536/DRO/DU:30030233

Reproduced with the kind permission of the copyright owner

Copyright : 1995, American Institute of Physics
Molecular dynamics simulations of ion clustering and conductivity in NaI/ether solutions. I. Effect of ion charge

Vilia Ann Payne, Jian-hua Xu, Maria Forsyth,a) Mark A. Ratner,b) and Duward F. Shriver
Northwestern University, Department of Chemistry and Materials Research Center,
Evanston, Illinois 60208-3113

Simon W. de Leeuw
Faculty of Applied Physics, Lorentzweg 1, 2628 CJ Delft, The Netherlands

(Received 4 April 1995; accepted 11 August 1995)

Model systems of sodium iodide dissolved in dimethyl ether were studied in order to investigate the structural and dynamic properties of ionic solutions in small and polymeric ethers having low dielectric constants. Full molecular dynamics simulations were performed at ion charges ranging from 0.5 to 0.1 e, and an algorithm designed to assign ions to clusters and calculate all the terms contributing to ionic conductivity was implemented. Quantitative results were obtained for the contributions of various ionic species to the conductivity. These model systems are stable for ion charges at or below 0.3 e, and a maximum in conductivity is observed at 0.3 e. A range of ion cluster sizes is observed in each system, but the current giving rise to ionic conductivity is due primarily to the movement of free ions and the relative movement of ions within loosely bound pairs. © 1995 American Institute of Physics.

I. INTRODUCTION

The basic mechanisms of ion transport in complex materials such as polymer electrolytes has been a subject of debate for some time. The difficulty lies in the complexity of these materials, which contain large amorphous polymer molecules and some combination of free ions and ion clusters. Ion transport in these amorphous materials occurs through a liquidlike mechanism in which local movement of the polymer is believed to be essential, although the material as a whole must behave as a solid with good mechanical stability. Most polymer electrolytes have a solvating oxygen-containing group, most often an ether group, on either the backbone or side chains of the polymer.

An understanding of the essential mechanism of ion transport in these systems is needed in order to design better materials with higher conductivities for polymer electrolytes. Development of polymer electrolytesb) remains in the prototype stage due to low conductivity. The best polymer electrolytes to date have conductivities on the order of $10^{-4}$ Siemens/cm (S/cm) at room temperature, as compared to $10^{-2} - 10^0$ S/cm for typical liquid electrolytes.c) In spite of excellent experimental work by a number of researchers, however, the properties of these systems on a microscopic level are still not completely understood.

The simulations discussed here were designed to investigate the behavior of ions in a solvent model of liquid dimethyl ether. The solvent corresponds to one monomer subunit in the formula for poly(ethylene oxide), $\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, which is a typical component of polymer electrolytes. The salt chosen for study was sodium iodide, which is one of the alkali halides that can form polymer electrolytes. Monoatomic ions, as opposed to a salt such as lithium perchlorate, were chosen to reduce the number of sites required and speed the computations.

Progress on the understanding of polymer electrolytes has previously been reported.1–6 In particular, the “salting-out” effect in which the ionic salt becomes less soluble at higher temperatures has been shown to be an entropic effect. This result has been demonstrated clearly through determining the separate components of the potential of mean force for two ions of opposite charge. Free ions have a strong ordering effect on a polar solvent. When ions form pairs, they interact with the solvent through dipolar instead of Coulomb forces. The solvent becomes less ordered, and the total entropy of the system increases.7–9 Other research groups have also been engaged in the theoretical study of polymer electrolytes using a variety of approaches.10–16

This paper discusses a series of model systems in which the ion charge is varied from 0.5 to 0.1 e. Each simulation used 15 sodium ions, 15 iodide ions, and 300 dimethyl ether solvents, corresponding to a salt molarity of 0.68. The choice of ion charge as the variable allows control of the degree of ion pairing and clustering during the simulations. In the real world, this choice of variable corresponds to using salts with a wide range of lattice energies. The nature and magnitude of ionic conductivity in each simulation is determined and compared with the others, leading to an understanding of the origin of conductivity in these model systems. The specific ionic species contributing to the current are examined.

II. COMPUTATIONAL METHODOLOGY

Molecular dynamics (MD) simulations provide both dynamic and structural information. Here, the MD study of polymer electrolytes is simplified by replacing the polymer with a number of independent ether molecules representing monomer units. The resulting model remains a complicated but workable one. The ions and the sites in each solvent are treated as partial charges inside Lennard-Jones soft shells,
TABLE I. Standard site parameters for this paper and the following companion paper.

<table>
<thead>
<tr>
<th>Site type</th>
<th>LJ or Value</th>
<th>LJ ε Value</th>
<th>Mass m</th>
<th>Charge q/ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl</td>
<td>3.775</td>
<td>104.0</td>
<td>15.0</td>
<td>+0.15</td>
</tr>
<tr>
<td>methylene</td>
<td>3.775</td>
<td>59.4</td>
<td>14.0</td>
<td>+0.15</td>
</tr>
<tr>
<td>oxygen</td>
<td>3.070</td>
<td>85.6</td>
<td>16.0</td>
<td>−0.30</td>
</tr>
<tr>
<td>sodium ion</td>
<td>1.900</td>
<td>58.2</td>
<td>23.0</td>
<td>+0.30</td>
</tr>
<tr>
<td>iodine ion</td>
<td>4.200</td>
<td>420.0</td>
<td>127.0</td>
<td>−0.30</td>
</tr>
</tbody>
</table>

thus reducing the types of interactions to Coulomb and Lennard-Jones potentials. Any explicit treatment of polarizability has been neglected at this stage of the research.

The ions are given partial charges because full charges lead to phase separation. Although large organic ions are somewhat soluble in small ethers such as in diethyl ether, salts such as alkali halides will only dissolve in polymeric ethers. This effect may be explained through entropic considerations. The entropy loss when a salt dissolves in a polymeric ether is reduced compared to a small-molecule solvent due to the lower initial entropy of the polymer. The lower charge given to the ions in these simulations allows the salt to dissolve in the monomeric ether and also compensates for the neglect of polarizability.

