Electrostatic Interactions of a Neutral Dipolar Solute with a Fused Salt: A New Model for Solvation in Ionic Liquids[†]

Mark N. Kobrak*

Department of Chemistry, Brooklyn College and the Graduate Center of the City University of New York, 2900 Bedford Avenue, Brooklyn, New York 11210

Received: September 18, 2006; In Final Form: November 28, 2006

Ionic liquids represent a novel and poorly understood class of solvents, and one challenge in understanding these systems is how one should view the electrostatic character of solute−solvent interactions. The highly structured nature of a fused salt makes a dielectric continuum approximation difficult to implement, and there is no obvious connection between the structure of an individual ion and the polarization character of the medium. We address this problem by making the ansatz that rather than polarizing the medium, the solute may be viewed as intercalating in the charge distribution of the neat liquid such that the solvent screens the electric field of the solute. This approach allows derivation of an analytical expression for the distribution of solvent charge about the solute, and this distribution is found to be a close match to simulation data. The theory also predicts that the electrostatic character of solute−solvent interactions should be determined primarily by the number density of solvent ions, a prediction proven correct by analysis of existing experimental data. The approach represents a new model for the interpretation of solvation phenomena in ionic liquids.

I. Introduction

Ionic liquids are a class of salts that are molten at or near room temperature. Many different species are known,[1−3] and these systems offer great promise as solvents for chemical processing. In addition to useful physical properties such as low flammability and very low vapor pressures, ionic liquids have been found to be useful solvents for a wide range of organic and inorganic species. They show considerable promise as solvents for commercial chemical processing, and have even been hailed as environmentally benign ("green") solvents,[4] though this aspect is questionable for at least some species.[5]

Despite a substantial body of work exploring ionic liquids, the physics underlying their solvation behavior remain poorly understood. Existing theories of solvation thermodynamics in molecular liquids, commonly cast as descriptions of "solvent polarity", rely heavily on the concept of a molecular dipole moment to explain the connection between the structure of a solvent molecule and its operation as a solvent. However, an ion does not have a well-defined dipole moment,[6] and the use of the concept is inappropriate in the description of ionic liquids. The development of a theoretical description of molecular solute−ionic solvent interactions is therefore necessary if chemists are to explain the properties of a given ionic liquid as a solvent.

Experimental measurements of solvent polarity, including spectroscopic,[7−11] chromatographic,[12,13] and reactive[14,15] methods generally suggest ionic liquids possess a polarity comparable to that of moderately polar organic solvents such as short-chain alcohols. Measurements of the dielectric constant of ionic liquids, however, give values far lower than the dielectric constants associated with those liquids.[16,19] This suggests that while specific interactions such as hydrogen bonding appear comparable in molecular and ionic liquids, nonspecific elec-

trostatic interactions operate through a qualitatively different mechanism, leading to the discrepancy in measured dielectric values.

This discrepancy is perhaps unsurprising. Ionic liquids are conductive media and thus interact with applied electric fields in a qualitatively different way than do dielectric materials. Basic physics demands that an applied electric field should be screened at the surface of a conductor, retaining a constant electrostatic potential within the bulk. In the context of solvation, this would imply that the dipole moment of a molecule should be screened by solvent ions near the solute, as indeed is observed in previous simulations.[20] However, this contrasts with another expectation, that the dipole−ion forces characteristic of solute−solvent interactions should be weaker and shorter-ranged than the ion−ion forces associated with solvent−solvent interactions. This weakness would suggest that the presence of the solute dipole should not significantly disrupt the ordering of ions in the liquid. How, then, can one have screening of a solute without polarization of the liquid?

The answer to that question is the central goal of this paper. We begin by reviewing the basic electrostatics of solute−solvent interactions in ionic liquids and make the following ansatz: The solute intercalates in the ionic liquid in a way that does not significantly perturb the electrostatic structure of the neat liquid. Instead, the solute diffuses through configurations of the neat liquid that provide screening in the statistical limit. We present a mathematical expression describing the average distribution of charge about the solute and use simulation to show that it correctly describes the observed distribution. We use this model to make predictions about the nature of solute−solvent electrostatic interactions in ionic liquids and use existing experimental data to prove these predictions correct.

II. Theory

A. Classical Electrostatic Description of Solvation. The basic model for electrostatic interactions between a dipolar solute

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and a molecular solvent was laid out by Kirkwood and others in the first half of the twentieth century.[21,22] In its simplest form, the model is based on a spherical solute containing a point dipole interacting with a dielectric continuum; the energy of interaction can be calculated analytically for given values of the dielectric constant for the solute and solvent regions. Modern implicit solvation models such as the polarized continuum model[23] are far more sophisticated in that they include the effects of solute geometry and specific solute−solvent interactions, but they are ultimately extensions of this basic approach.

This model cannot be easily applied to ionic liquids. In principle, conductive media can be assigned a dielectric constant, though it must be complex-valued to account for conductivity.[24] However, molten salts are highly structured materials on molecular length scales, and one may expect any dielectric constant employed in such a model of solvation to be strongly dependent on the length scale of the applied electric field of the solute.