The Lennard-Jones (LJ) potential and parameters follow the general form of Jorgensen and co-workers. Table I lists the standard parameters used for the Lennard-Jones well depth $\epsilon$, diameter $\sigma$, mass $m$, and charge $q$. All simulations conform to these specifications unless otherwise noted. The Coulomb potential is implemented in the form of the Ewald summation. The details of the proper use of the Ewald summation were worked out in the 1980s and have been extensively discussed in the literature.

Each chemical species is represented by one or more sites, each having a partial charge and a Lennard-Jones 6–12 potential. Fixed bond lengths are held constant with Lennard-Jones constraints.

### Equations of Motion

The equations of motion are solved numerically by the six-value Gear predictor–corrector method for second-order equations. The time step is one femtosecond (fs). The Lagrangian multipliers to correct the constrained distances are calculated during the solution of the equations of motion. The constrained distances and associated velocities are corrected for numerical inaccuracies on an occasional basis.

The program was set up to simulate a one-component system of a rigid dimethyl ether model, as described above. The molecule consists of three sites representing the oxygen and the methyl groups. The distances among all three sites are constrained, so that the bond lengths and the methyl–oxygen–methyl angle are all fixed.

Dimethyl ether is a low dielectric solvent, having a dielectric constant of 5 at 298 K. The dielectric constant of approximately 3 for the pure solvent model compares well to this value. It changes little when ions are added to the solution. An addition of ions to a polar solvent normally results in a decreased dielectric constant because the ions decrease the ability of the solvent to rotate. The lack of change in the dielectric constant is probably due to the lack of polarizability and the completely rigid solvent.

For two sites $A$ and $B$, which are not in the same molecule, the intermolecular pair distribution function $g_{AB}$ at distance $r$ is defined

$$g_{AB}(r) = \frac{N_B^A(r)}{\langle N_B^A \rangle_{\text{ideal}(r)}}$$

where $N_B^A$ is the number of $B$ sites located on the surface of a sphere of radius $r$ with center at the $A$ site. $N_B^A_{\text{ideal}}$ is the same quantity that would be calculated if the fluid behaved as an ideal gas at the same density. The integral of $g_{AB}(r)$ is defined as the number of $B$ particles inside the sphere of radius $r$ with center at site $A$.

### Velocity Time Correlation Functions (TCF)

Velocity time correlation functions (TCF) are defined for the tracer diffusion of the cations, anions, and solvents, and for the cross-diffusion among the different species. The velocity TCF discussed in this work are all normalized with respect to the mean squared velocities of the particles. The time zero values of all autocorrelation functions are therefore unity. The time zero values of all cross-correlation functions are zero, within the limits of accuracy of the calculation. For example, the mean squared velocity of the cations is symbolized $v_{c0}$. The autocorrelation function and cross-correlation functions for the cations are respectively written

$$\Phi_c(t) = \frac{1}{V C_{0}} \langle v_{c}(t) \cdot v_{c}(0) \rangle$$

$$\Phi_{cc}(t) = \frac{1}{V C_{0}} \langle v_{c}(t) \cdot v_{c}(0) \rangle$$

where the subscripts $i$ and $j$ refer to individual particles and the subscript $c$ refers to cations. In practice, the statistical accuracy of the calculations is improved by averaging over all possible particles or pair of particles. The accuracy of the time correlation functions is also improved by the use of "sliding averages." This technique increases the number of data points used in an average without requiring a longer simulation.

Both tracer and cross-diffusion coefficients are calculated from the TCF. The data was not smoothed before the transform. Cross-diffusion coefficients are also known as dis-
distinct diffusion, \(^3\) mutual diffusion, \(^3\) or intradiffusion \(^9\) coefficients. Symbolizing the half-Fourier transform, or Fourier–Laplace transform, \(^{40,41}\) as \(\mathcal{F}_u\), and the number of cations as \(N_{c}\), the tracer (\(D_c\)) and cross-diffusion (\(D_{cc}\)) coefficients for the cations are expressed

\[
D_c(\omega) = \frac{1}{3N_c} \sum_{i=1}^{N_c} \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle_{\omega},
\]

(5)

\[
D_{cc}(\omega) = \frac{1}{3N_c(N_c-1)} \sum_{i=1}^{N_c} \sum_{j \neq i} \langle \mathbf{v}_i(t) \cdot \mathbf{v}_j(0) \rangle_{\omega}.
\]

(6)

### III. CONDUCTIVITY ANALYSIS FOR ION CLUSTERS

When the charge and velocity of the \(i\)th ion are \(q_i\) and \(\mathbf{v}_i(t)\), the current vector is found as

\[
J(t) = \sum_{i=1}^{N_{\text{ion}}} q_i \cdot \mathbf{v}_i(t).
\]

(7)

The dc (direct current or zero frequency) conductivity in a nonpolarizable ionic solution can be exactly expressed\(^{40,42}\)

\[
\sigma_{\text{DC}} = \frac{1}{3V_bk_B T} \int_0^\infty dt \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle,
\]

(8)

which leads to the complete expression for the dc conductivity

\[
\sigma_{\text{DC}} = \frac{1}{3V_bk_B T} \int_0^\infty dt \left( \sum_{m=1}^{N_{\text{ion}}} q_m \mathbf{v}_m(t) \cdot \sum_{n=1}^{N_{\text{ion}}} q_n \mathbf{v}_n(0) \right).
\]

(9)

By dividing the ions into groups or “clusters,” whose composition may change with time, the order of summation can be changed. Then \(\sigma_{\text{DC}}\) may be written

\[
\sigma_{\text{DC}} = \frac{1}{3V_bk_B T} \int_0^\infty dt \left( \sum_{m=1}^{N_{\text{ion}}} \sum_{l=1}^{N_{\text{cl}(m)}} q_m \mathbf{v}_m(t) \cdot \sum_{n=1}^{N_{\text{ion}}} \sum_{j=1}^{N_{\text{cl}(n)}} q_n \mathbf{v}_n(0) \right),
\]

(10)

where \(N_{\text{cl}(m)}\) refers to the number of clusters at time \(t\) and \(N_{\text{ion}l}\) refers to the number of ions in a given cluster.

By making three assumptions: (1) the sum over the ions in a cluster may be replaced by the center-of-mass (COM) motion of the cluster, (2) the individual clusters do not change identity over time, and (3) the correlations between different clusters (off-diagonal terms) are negligible, the following equation may be derived:

\[
\sigma_{\text{DC}} \approx \frac{1}{3V_bk_B T} \int_0^\infty dt \left( \sum_{k=1}^{N_{\text{cl}(m)}} q_k \mathbf{v}_{\text{com}}(t) \cdot \mathbf{v}_{\text{com}}(0) \right).
\]

(11)

The definition of diffusion coefficients and the Einstein relation, \(^{43}\) \(\mu = q/k_B T\), where \(\mu\) is mobility and \(D\) is the diffusion coefficient, leads to the following expression for \(\sigma_{\text{DC}}\). It is often applied to ionic or electronic conductors\(^{44}\) where the identities of the \(N_{\text{species}}\) types of charge carriers are known:

\[
\sigma_{\text{DC}} \approx \sum_{k=1}^{N_{\text{species}}} q_k n_k \mu_k,
\]

(12)

where \(n_k\) is density of carriers of species \(k\), \(q_k\) is charge, and \(\mu_k\) is mobility. In polymer electrolyte literature this relationship is expressed as the Nernst–Einstein equation\(^{45}\) for a given carrier species with diffusion coefficient \(D\)

\[
\sigma_{\text{DC}} = \frac{n q^2}{k_B T} D.
\]

(13)

However, the three assumptions mentioned above may lead to gross errors. The standard method for discussing such deviations has been to use the Haven ratio,\(^{46–48}\) which is the ratio of the diffusion coefficient \(D\) calculated from the velocity correlation functions to the diffusion coefficient \(D_\sigma\) calculated from the conductivity through use of the Nernst–Einstein relation. \(D\) is taken as the mean of the cation and anion tracer diffusion coefficients.\(^{47}\) A Haven ratio much greater than unity indicates a high degree of pairing and clustering in the conductive system. As ions group together, the number of effective charge carriers decreases, and so does the apparent diffusion coefficient calculated from the conductivity.

However, the notion that the dynamic properties may be attributed to one particular ionic species is an oversimplification that may impede understanding of the real mechanisms involved in transport. A more complete analysis begins by returning to Eq. (10). The conductivity may be thought of as a result of four different types of motions of ion clusters. The first type is the COM motion of a cluster through space. For example, a lone cation is a cluster of one ion which creates a current when moving. COM displacement will not contribute to the conductivity if the charge on the cluster is zero. The second type of motion is the relative movement of ions within a cluster. For example, a loosely bound ion pair creates a current if the cation and anion move relatively to one another. These two types of motion are “self” contributions in the sense that only one cluster at a time is considered.

The other motion types are the “cross” contributions because they refer to the pairwise interactions of clusters. The third type is the movement of different cluster COMs with respect to each other. The simplest example is the decrease in conductivity found when cations and anions move in the same direction. The fourth type of motion is the movement of ions in different clusters with respect to one another without relative displacement of their COMs. An example would be two large clusters that are close to each other. A rearrangement of ions within each cluster takes place due to the influence of the other. More complicated examples could include mixtures of all four types of motion along with changes in identities of clusters.

The latter three types of contributions may be positive (increase conductivity) or negative (decrease conductivity). The COM self contribution mentioned first must always be positive. Using \(S\) to refer to self terms, \(X\) to refer to cross terms, the indices \(m\) and \(n\) to refer to cluster COMs, and the indices \(i\) and \(j\) to refer to any two individual ions, the following four terms are defined in order to rewrite Eq. (10) in a new form.
\[
S_m(t) = q_m^2 \langle \mathbf{v}_m(t) \cdot \mathbf{v}_m(0) \rangle,
\]

(14a)

\[
S_{ij}(t) = q_i^2 \langle \mathbf{v}_i(t) \cdot \mathbf{v}_j(0) \rangle,
\]

(14b)

\[
X_{mn}(t) = q_m q_n \langle \mathbf{v}_m(t) \cdot \mathbf{v}_n(0) \rangle,
\] and

(14c)

\[
X_{ij}(t) = q_i q_j \langle \mathbf{v}_i(t) \cdot \mathbf{v}_j(0) \rangle,
\]

(14d)

where the cluster charge is

\[
q_m = \sum_{i=1}^{N_{\text{ion}i}} q_i,
\]

(15a)

and the cluster COM velocity is

\[
v_m(t) = \frac{\sum_{i=1}^{N_{\text{ion}i}} \text{mass}_i \mathbf{v}_i(t)}{\sum_{i=1}^{N_{\text{ion}i}} \text{mass}_i}.
\]

(15b)

Equation (10) is therefore rewritten

\[
\sigma_{DC} = \frac{1}{3N_{\text{vol}}} \int_0^\infty \left[ \sum_{m=1}^{N_{\text{cl}}} S_m(t) + \sum_{m=1}^{N_{\text{cl}}} \sum_{i=1}^{N_{\text{ion}i}} S_m(t) - \sum_{m=1}^{N_{\text{cl}}} S_m(t) \right]

+ \sum_{m=1}^{N_{\text{cl}}} \sum_{i=1}^{N_{\text{ion}i}} X_{mn}(t)

+ \sum_{m=1}^{N_{\text{cl}}} \sum_{i=1}^{N_{\text{ion}i}} \sum_{j=1}^{N_{\text{ion}j}} X_{mn}(t)

- \sum_{m=1}^{N_{\text{cl}}} \sum_{i=1}^{N_{\text{ion}i}} X_{ij}(t) \right] dt.
\]

(16)

The four terms of Eq. (16), each enclosed with \( \langle \rangle \), are equivalent to the four types of motion described above in the same order. Note that by adding and subtracting the \( S_m(t) \) and \( X_{mn}(t) \) terms, the contributions from COM motions are separated from those due to individual ion movements. Also note that the off-diagonal terms \( [X_{mn}(t) \times X_{mn}(t)] \) involving different clusters may further be divided into contributions from two different clusters of the same species and contributions from clusters of different species. A cluster species or type is defined by number of cations and number of anions.