To see this, consider that the dielectric constant is defined by the relationship[25]

$$\frac{1}{\epsilon(k)} = \frac{\mathbf{k} \cdot \mathbf{E}(k)}{\mathbf{k} \cdot \mathbf{D}(k)} \tag{1}$$

where $\mathbf{E}(k)$ represents the applied electric field, $\mathbf{D}(k)$ is the electric displacement (field produced by the response of the medium), and k is the characteristic wavelength of the field. In the limit of a salt containing only one type of cation and anion, linear response theory gives[25]

$$\frac{1}{\epsilon(k)} = 1 - \frac{4\pi\rho e^2}{k^2 k_B T} S_{\alpha\alpha}(k) \tag{2}$$

where $S_{\alpha\alpha}(k)$ is a normalized form of the concentration−concentration structure factor. For the salt system described above, it is[25]

$$S_{\alpha\alpha}(k) = S_{++}(k) + S_{--}(k) - 2S_{+-}(k) \tag{3}$$

where $S_{++}(k)$, $S_{--}(k)$, and $S_{+-}(k)$ denote the cation−cation, anion−anion, and cation−anion structure factors, respectively.

This equation is not directly applicable to ionic liquids because it is restricted to nonpolarizable, monatomic ions but offers some qualitative insight. $S_{\alpha\alpha}$ may vary strongly with k for values on the order of ionic size and lattice spacing, implying that $\epsilon(k)$ is apt to be highly wavelength-dependent on molecular length scales. The wavelength dependence of $\epsilon(k)$ in molecular liquids is generally relatively weak, making it possible to use comparable values of the dielectric constant for experiments on macroscopic length scales (e.g., capacitance measurements),[26] spectroscopic measurements of the dielectric constant such as dielectric reflectance spectroscopy,[27] and spectroscopic studies of molecular probes that are indexed to the dielectric constant (e.g., Reichardt's betaine 30 scale[28] and Kamlet and Taft's linear free energy parametrization[29,30]). Results by Weingärtner and others[16−19] suggest that this is not the case for ionic liquids (ILs), however, as dielectric relaxation studies yield dielectric constants for ILs that are inconsistent with values inferred from solvatochromic[7−11] and chromatographic[12,13] experiments using molecular probes. Efforts to employ dielectric models to describe ionic liquid solvation dynamics have also been met with limited success,[31] though at least some of the problem in this case may arise from the limited availability of high frequency dielectric data. Nevertheless, the wavelength dependence of the dielectric

constant seems to be the most likely explanation for the discrepancies in the static dielectric phenomena.

B. Distribution of Solvent Charge Density in Solution. Setting aside the issue of the dielectric constant for the moment, let us consider the general physics of molecular solute−ionic solvent interactions. Given the strength of Coulomb interactions, the magnitude of the electrostatic interactions between solvent ions should be much larger than the dipole−ion forces characterizing solute−solvent interactions. This suggests that, rather than viewing the solute as polarizing the medium, we should assume that the presence of a dipolar solute represents a weak perturbation on the charge distribution of the neat liquid. While dispersive interactions will perturb nearby ions, electrostatic interactions with small molecular species will not significantly alter the distribution of charge in the liquid over a long distance.

However, this hypothesis conflicts with the basic physics of a conductive medium. Ionic liquids are conductors, and must therefore cancel an applied electric field at their surface (or near it, for systems composed of granular charge carriers). Screening of charged surfaces by molten salts is well-established in simulation,[32,33] and previous simulation results from this group[20] have shown that the net electrostatic interaction between a dipolar solute and an ionic medium is zero past the first two solvation shells. While dynamic fluctuations in solvent structure lead to significant long-range interactions on time scales of up to hundreds of picoseconds, long-time statistical averaging leads to cancellation of these interactions. Thus, the solute dipole is screened.

How can an unpolarized solvent screen the dipole? The answer is that we should not assert that the solvent polarizes in response to the dipole but rather assert that *the solute positions itself within the liquid so that the dipole is screened by the unperturbed charge density of the liquid.* The charge density of the ions in the solution remains nearly identical with that of the neat liquid, and the solute intercalates in configurations that screen its electric field.

Screening of ions in an ionic liquid is explained by Debye−Hückel theory, and the charge distribution about an ion in a concentrated electrolyte is known.[34] Any dipole can be modeled as a pair of opposite unit charges spaced at a distance, δ, to reproduce the magnitude of the dipole. We will refer to these sites as the foci of the dipole and make the following ansatz: The distribution of charge about a dipolar solute in an ionic liquid is equivalent to the sum of the charge distributions about oppositely charged point charges positioned at the foci of the dipole. Given this ansatz, we may use the Debye−Hückel treatment of charge distribution about ions in a concentrated electrolyte to predict the charge density about the foci.

The ansatz is justified by consideration of the nature of screening in a fused salt. Because the charge carriers in an ionic liquid are granular, charge density cannot be distributed continuously and screening can only be obtained in the statistical limit. In the case of ions, screening is achieved by the accretion of layers of charge density. Each ion is associated with a certain number of counterions, which diffuse about it in a spherical shell. In a concentrated electrolyte or fused salt, multiple layers of charge emerge, screening the charge in the thermodynamic limit.

For the purposes of developing the formalism for a dipolar solute, we take the view that the solute shuttles between two sets of configurations, one in which the positive focus occupies a cationic vacancy in the liquid and one in which the negative focus occupies an anionic vacancy. Screening is obtained in the statistical average over these configurations.

Solvation in Ionic Liquids

J. Phys. Chem. B, Vol. 111, No. 18, 2007 **4757**

Physically, the solute must occupy a large number of intermediate configurations, and the steric structure of the solute may prevent it from occupying sites that can clearly be labeled as either cationic or anionic vacancies. Nevertheless, if the ionic liquid is not polarized by the dipolar solute, it is reasonable to expect that the most important contributions to screening will arise from configurations "designed" to screen individual ions, and the charge distributions of intermediate configurations will cancel out on statistical averaging.