An equivalent definition with a uni-univalent salt such as sodium iodide is to define the cluster by number of cations and number of anions. A good estimate of the true system properties. The second source of error arises because the conductivity calculated by this algorithm will exactly equal the conductivity found directly from Eq. (8) only in the thermodynamic limit of a large equilibrated system. This difference occurs because the individual contribution from each cluster or pair of clusters is approximated by the average contribution calculated from the average time correlation function for that cluster type or pair of types. An idea of the magnitude of the latter error can be obtained by comparing the conductivity calculated by the clustering algorithm to the conductivity calculated from Eq. (8). This comparison is quantified by the \( \Theta \) parameter, which gives the percent ratio of the former to the latter. For phase separated systems, this error can lead to an unsuccessful analysis.

The \( \Theta \) parameter typically ranges from 90% to 110% for stable systems. A value in this range indicates a successful analysis. However, the analysis can be very poor for systems which are undergoing phase separation. The \( \Theta \) value calculated during the clustering analysis can be negative in such cases. Negative values occur when some of the individual terms making up the total conductivity are large and negative. When these values have large errors associated with them, then the total of all the conductivity terms can be negative.

The analysis described above depends on finding a reasonable definition of a cluster. Concepts such as a Bjerrum ion pair can be applied only in dilute solutions. For the analysis of polymer electrolytes, the following definition is suggested here: An ion cluster is a group in which each ion is within some minimum distance \( r_{\text{pair}} \) of some other unlike ion in the group. This concept is based on the idea that each ion in a cluster affects other ions in the cluster either directly or through multiple particle interactions. Any ion which is paired to an ion within the cluster is also part of the cluster. The identity of the cluster changes when any ion moves close enough to join in the interactions or moves away so that it is no longer strongly affected by the cluster. Other researchers have approached this problem in similar fashion.

The distance \( r_{\text{pair}} \), typically between 4 and 5 Å, is first estimated from the cation–anion pair distribution function for a particular simulation. The choice of \( r_{\text{pair}} \) is then refined so that the minimum number of cluster identity changes \( I_{\text{min}} \) occur over the length of the simulation. Choosing a value of \( r_{\text{pair}} \), which is too small, leads to failure to include all the ions in each group which are interacting with each other. The vibrations of ions in and out of the incomplete groups leads to an increase in \( I_{\text{min}} \). Choosing a value of \( r_{\text{pair}} \) which is too large leads to several ion groups which are not interacting strongly with each other being defined as a cluster, and the separate motions of these groups in different directions also leads to an increase in \( I_{\text{min}} \). A natural minimum in \( I_{\text{min}} \) is observed to occur at appropriate \( r_{\text{pair}} \) values between 4 and 5 Å.

The definition of the pairing parameter \( r_{\text{pair}} \) corresponds approximately to the size of the hole inside which a molecule dissolved in a polymer is undergoing vibration. Recent literature results have used a pairing parameter of 5 Å to define
cluster sizes in poly(ethylene oxide)–lithium iodide materials. Of course, a second minimum will occur in $r_{\text{min}}$ at a value for $r_{\text{pair}}$ large enough to include all the ions in the simulation cell in one cluster. This minimum depends on the size of the box and has no physical meaning.

IV. STRUCTURAL PROPERTIES

A detailed examination of how structural and transport properties depend on the ion charge provides much information about the MD model systems. A series of six simulations at five different ion charges was carried out at 298 K with 15 cations, 15 anions, and 300 dimethyl ether solvents. The conditions correspond to a salt molarity of 0.68. All parameters other than the ion charges used the standard values outlined in Table I. The length of each cubic simulation cell was 33.22 Å.

The simulation with ion charge of 0.5 e began phase separation at a rapid rate. One simulation at 0.4 e provided inconclusive results, so a second simulation from the end coordinates of the first was also carried out. It appears that systems with ion charge of 0.4 e at 298 K are unstable and will eventually undergo phase separation. Systems with ion charges of 0.3, 0.2, and 0.1 e are stable. The simulations with ion charges of 0.5, 0.4 (first), 0.4 (second), 0.3, 0.2, and 0.1 e lasted 100, 100, 65, 80, 100, and 100 ps, respectively, following an equilibration period of similar length beginning from the coordinates of a previous simulation.

Figure 1 shows the mean cation–anion distance averaged over all possible pairs of unlike ions) for all these systems as a function of simulation length. Although this distance is not a thermodynamic property, since it depends on system size, it has proven to be a useful tool to illustrate the effect of phase separation. The mean cation–anion distance for a given system at equilibrium will fluctuate about some average value. For a system experiencing phase separation, the mean cation–anion distance will decrease over time. The range of values for unstable systems will therefore depend on the initial configuration and length of the simulation. In the same way, all the other structural and dynamic information obtained for unstable systems must be interpreted with the greatest care because equilibrium has not been reached.

An examination of Fig. 1 shows clearly that the system will be stable when the ion charge is 0.3 e or less. The distance for the 0.5 e simulation decreases approximately 3 Å within 100 ps. The distance for the two consecutive 0.4 e simulations starts at a higher value but drops about 4 Å within 165 ps. The distances for the three other simulations at lower charges do not change, indicating systems at equilibrium.

Figure 2 shows the cation–anion PDF at five different ion charges for simulations at 298 K with 15 cations, 15 anions, and 300 solvents. A few data points are marked with symbols. Units are normalized as described in the text.

![FIG. 1. The mean cation–anion distance as function of simulation length for five different values of the ion charge. Each point is an average over the preceding 10 ps. The average includes all possible pairs of unlike ions in the basic simulation cell, not just those which are in close proximity to each other.](image1)

![FIG. 2. The cation–anion PDF at five different ion charges for simulations at 298 K with 15 cations, 15 anions, and 300 solvents. A few data points are marked with symbols. Units are normalized as described in the text.](image2)

![FIG. 3. The oxygen–cation pair distribution function at five different ion charges.](image3)
that an ion charge of 0.3 e, small clusters containing a few ions exist, but larger clusters are rare. Further decreases in ion charge will therefore only affect small clusters. These conclusions are supported by examination of the cation–cation PDF and anion–anion PDF. Only small differences can be observed for ion charges of 0.3 e and below.

Figure 3 displays the oxygen–cation PDF for the simulations. The first peak indicates that the short-range interactions between cations and solvent–oxygen sites increases with decreasing ion charge from 0.5 to 0.3 e, and then decreases again at lower charges. The strongest cation–solvent interactions occur when the cation and oxygen site charges have the same absolute value (~0.3 e!). Methyl sites and anions also have an attractive interaction due to the 0.15 e positive charge on methyl sites. Figure 4 presents the methyl–anion PDF. The first peak shows an increase at decreasing values of the ion charge from 0.5 to 0.3 e. Lower charges give almost identical results.

It is also instructive to look at the repulsive oxygen–anion and methyl–cation interactions. Figures 5 and 6 show the PDF for these sites. In the oxygen–anion PDF, a shift for the first peak to larger distances is seen for ion charges of 0.3 e and below. This phenomenon may be attributed to the decrease in the amount of ion clustering. At larger values of the ion charge, a cation may keep both an anion and an oxygen site in close proximity. The methyl–cation PDF has a maximum for the first peak at ion charges of 0.3 and 0.2 e.

The conclusions from examination of all the pair distribution functions is that stable systems without large clusters exist for ion charges at or below 0.3 e. However, an ion charge of 0.1 e is too small for significant ion–solvent interactions. Table II shows the mean total coordination numbers for the cations at 3.6 Å. Ion charges of 0.5 and 0.4 e result in fourfold coordination for the cation in its first solvation shell. The standard coordination for a sodium ion in water is octahedral, but with the lower ion charge and less polar solvent in these simulations, the coordination number is also lower. Some NMR evidence of four-coordinate solvent:solute species for solutions of NaAlBu₄ in tetrahydrofuran (THF) has been reported in the literature. At lower charges, each cation tends to be in close proximity to two oxygen sites and either one or zero anions. At an ion charge of 0.1 e, almost no anions are found near the cations.

V. DYNAMIC PROPERTIES

A study of the dynamic properties of these systems begins with an examination of the time correlation functions. The time correlation functions for the two simulations at 0.4 e show little difference between the two simulations. Only the results from the first simulation are plotted in the graphs described here. Figure 7 shows the current correlation func-

---

**TABLE II. Mean coordination numbers for cations at 3.6 Å.**

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Number of anions</th>
<th>Number of oxygens</th>
</tr>
</thead>
<tbody>
<tr>
<td>q = 0.5 e</td>
<td>2.53</td>
<td>1.17</td>
</tr>
<tr>
<td>q = 0.4 e (first)</td>
<td>1.67</td>
<td>1.87</td>
</tr>
<tr>
<td>q = 0.4 e (second)</td>
<td>1.88</td>
<td>1.62</td>
</tr>
<tr>
<td>q = 0.3 e</td>
<td>0.87</td>
<td>2.36</td>
</tr>
<tr>
<td>q = 0.2 e</td>
<td>0.36</td>
<td>2.42</td>
</tr>
<tr>
<td>q = 0.1 e</td>
<td>0.17</td>
<td>1.95</td>
</tr>
</tbody>
</table>
tions for the simulations. The troughs seen in the functions grow progressively less with decreasing ion charge. These troughs are the result of the vibration of cations in the potential well of adjacent anions. Figure 8 shows the cation velocity correlation functions. The cation functions also exhibit definite troughs at the two highest charges, and they flatten out at lower charges.

Table III reports the conductivities and self-diffusion coefficients for the six systems. To obtain the molar conductivity $\sigma$ in $10^{-5}$ S cm$^{-2}$ mol$^{-1}$, multiply the conductivity $\sigma$ in $10^{-3}$ S cm$^{-1}$ by 0.1472. The most striking effect seen from this data is a maximum in the conductivity at an ion charge of 0.3 e, which is three times that of the 0.5 e value. The value for 0.2 e also is high. The diffusion coefficient for the solvent remains about the same, but the diffusion coefficients for both ions increase, with the cation showing an impressive jump. The increase in the diffusion coefficients can only be attributed to a decrease in the size of clusters, so that the total mass of the moving particles is less.

The maximum in the conductivity at 0.3 e can be simply explained. As noted above, at an ion charge of 0.3 e the maximum cation–oxygen interaction in the first shell is obtained. At lower charges both cation–solvent and cation–anion interactions are decreased. At ion charges of 0.3 e and below, the degree of ion clustering is low enough so that the system is stable. At lower charges, the diffusion coefficients increase and the ion pairing decreases, which leads both to greater mobility and more charge carriers. This trend is counteracted by the effect of the decreasing magnitude of the charge, because the conductivity is directly related to the square of the charge on the carriers. These two trends balance at an ion charge of 0.3 e to provide the maximum in conductivity.

Table IV reports the cross-diffusion coefficients and Haven ratios for the six simulations. A decrease in the Haven ratio is observed with decreasing ion charge, until a value close to unity is obtained for 0.1 e. The cross-diffusion coefficients are correlated with the degree of ion pairing and clustering found in the system. High positive values indicate a strong correlation among the velocities of the ions. The table shows a decrease in the anion–anion, cation–cation, and cation–anion cross-diffusion coefficients with a decrease in ion pairing as established by the pair distribution functions. A notable exception is the large positive value of $D_{ca}$ at an ion charge of 0.1 e. That exception will be discussed further after the clustering analysis results are presented.