C. The Model. Here, we derive an analytical expression for the charge distribution about a dipole based on the ansatz above. In a concentrated electrolyte, the distribution of charge about an ion is often taken to have the following asymptotic form[34]

$$Q_v(r) = \frac{A}{r} \exp[-r/\lambda_d] \sin[2\pi r/d + \phi] \quad (4)$$

where r is the distance from the ion, d is the period of oscillations (i.e., the distance between like ions in the IL), ϕ is a phase factor, and λ_d is the Debye screening length of the liquid. Given the ansatz described above, our goal is to describe the solvent charge density about a dipolar solute as the sum of that about two oppositely charged ions, each possessing the charge distribution given in eq 4. We will assume a monovalent ionic liquid in the present study.

Consider a solute with a dipole moment of magnitude p. The dipole is approximated by a pair of opposite point charges (the foci) placed a distance, δ, apart, such that

$$p = e\delta \quad (5)$$

where e is the magnitude of a unit charge. For convenience, we orient the solute to the z-axis such that the positive focus resides at $(0,0,\delta/2)$ and the negative focus resides at $(0,0,-\delta/2)$. The distribution of charge about the dipole is then

$$Q_d(r_+,r_-) = \frac{A}{r_+} \exp\left[\frac{-r_+}{\lambda_d}\right] \sin\left[2\pi\frac{r_+}{d} + \phi_1\right] + \frac{A}{r_-} \exp\left[\frac{-r_-}{\lambda_d}\right] \sin\left[2\pi\frac{r_-}{d} + \phi_2\right] \quad (6)$$

where r_+ and r_- denote the distances to the positive and negative foci, respectively. Because the charges on the two sites have opposite signs, $\phi_1 - \phi_2 = L\pi$, where L is any positive or negative odd integer. We chose $L = 1$ for convenience and note that, with these conventions, A can be a negative number depending on the values of ϕ_1 and ϕ_2. We then write

$$Q_d(r_+,r_-) = \frac{A}{r_+} \exp\left[\frac{-r_+}{\lambda_d}\right] \sin\left[2\pi\frac{r_+}{d} + \phi_1\right] - \frac{A}{r_-} \exp\left[\frac{-r_-}{\lambda_d}\right] \sin\left[2\pi\frac{r_-}{d} + \phi_1\right] \quad (7)$$

Equation 7 lends itself naturally to ellipsoidal coordinates, in which the variables λ, μ, and θ are defined such that[35]

$$\lambda = \frac{r_+ + r_-}{\delta}$$

$$\mu = \frac{r_+ - r_-}{\delta} \quad (8)$$

The ellipsoid is defined by the position of two foci, representing the charged sites in the present application. λ represents the sum of the distances between the foci and the point of interest,

and μ represents the difference between the distances. If, as in the current definition, the foci lie along the z-axis, λ and μ describe the position in any half-plane containing the z-axis (e.g., $x = 0$, $y \geq 0$), and θ represents an angular variable for rotation about the z-axis. The coordinates are scaled by δ, the distance between the two points, so μ can be any value between -1 and 1 and λ can be any value between 1 and ∞.

In these coordinates, eq 7 may be rewritten

$$Q_d(\lambda,\mu) = A\left[\frac{1}{\frac{\delta}{2}(\lambda + \mu)} \exp\left[-\frac{\delta}{2\lambda_d}(\lambda + \mu)\right] \times \right.$$
$$\sin\left[\left(\frac{2\pi}{d}\frac{\delta}{2}(\lambda + \mu) + \phi_1\right)\right] - \frac{1}{\frac{\delta}{2}(\lambda - \mu)} \exp\left[-\frac{\delta}{2\lambda_d}(\lambda - \mu)\right] \times$$
$$\left. \sin\left[\left(\frac{2\pi}{d}\frac{\delta}{2}(\lambda - \mu) + \phi_1\right)\right] \right] \quad (9)$$

Considerable simplification in the form of eq 9 is possible. For brevity, we will make the substitutions $a_d = (\delta/2\lambda_d)$ and $c_d = (\pi\delta/d)$. We can also use the trigonometric identity $\sin(\alpha \pm \beta) = \sin(\alpha) \cos(\beta) \pm \cos(\alpha) \sin(\beta)$ to write

$$Q_d(\lambda,\mu) = \frac{A}{\frac{\delta}{2}(\lambda^2 - \mu^2)} \times [(\lambda - \mu) \times$$
$$\exp[-a_d(\lambda + \mu)](\sin(c_d\lambda + \phi_1) \cos(c_d\mu) + \cos(c_d\lambda + \phi_1) \times$$
$$\sin(c_d\mu)) - (\lambda + \mu) \exp[-a_d(\lambda - \mu)][\sin(c_d\lambda + \phi_1) \times$$
$$\cos(c_d\mu) - \cos(c_d\lambda + \phi_1) \sin(c_d\mu)] \quad (10)$$

Grouping terms of like trigonometric function and using the definitions of the hyperbolic trigonometric functions, this expression simplifies to

$$Q_d(\lambda,\mu) = \frac{2A \exp[-a_d\lambda]}{\frac{\delta}{2}(\lambda^2 - \mu^2)}[\sin(c_d\lambda + \phi_1) \cos(c_d\mu) \times$$
$$[-\lambda \sinh(a_d\mu) - \mu \cosh(a_d\mu)] + \cos(c_d\lambda + \phi_1) \sin(c_d\mu) \times$$
$$[\lambda \cosh(a_d\mu) + \mu \sinh(a_d\mu)]] \quad (11)$$

This represents the charge density about the solute predicted by the ansatz.