### VI. CONDUCTIVITY ANALYSIS RESULTS

Table V presents the results of the clustering analysis for the simulations using a value of the pairing parameter of 1.0 Å. All ions are therefore treated as free during the calculations, since an iodide ion can never approach within an angstrom of a sodium ion due to their finite radii. $S$ refers to self-terms and $X$ refers to cross-terms. Cations and anions

<table>
<thead>
<tr>
<th>Simulation</th>
<th>HR</th>
<th>$D_{c} / 10^{-5}$ cm$^2$ s$^{-1}$</th>
<th>$D_{a} / 10^{-5}$ cm$^2$ s$^{-1}$</th>
<th>$D_{ca} / 10^{-5}$ cm$^2$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td></td>
<td>$\ldots$</td>
<td>$\ldots$</td>
<td>$\ldots$</td>
</tr>
<tr>
<td>$q=0.5$ e</td>
<td></td>
<td>$5.09$</td>
<td>$6.5 \pm 0.1$</td>
<td>$2.2 \pm 0.1$</td>
</tr>
<tr>
<td>$q=0.4$ e</td>
<td></td>
<td>$3.68$</td>
<td>$5.3 \pm 0.1$</td>
<td>$0.50 \pm 0.01$</td>
</tr>
<tr>
<td>(0–100 ps)</td>
<td></td>
<td>$3.35$</td>
<td>$5.5 \pm 0.1$</td>
<td>$0.93 \pm 0.01$</td>
</tr>
<tr>
<td>$q=0.3$ e</td>
<td></td>
<td>$1.44$</td>
<td>$1.6 \pm 0.1$</td>
<td>$0.47 \pm 0.01$</td>
</tr>
<tr>
<td>$q=0.2$ e</td>
<td></td>
<td>$1.30$</td>
<td>$0.25 \pm 0.01$</td>
<td>$-0.81 \pm 0.01$</td>
</tr>
<tr>
<td>$q=0.1$ e</td>
<td></td>
<td>$0.94$</td>
<td>$0.14 \pm 0.01$</td>
<td>$2.2 \pm 0.1$</td>
</tr>
</tbody>
</table>
are denoted by c and a subscripts. All values are reported as a percentage of the total conductivity for the appropriate simulation. The percentage is rounded off to the nearest integer. The following equations may be used to understand the table:

\[
S_c + S_a = S_{tot}, \quad (17)
\]

\[
X_{cc} + X_{aa} + X_{ca} = X_{tot}, \quad \text{and} \quad (18)
\]

\[
S_{tot} + X_{tot} = 100\%. \quad (19)
\]

The results provide further confirmation of previous conclusions. At the two higher charges, the totals of the cross-terms are large in negative, so that ion pairing and clustering serves to decrease the conductivity by a great deal. At 0.3 and 0.2 e, the totals of the cross-terms are also negative, but the magnitudes are much smaller. This decrease in the amount of clustering is responsible for the maximum in conductivity at these values of the ion charge. At all values of the ion charge, the self-terms for cations are greater than the self-terms of anions, which may be attributed to the lighter mass of sodium.

At the lowest ion charge, something peculiar is observed. The cross-term between cations, which had been negative at 0.3 and 0.2 e, is again positive and contributes 11% of the conductivity. It is this cross-term that leads to the Haven ratio of a little less than unity for this simulation (see Table IV). It is possible that the solution is partially behaving as a single-ion conductor of cations, which would lead to a Haven ratio of less than unity.\textsuperscript{48} Supporting evidence is the high value of the cation cross-diffusion coefficient at 0.1 e. However, 11% is within the error of the analysis for the system, so no firm conclusions will be made.

Repeating the cluster analysis with a larger value of the pairing distance parameter allows a more detailed analysis of these systems. Figure 9 shows how the number of cluster identity changes is affected by the value of the pairing parameter. A broad minimum for all simulations occurs between 4.0 and 5.5 Å. The origin of this minimum was discussed previously. The value of \(r_{pair}=4.8\) Å was selected as the pairing parameter for all simulations.

Using the pairing parameter of 4.8 Å, the cluster species and their contributions to the current were analyzed. At the three lower charge values, no clusters with more than seven ions are observed. The simulations at 0.4 e show the largest number of different sizes, ranging from free ions to very large clusters. This difference is probably due to the partial phase separation of the system. A smaller number of ions at 0.4 e might be within the solubility limit and show no phase separation. At 0.5 e, the system is at an advanced stage of phase separation, and most of the ions are in a few large clusters.

The thought may occur that if free cations are more solvated by oxygen sites than free anions are by methyl sites, due to the larger partial charge on the oxygen sites, then there may be a difference in the stabilities of the two ion types. One possibility might be that an extra free cation is balanced by an ion triplet with an extra anion. To investigate this possibility, the number concentration of free ions was graphed as a function of ion charge in the simulations. The number concentration of a species is simply the average number of that species present during the simulation at any time. Figure 10 shows a remarkably symmetrical distribution. The concentration of free ions increases with decreasing absolute value of the charge, and free anions have about the same average concentration as free cations at each value of the charge. The one exception is in the unstable system with ion charge of 0.4 e, where a larger concentration is observed for free cations than free anions, although both have small concentrations. No free ions were observed in the simulation using 0.5 e ion charge.

The relative concentrations of other cluster types are also

---

**TABLE V.** Clustering analysis with pairing parameter of 1.0 Å. S refers to self terms, X refers to cross terms, and c and a refer to cations and anions, respectively.

<table>
<thead>
<tr>
<th></th>
<th>0.5 e (First)</th>
<th>0.4 e (Second)</th>
<th>0.4 e</th>
<th>0.3 e</th>
<th>0.2 e</th>
<th>0.1 e</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_{tot})</td>
<td>479</td>
<td>347</td>
<td>398</td>
<td>142</td>
<td>126</td>
<td>94</td>
</tr>
<tr>
<td>(S_c)</td>
<td>263</td>
<td>188</td>
<td>231</td>
<td>89</td>
<td>90</td>
<td>74</td>
</tr>
<tr>
<td>(S_a)</td>
<td>216</td>
<td>160</td>
<td>167</td>
<td>52</td>
<td>36</td>
<td>20</td>
</tr>
<tr>
<td>(X_{total})</td>
<td>-379</td>
<td>-248</td>
<td>-299</td>
<td>-42</td>
<td>-26</td>
<td>6</td>
</tr>
<tr>
<td>(X_{cc})</td>
<td>404</td>
<td>39</td>
<td>76</td>
<td>-11</td>
<td>-17</td>
<td>11</td>
</tr>
<tr>
<td>(X_{aa})</td>
<td>351</td>
<td>75</td>
<td>136</td>
<td>-6</td>
<td>-8</td>
<td>-3</td>
</tr>
<tr>
<td>(X_{ca})</td>
<td>-1134</td>
<td>-362</td>
<td>-510</td>
<td>-24</td>
<td>-1</td>
<td>-2</td>
</tr>
</tbody>
</table>