We will now test the validity of this hypothesis by conducting a simulation of a model salt system and examining the distribution of ions about a neutral, dipolar solute.

D. Simulation Results and Discussion. For simplicity, we will study a diatomic solute dissolved in a univalent salt composed of monatomic ions. We will use sodium chloride for the salt, making use of the Born–Huggins–Meyer potential as parametrized by Tosi and Fumi,[36] which is of the form

$$U(r_{ij}) = A \exp[-B(r_{ij} - \sigma)] - \frac{C}{r_{ij}^6} - \frac{D}{r_{ij}^8} + \frac{q_i q_j}{4\pi\epsilon r_{ij}} \quad (12)$$

The van der Waals parameters employed are reported in Table 1, and electrostatic interactions were treated in the Ewald summation.[37]

The solute is taken to be a diatomic molecule with two sites of unit charge separated by a distance of 1.00 Å. This creates an electrostatic dipole moment of 4.80 D, corresponding to a polar molecule but well within the range of known species. The two molecular sites were treated as separate atoms with

TABLE 1: Van der Waals Potential Energy Parameters Used in Simulation (Solute Sites Possess Equivalent Van der Waals Interactions and Are Denoted by the Letter X)

	A (kJ/mol)	B (Å^{-1})	σ (Å)	C (kJ/mol)	D (kJ/mol)
Na$^+$−Na$^+$	0.2544	3.1545	2.340	1.0117	0.48177
Na$^+$−Cl$^-$	0.2035	3.1545	2.755	6.7448	8.3708
Cl$^-$−Cl$^-$	0.1527	3.1545	3.170	69.857	140.32
Na$^+$−X	0.2035	3.1545	2.755	6.7448	8.3708
Cl$^-$−X	0.1527	3.1545	3.170	69.857	140.32

van der Waals parameters equal to those of a chloride ion (see Table 1).

Molecular dynamics simulations were performed using the DL_POLY molecular dynamics suite.[38] Simulations were carried out in the NPT ensemble maintained using a Nóse−Hoover thermobarostat, with a temperature time constant of 2.0 ps and a pressure time constant of 0.5, as defined in eq 2.192 of the DL_POLY 2 User Manual.[38] The temperature and pressure were 2000 K and 1 atm, respectively.

Two sets of simulations were performed, one of the neat liquid and one of a solution containing the dipolar solute. The neat liquid consisted of 1000 ion pairs equilibrated for 20 ps, followed by data collection over 50 ps. The solution consisted of one solute molecule in combination with 999 ion pairs, simulated in the same NPT ensemble. Equilibration was accomplished in 20 ps, and a total of 600 ps of data accumulation were acquired from five separate trajectories. The longer acquisition phase was mandated by the existence of only a single solute, which yielded less data per time step and thus required additional sampling for statistical convergence. Convergence in the reported parameters with respect to trajectory length was confirmed.

The first issue to consider is the accuracy of eq 4 in describing the distribution of charge density in a neat liquid. Figure 1 shows the charge density about a chloride ion, as calculated from simulation. As expected, van der Waals interactions set a minimum distance for association of the ions, which is not accounted for in eq 4. We modify this using the Heaviside function, $\Theta(x)$,

$$\Theta(x) = 0 \qquad x < 0$$
$$= 1 \qquad x \geq 0 \qquad (13)$$

The fitted function becomes

$$Q_v(r) = \Theta(r - r_0)\frac{A}{r}\exp[-r/\lambda_d]\sin[2\pi r/d + \phi] \quad (14)$$

The parameters for this fit are given in Table 2, and a graphical comparison to simulation data is presented in Figure 1. Even when the van der Waals repulsion is crudely accounted for, as in eq 14, short-ranged interactions perturb the distribution, making the fit imperfect. This problem is reflected in an underestimation of the value of d, as evidenced by the fact that the oscillations of the fitted form are out of phase with the simulation data at long range. However, the functional form certainly reproduces the correct qualitative features. We may therefore be satisfied that if a fit of eq 11 describes the distribution of charge about the dipole at a comparable accuracy to that observed in Figure 1, our ansatz concerning the distribution of charge about the dipole is valid to a useful degree.

The simulation data must be converted to a distribution in the form of eq 11 by integration of the ion distribution about the solute axis. We will describe this transformation in Cartesian coordinates and take the plane represented by eq 14 to lie in
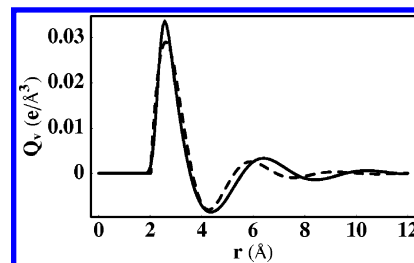

Figure 1. Charge density distribution about a chloride ion: solid, simulation data; dashed, fit to simulation data according to eq 14.
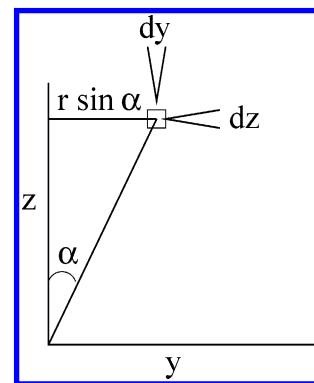

Figure 2. Projection of charge into the $y-z$ plane via rotation about the z-axis, as described in the text.

the positive y region of the $y-z$ plane, as shown in Figure 2. The simulation data are projected into the $y-z$ plane via integration in a cylinder about the z-axis. Each area unit, dy dz, thus corresponds to a ring-shaped volume element, d$v(y,z) = 2\pi r \sin \alpha$ dy dz, where $r = \sqrt{y^2+z^2}$. The charge density is then taken to be

$$F(y,z) = \frac{(N_+(y,z) - N_-(y,z))}{\mathrm{d}v(y,z)} \qquad (15)$$

where $N_+(y,z)$ and $N_-(y,z)$ correspond to the number of positive and negative ions observed in the given area element, respectively.

The resulting distribution is shown in Figure 3A. As one would expect, the distributions of charge are strongly peaked near the molecular axis, where the distance from an ion to the oppositely charged focus is minimized and that to the like-charged focus is maximized. As one rotates through the plane at constant r, the magnitude of the charge density decreases until $\alpha = 90°$, where interaction with the oppositely charged sites cancels the net Coulombic interaction. The distribution clearly shows alternating layers of opposite charge as the distance to a given focus increases; note that these layers are 180° out of phase for the two foci, as one would expect on the basis of their opposite charges.

To test the model, the simulation data were fit to the form of eq 11. We account for dispersive interactions by rewriting eq 11

$$Q_d(\lambda,\mu) = \Theta(r(\lambda,\mu) - r_0)\frac{2A\exp[-a_d\lambda]}{\frac{\delta}{2}(\lambda^2 - \mu^2)}[\sin(c_d\lambda + \phi_1) \times$$
$$\cos(c_d\mu)[-\lambda\sinh(a_d\mu) - \mu\cosh(a_d\mu)] +$$
$$\cos(c_d\lambda + \phi_1)\sin(c_d\mu)[\lambda\cosh(a_d\mu) + \mu\sinh(a_d\mu)]] \quad (16)$$

Solvation in Ionic Liquids

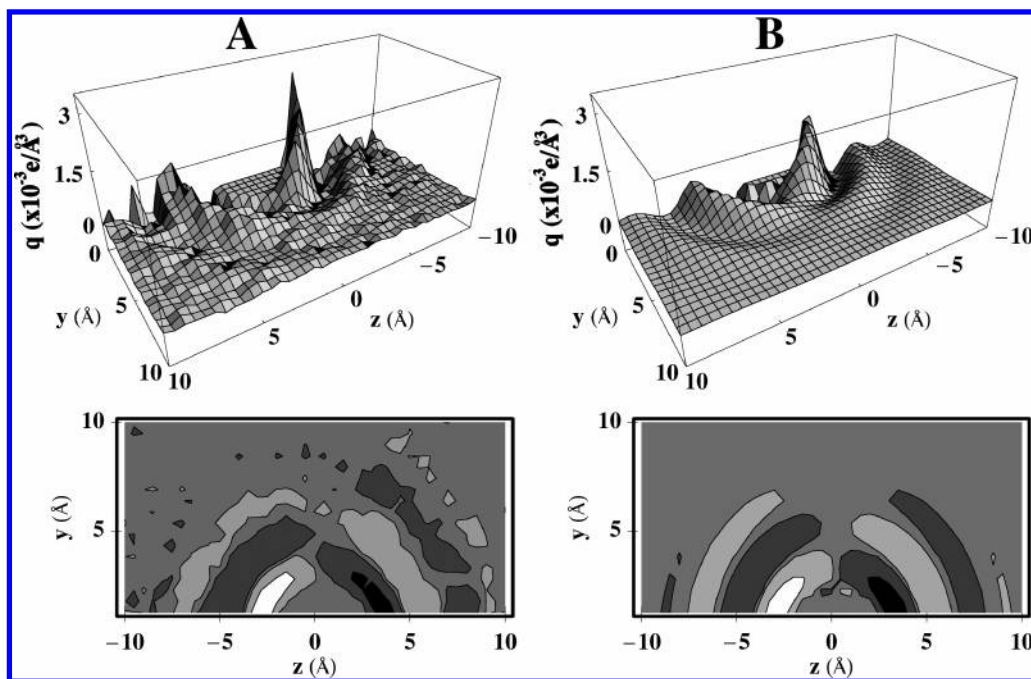*J. Phys. Chem. B, Vol. 111, No. 18, 2007* **4759**

Figure 3. Charge density distribution about the dipolar solute, presented in both three-dimensional and contour forms: column A, simulation data; column B, fit to simulation data according to eq 16. The contours are the same in both figures, and their scale is logarithmic.

TABLE 2: Parameters for eq 14 (Ionic Case) and eq 16 (Molecular Case), Fitted to Simulation Data (Brackets Indicate Confidence Intervals; Uncertainty in r_0 Was Negligible)

	A (e/Å^2)	λ_d (Å)	d (Å)	ϕ (rad)	r_0 (Å)
ionic	0.302 {0.241,0.363}	2.02 {1.78,2.33}	3.25 {3.17,3.34}	2.39 {2.26,2.53}	2.03
molecular	0.011 {0.010,0.11}	3.27 {3.10,3.44}	3.76 {3.74,3.79}	0.15 {0.10, 0.19}	2.17

where r is the distance from the solute center, midway between the two sites (making it a nontrivial function of λ and μ). This spherical form will be somewhat inaccurate, both because of the nonspherical nature of the solute and the asymmetry in the sizes of sodium and chloride ions, but is acceptable in the present qualitative study.