---

![FIG. 9. The number of cluster identity changes as a function of the pairing distance parameter.](image)
worth thorough investigation. The stable systems have no clusters with more than 7 ions. The concentrations of clusters with 7 ions is small in all the systems studied. Therefore, free ions, neutral ion pairs, and clusters with 3 to 6 ions may be deemed important in stable systems. For the systems with 0.4 e ion charge, only the results from the second simulation will be discussed to prevent confusion. The number concentrations of neutral ion pairs observed in the different simulations are shown in Fig. 11. Significant concentrations of pairs are observed in the three stable systems, with the largest concentration at 0.3 e.

Figure 12 shows the number concentrations of clusters with one unbalanced ion and a total of 3 or 5 ions. By comparing this graph and Fig. 10, it is easy to see that, for stable systems, free ions are more prevalent than ion triples, and ion triples are more prevalent than clusters of 5. Although the data is noisy, concentrations in the stable systems of either triples or clusters of 5 appear to increase with increasing ion charge for both negatively and positively charged clusters. Figure 13 displays a similar plot for neutral clusters having 4 or 6 ions. Again, concentration increases with increasing ion charge for the stable systems. For the unstable systems at 0.4 and 0.5 e, lower concentrations are observed for all these small species because each ion spends most of the time in a large cluster. It should also be mentioned that at the two lowest ion charges, a few clusters are observed with two extra unbalanced ions. Some energetically favorable solvent configuration is probably important in the formation of these rare clusters.

The number concentration can be converted to the average percentage of ions found in that cluster type. Table VI shows the mean percentages of cations and anions found in the different small species. A dash mark means the cluster was not observed during the simulation. If the cluster is neutral, the percentages of cations and anions are equal. Separate percentages for cations \( C \) and anions \( A \) are reported for charged clusters. The symbols \( \delta^+ \) and \( \delta^- \) stand for partial charges. For example, the table shows that at an ion charge of 0.1 e, 72% of the cations are free, and 73% of the anions are also free. Also, 18% of cations and 18% of anions are in
neutral ion pairs. The percentages for all species containing cations add up to 100%, and the percentages for all species containing anions also add up to 100%. The table shows that in the three stable systems, the concentrations of species with the same number of ions and opposite charges are approximately equal. In the 0.4 e system, a trend may exist for more free cations and anions, but the statistics are not good enough for firm conclusions on this question.

The difference between the unstable and stable systems is quite striking. At ion charges at or above 0.4 e, most of the ions exist in clusters larger than 6 ions. The first and second simulations at 0.4 e show the progress of phase separation as the number of ions in the large clusters increases. At ion charges at or below 0.3 e, less than 1% of the clusters cannot be accounted for by free ions, ion pairs, neutral clusters of 4 or 6 ions, and charged clusters of 3 or 5 ions. A hypothesis can be formed from this data that stable systems have no significant concentrations of clusters larger than six ions.

The focus can now be shifted from the structural properties of the clusters to their dynamic properties. Table VII presents the clustering analysis for each simulation using a pairing parameter of 4.8 Å. Here, the subscript 1 refers to any cluster type and the subscript 2 refers to any cluster type 2≠1. The underlined values include both the COM contributions and the contributions due to the motions of individual ions. The values which are not underlined include only the COM contributions. The following equations may be used to understand the table:

\[
S + X_{11} + X_{12} = \text{Total}=100\% \quad \text{and} \quad (20)
\]

\[
S + X_{11} + X_{12} = \text{Total}=100\% . \quad (21)
\]

The final row contains the parameter \(\Theta\), which is the percentage of the total conductivity calculated using \(r_{\text{pair}}=4.8\ \text{Å}\) with respect to the total conductivity calculated using \(r_{\text{pair}}=1.0\ \text{Å}\). If the \(\Theta\) parameter is positive, a positive value for any of the other terms indicates a contribution which increases the conductivity, and a negative value indicates a contribution which decreases the conductivity. The opposite is true if the \(\Theta\) parameter is negative. For the highest ion charge, the \(\Theta\) parameter shows that the analysis with \(r_{\text{pair}}=4.8\ \text{Å}\) is unable to account for any of the conductivity. This failure occurs for highly clustered systems, as discussed in Sec. III.

The COM approximation to the conductivity is poor in all cases. Even at the lowest ion charge, the COM contributions account for only 64% of the conductivity. Therefore,
TABLE VIII. Percent contributions of small clusters to the conductivity. Two species are reported for terms involving cross correlations.

<table>
<thead>
<tr>
<th>Ion charge</th>
<th>% Value</th>
<th>Type of Term</th>
<th>Species one</th>
<th>Species two</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 e</td>
<td>14.8</td>
<td>( S_1 )</td>
<td>Na(_{12} )</td>
<td>...</td>
</tr>
<tr>
<td>0.4 e (1st)</td>
<td>58.4</td>
<td>( S_1 )</td>
<td>NaI</td>
<td>...</td>
</tr>
<tr>
<td>0.4 e (2nd)</td>
<td>11.8</td>
<td>( S_1 )</td>
<td>Na(_{12} )</td>
<td>Na(_{12} )</td>
</tr>
<tr>
<td>0.3 e</td>
<td>29.4</td>
<td>( S_1 )</td>
<td>NaI</td>
<td>...</td>
</tr>
<tr>
<td>0.2 e</td>
<td>46.5</td>
<td>( S_1 )</td>
<td>Na(_{12} )</td>
<td>...</td>
</tr>
<tr>
<td>0.1 e</td>
<td>51.5</td>
<td>( S_1 )</td>
<td>Na(_{12} )</td>
<td>...</td>
</tr>
</tbody>
</table>

The underlined values will be used in further discussion. The amount of conductivity due to self-terms peaks at an ion charge of 0.2 e.