With regard to the fitting of the data, the process of integration about the molecular axis implies a higher degree of statistical accuracy for points falling further from the molecular axis (where integration yields higher total populations). Therefore, the fitting procedure excluded all points within 1.25 Å of the molecular axis to reduce statistical noise.

The fitted function and the data obtained from simulation are shown in Figure 3B. Except for the region near the z-axis, where statistical noise is greatest, the distributions are strikingly similar. The similarity holds even at relatively short range where steric and dispersive interactions would be expected to disrupt the liquid structure in a manner more complicated than the simple inclusion of $\Theta(x)$. Thus, we can be confident that the ansatz presented in section 2.3 captures the essential physics of the situation.

Additional confirmation can be obtained by examination of the fitted function. Values of the parameters obtained by fitting eq 16 and their confidence intervals are presented in Table 2. We compare these parameters with those obtained for the distribution of charge about a solvent ion according to the Debye–Hückel equation, reported in eq 14. Most of the fitted parameters depend on both the character of the solvent and the solute, and differences between the solute in the two cases make comparison moot. The values of r_0 and ϕ_1 fall in this category. However, d is a function purely of the solvent, and its value should not vary between the molecular and ionic cases. The values reported in Table 2 are indeed very close together, and

their discrepancy may arise from error in the fit of the charge distribution about the ion shown in Figure 1 rather than any error introduced by the ansatz. Thus, we obtain further evidence that our ansatz concerning the distribution of charge about the solute is correct.

The A and λ_d terms do vary significantly between the two cases, however, and their comparison is informative. In the ionic case, λ_d represents the Debye screening length, which is the distance required by the solvent to screen the potential produced by one of its own ions. The fact that the dipolar solute possesses a longer Debye length implies that the dipole is less efficiently screened by the solvent than is an ion. This is acceptable, in that the ansatz requires only that the form of the charge distribution about each focus match the Debye–Hückel distribution, and not that the parameters match exactly. Indeed, the idea that the solute must shuttle between solute configurations to achieve screening implies that the mechanism of screening should be less efficient in the molecular case, consistent with a longer Debye screening length. In a similar vein, the fact that the value of A is more than an order of magnitude smaller for the molecular solute indicates that the distribution of charge is less sharply peaked, consistent with the idea that the solvent is sampling a wide range of configurations, many of which cancel out on average. The overall picture is thus one of weak and inefficient screening, consistent with the idea that the solvent is not polarized.

III. Electrostatic Energy

A. Solute–Solvent Interactions. Having ascertained that the distribution given in eq 4 is at least qualitatively correct, it is desirable to use this equation to estimate the charge–dipole interaction energy between a solute and the medium. The most

obvious approach is to calculate the energy of interaction between the solute foci and the charge distribution, given by

$$E_{\text{dip}} = \frac{q}{4\pi\epsilon} \int_1^\infty d\lambda \int_{-1}^1 d\mu \int_0^{2\pi} d\theta (\delta/2)^3 (\lambda^2 - \mu^2) \times$$

$$Q_{\text{d}}(\lambda, \mu) \frac{(\delta/2)[(\lambda - \mu) - (\lambda + \mu)]}{(\delta/2)^2 (\lambda^2 - \mu^2)}$$

$$= -\frac{q}{4\pi\epsilon} \frac{\delta^2}{2} \int_1^\infty d\lambda \int_{-1}^1 d\mu \int_0^{2\pi} d\theta \, \mu Q_{\text{d}}(\lambda, \mu). \tag{17}$$

Note that in ellipsoidal coordinates, the volume element is given by $dv = d\lambda \, d\mu \, d\theta \, (\delta/2)^3 (\lambda^2 - \mu^2)$, and we have used the coordinate transformations given in eq 8. However, integration over θ and μ yields an expression that is singular for $\lambda = 1$, corresponding to the line segment containing the solute sites. This singularity arises from the existence of finite charge density on those sites, and despite the fact that the volume element converges to zero at the foci, the formalism breaks down in this limit. Possible solutions include the imposition of a finite size on the solute, excluding charge density from this region. While this could be easily achieved by setting a lower limit on the integration of λ, the variable λ depends on δ. Imposing such a limit therefore mandates that the geometry of the solute be determined by its dipole moment, an unphysical restriction, and other solvent geometries are complicated to implement. Alternative approaches to the interaction energy, such as the positioning of a point dipole at the origin, are also not readily soluble.

Even without an analytical solution to eq 17, one can gain important insight on the nature of the solute−solvent interaction energy. At this level of approximation, the energy of interaction depends exclusively on the parameters A, ϕ_1, d, and λ_{d}. ϕ_1 will be determined primarily by local interactions about the solute, so it is the other parameters that determine charge−dipole interactions. The value of d represents the distance between ions of like type in the liquid, and thus, it has an algebraic relationship with the number density of the liquid. The value of λ_{d}, the Debye screening length, is a more subtle property. In an electrolyte composed of monovalent ions of a single salt (i.e., ions of only two types are present in solution), λ_{d} is given by[34]

$$\lambda_{\text{d}} = \sqrt{\frac{k_{\text{B}}T}{8\pi\rho q^2}} \tag{18}$$

where ρ denotes the number density and q is the magnitude of the unit charge. At higher concentrations, the screening length becomes dependent on the ionic radius in a nontrivial way.[34] However, both this ionic radius and the value of λ_{d} given in eq 18 will be correlated strongly with the solvent number density. Thus, both d and λ_{d} are expected to vary strongly with ρ.