A comparison of the \( S_{total} \) and \( X_{ca} \) terms in Table V with the \( S_1 \) and \( X_{12} \) terms in Table VII is in order. The \( X_{12} \) terms have smaller magnitudes and in some cases are of opposite sign than their \( X_{ca} \) counterparts. When all ions are counted as free, the presence of clusters in which ions are moving together decreases the conductivity and gives a negative value to \( X_{ca} \). By dividing the ions into clusters, this negative contribution is shifted into the \( S_1 \) term. The magnitude of the \( S_1 \) term is therefore decreased compared to the \( S_{total} \) term. The \( X_{12} \) term then reflects the relative motions of different clusters of ions instead of individual ions, and for charges of 0.3 e or less, this contribution is no more than 20%.

The analysis also provided an estimate of the positive or negative contribution to the conductivity from a cluster type (self term) or pair of types (cross term) if the magnitude was greater than 0.01%. For the 0.5, 0.4 (first), 0.4 (second), 0.3, 0.2, and 0.1 e simulations, there were 24, 172, 169, 61, 63, and 56 such terms, respectively. The contributions will be reviewed here for free ions, neutral pairs, and clusters with 3 to 6 ions. Table VIII presents the contributions of these small clusters to the conductivity found in the different simulations. The values reported include both COM and relative ion motion contributions. The meanings of the terms \( S_1 \), \( X_{11} \), and \( X_{12} \) are the same as in the previous table and refer to self and cross terms. Only values over 5% are reported, and the results are ordered by size of the value.

In the unstable system with 0.5 e charge, the conductivity is entirely due to the relative motion of ions within clusters. All clusters observed in the simulation were neutral, so there are no COM contributions. The ions spend most of the time in large clusters containing 14 or more ions. The contributions of small clusters are not large when compared with the term totals from Table VII. In the two simulations of the system with 0.4 e charge, many different terms made contributions to the conductivity. The relative contributions of the small clusters shift a great deal from the first to second simulation, indicating the unstable nature of this system. In particular, the contribution of neutral pairs disappears, which correlates with the drop in concentration for ion pairs seen in Table VI.

For the stable systems, the most important species in conductivity are free ions and ion pairs. These results show that ions in the loosely bound pairs create currents by their relative movement. The contributions of free ions increase and that of pairs decrease as the charge decreases, which matches with the changes in concentration seen in Table VI. The free cation also contributes more than the free anion, and the difference increases with the decrease in charge. As the concentrations of free anions and cations are almost equal, this difference must be attributed to greater mobility for the lighter cation.

The clustering analysis which treated all ions individually was shown in Table V. The differences observed between the dynamic properties of cations and anions have increased by using the clustering analysis with a pairing parameter of 4.8 Å when compared to the previous analysis. In the new analysis, only the ions which are not in clusters are treated as free particles. Therefore, the effect of ion pairing is separated away from the effect of the free particles. The second analysis provides a much clearer picture of the origin of conductivity.

VII. CONCLUSIONS

This article offers an analysis of ionic conductivity in low dielectric dimethyl ether solutions at 298 K by varying the ion charge from 0.5 to 0.1 e. Both dynamic and structural information clearly demonstrated that this system is stable for ion charges at or below 0.3 e. The pair distribution functions indicate that the ion–solvent interaction reaches a maximum when the oxygen site and the cation have charges of equal magnitude (0.3 e). The cation–anion interaction decreases steadily as the charge decreases.

In highly clustered systems, the cation and anion show similar magnitudes for self-diffusion coefficients because ions within clusters travel at the same velocity. The cross-diffusion coefficients, especially the cation–anion diffusion coefficient, have positive values comparable to the ion self-diffusion coefficients. These similarities are all indicative of a highly clustered or phase separated system.

As the ion charge decreases, the diffusion coefficients of both ions increase (see Table III). Of course, this change is directly related to the decrease in cluster size. At an ion charge of 0.1 e, the cation has a diffusion coefficient about four times greater than the anion, reflecting the fact that it is the lighter particle. Although the diffusion coefficients continue to increase with decreasing ion charge, the conductivity
reaches a maximum at 0.3 e. This maximum is the result of the dependence of the conductivity on two opposing trends, which are the square of the ion charge and the degree of clustering. It makes sense that the conductivity reaches a maximum when the charge magnitudes for the oxygen sites, anions, and cations are all equal, for then the solvent can compete successfully with the anion to reduce clustering around a given cation.

The structural results of the clustering analysis (Table VI) provided estimates of the concentrations of various cluster species present in the system and, at these concentrations of cluster types with the same number of ions but opposite charges are about equal. The percentage of ions that are free increased steadily with decreasing ion charge. About 70% of the ions at 0.1 e are free. The concentration of pairs reached a maximum of 44% of the ions at a charge of 0.3 e. Clusters of 3 or 4 ions were observed to be more common in the stable systems than clusters of 5 or 6 ions.

It has been demonstrated that the movement of free ions and the relative movement of ions within pairs give rise to the largest part of the current in stable model systems. Both the concentration of pairs and the ionic conductivity reach a maximum at an ion charge of 0.3 e. In this context, a significant percentage of pairs must be regarded as loosely bound, and a dynamic equilibrium exists between ion pairs and free ions. In fact, this dynamic equilibrium exists among all the cluster species present in the system and, at these concentrations, cluster formation dynamics makes the Nernst–Einstein relation [Eq. (13)] invalid for ion charges greater than 0.1 e.

ACKNOWLEDGMENTS

This work was supported by the NSF/MRC through the Northwestern MRL, Grant No. DMR 9120571, and by the LBL Advanced Battery Project (No. 4594110). Supercomputer support was provided by the Pittsburgh Supercomputing Center, Grant No. DMR 910014P. M.F. and V.A.P. acknowledge a Fulbright Postdoctoral Fellowship and a NSF Graduate Fellowship, respectively.