The parameter A represents a magnitude of charge density fluctuations. Viewed as the charge density about a solvent ion, as indicated in eq 4, it contains information about the competition between thermal energy and ion−ion interactions. One would expect a highly disordered ionic fluid to have a relatively small value of A while those for which ion association was strongest to have very large values of A (the value of λ_{d} in either case notwithstanding). Since Coulomb interactions dominate ion−ion interactions, the value of A is apt to be correlated with inter-ion distances and thus depend on liquid density.

Thus, all of the parameters relevant to the calculation of dipole−solvent interaction are expected to depend on solvent

number density. However, eq 17 contains no information about the electrostatic structure of an individual ion. That is, the theory includes the total charge on each ion but does not at this level incorporate any other electrostatic property specific to a given ion. This is markedly different than the case of molecular liquids, where knowledge of the dielectric constant (and, vide infra, the molecular dipole) is essential to calculations of energy. This has an important consequence: According to this theory, two ionic liquids possessing the same number density and ionic valence must have identical dipole−solvent interaction energies. The model obviously neglects the possibility of specific interactions and geometric constraints, which may be significant. However, if it is true that Coulomb interactions are the dominant force in ionic liquids, the variation of electrostatic solvation energy and number density should be clear from experimental data. An examination of such data is presented in the next section.

B. Experimental Measurement of Solute−Solvent Electrostatic Interaction. We now explore the relationship between solvent number density and electrostatic solute−solvent interaction energy using experimental data. Because of the k dependence of the dielectric constant outlined in section 2.1, we must use a molecular probe to access the relevant length scale. The linear free energy relationship developed by Kamlet and Taft[29,30] is based on the solvatochromic shift of a series of dye molecules, and includes a measure of the electrostatic component of the solute−solvent interaction energy. In this model, the wavelength, ν, corresponding to the absorbance maximum of a series of dyes is modeled according to the equation

$$\nu = \nu_0 + a\alpha + b\beta + s\pi^* \tag{19}$$

where s, a, and b are susceptibilities of a given dye and α, β, and π^* correspond to solvent parameters describing hydrogen-bond acidity, hydrogen-bond basicity, and electrostatic polarization energy, respectively. The use of solvatochromic probe molecules in this way represents an electrostatic probe of a suitable length scale, and π^* is taken to be proportional to the electrostatic component of the solute−solvent interaction energy.

Values of π^* and the number densities of 16 ionic liquids are given in Table 3. We were not selective in our choice of data and used all systems for which both densities and π^* were available based on a compilation given in ref 39. The reported π^* values are compiled from a number of different studies, not all of which made use of the same spectroscopic probes. The number densities were calculated from reported mass densities. Values for the density at 25 °C were used where available, though in a few cases values at 22 and 20 °C were employed where the 25 °C densities were not available (temperatures at which π^* was measured were not always reported). The error introduced in these discrepancies is sufficiently small that it should not affect our conclusions. Further, no attempt was made to evaluate the quality or possible error associated with specific studies, and issues such as the purity (including water content) of the liquid were not considered. This issue does create the potential for error in the data.

The resultant data are shown graphically in Figure 4, and it is clear that π^* increases with number density for ILs. Statistical analysis of the covariance indicates a greater than 99.5% confidence that the variables are indeed correlated.[40]

As in any statistical study, the possibility that a sample is biased must be considered. We were not selective in our use of data from ref 39 and made use of every data point for which a π^* value and mass density were reported. The study is remarkably comprehensive, and there is no reason to assume

Solvation in Ionic Liquids

J. Phys. Chem. B, Vol. 111, No. 18, 2007 **4761**

TABLE 3: π^* vs Number Density for a Set of Ionic Liquids (These Data Were Assembled on the Basis of Citations Given in ref 39)[a]

liquid	ρ (mol/L)	π^*
BMIM BF$_4^-$	4.63[45]	1.05[7]
BMIM Cl$^-$	6.18[45]	1.17[2]
BMIM SbF$_6^-$	4.53[46]	1.04[7]
BMIM Tf	4.47[46]	1.01[7]
OMIM Cl$^-$	4.28[45]	1.09[2]
OMIM PF$_6^-$	3.60[2]	0.88[2]
P14 NTf$_2$	2.52[46]	0.95[7]
N2HHH NO$_3^-$	11.20[47]	1.24[48]
N3333 CHES	2.86[48]	1.00[48]
N3HHH NO$_3^-$	9.47[48]	1.17[48]
N33HH SCN$^-$	6.01[49]	1.16[49]
N4HHH SCN$^-$	7.18[49]	1.23[49]
N4444 BES	2.46[48]	1.07[48]
N4444 CHES	2.39[48]	1.01[48]
N4444 MOPSO	2.35[48]	1.07[48]
N5555 CHES	2.05[48]	1.00[48]

[a] Key: *Cations*: BMIM = 1-butyl-3-methylimidazolium; OMIM = 1-octyl-3-methylimidazolium; P14 = 1-butyl-1-methylpyrrolidinium; N*ijkl* denotes an alkylammonium species with *n*-alkyl substituents of lengths *i*, *j*, *k*, and *l*, respectively. An "H" denotes a hydrogen substituent. *Anions*: Tf = trifluoromethylsulfonate; NTf$_2$ = bis(trifluoromethylsulfonyl)imide; CHES = 2-(cyclohexylamino)ethanesulfonate; BES = 2-[bis(2-hydroxyethyl)amino]ethanesulfonate; MOPSO = 2-hydroxy-4-morpholinopropanesulfonate.
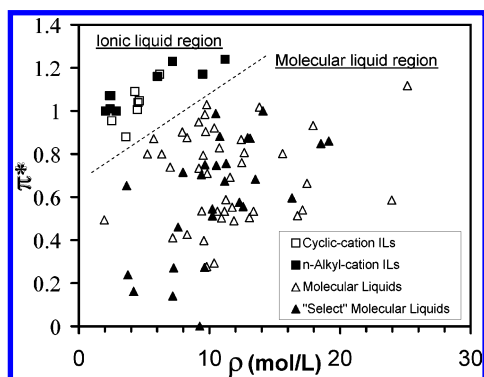

Figure 4. π^* vs number density for ionic and molecular liquids. Liquids composed of cyclic (imidazolium- and pyrrolidinium-based) cations and acyclic (ammonium-based) cations are distinguished to show the consistency of the observed trend. See text for additional discussion. Water (55.38 mol/L, 1.09) was excluded from the figure to maintain a wider scale on the features of interest.

any bias on the part of those authors in their compilation of data from literature sources. There is some possibility that the collection of the requisite data by researchers in the field is in some way biased toward a particular set of ionic liquids, though there is no reason to expect that either the value of π^* or the liquid density should correlate strongly with a variable relevant to a researcher's choice of species for study. The study includes only monovalent species, but as we have not considered polyvalency in the previous sections of this paper, that does not pose a problem for the exploration of the theory. A more serious issue is that certain classes of ionic liquids, such as phosphonium and pyridinium species, are not included in the sample set. However, imidazolium, alkylammonium, and pyrrolidinium species (albeit only a single example of the last) are represented in combination with a great variety of anions, offering a wide range of structures and capacities for specific interaction. Further, the imidazolium, pyrrolidinium, and alkylammonium species follow roughly the same trend, illustrating that the character of ions is of secondary importance to the

charge density. This is consistent with the hypothesis concerning solute−solvent interactions developed in this paper.

To see the significance of the correlation between π^* and the number density, we provide analogous data on molecular liquids. Our data are taken from Kamlet, Abboud, and Taft,[29,30] who report values of π^* for 71 known molecular solvents, represented by the set of open and closed triangles in Figure 4. The liquids, reported in refs 29 and 30, span a wide range of classes of organic molecules. The results show a high degree of scatter, but covariance tests indicate a statistical correlation between π^* and the number density that is better than 99.5%. This is unsurprising, as the polarizability of a molecular medium should depend both on the strength of molecular dipoles and on their number density, creating a correlation.

Nevertheless, it is clear from Figure 4 that the dependence of π^* on the number density is far weaker in molecular liquids than it is in ionic liquids. We may explore this question more fully by identifying a group of "select" liquids for which hydrogen bonding is negligible, and any trend in π^* versus ρ cannot be obscured by specific interactions. Abboud, Kamlet, and Taft[30] assembled exactly such a set of 29 solvents and demonstrated a clear correlation between the molecular dipole moment and π^* within this group. We have indicated this group with closed triangles in Figure 4. We observe that the scatter in the variation of π^* versus ρ is similar in degree to that of the general population, though covariance tests affirm a relationship at a similarly high level of certainty.

Note that no selection process was applied to ionic liquids, and the samples included are known to display a wide range of inter-ion specific interactions. The robustness of the trend in π^* versus number density for ionic liquids can only be due to the magnitude of inter-ion Coulomb interactions, which make hydrogen-bonding and steric interactions less important than they are in molecular liquids. It is also interesting to note that the region of Figure 4 in which ionic liquids are found is entirely different than that corresponding to molecular media, consistent with the idea that a fundamentally different mechanism governs electrostatic interactions in the two types of media. Thus, we both confirm our prediction that solute−solvent interaction energies are controlled by charge density and infer that the electrostatic structure of an ionic liquid is not significantly perturbed by either specific solvent−solvent interactions or specific solute−solvent interactions.

IV. Conclusions

We have presented a model for solute−solvent electrostatic interactions in ionic liquids. The model yields screening of the solute electric field without polarization of the medium, resolving an apparent contradiction between the weakness of solute−solvent interactions and the behavior of a conductive system. The results can be summarized by two observations:

(1) The electrostatic structure of an individual ion does not significantly affect the electrostatic energy of solute−solvent interactions, nor does its steric structure or capacity for specific interactions.

(2) The electrostatic energy of solute−solvent interactions is determined primarily by the number (charge) density of ions in the solvent.

Many issues remain to be considered. While the success of the theory in explaining Figure 4 indicates it is fundamentally correct, it must be explored in simulations of realistic systems to gain further insight. Likewise, there is also the need to consider polyvalent and mixed valency salts. Finally, other simulations have demonstrated both the existence of spatial

inhomogeneities in ionic liquids[41,42] and electrostriction about polar solutes.[43] Both of these phenomena may require extension of the model presented here.

The present theory offers a prediction that we have not yet been able to test: The value of π^* should vary with temperature according to the thermal expansivity of the liquid. The robust relationship shown in Figure 4 suggests that as the liquid expands or contracts, π^* should remain on the same trendline as the other liquids. This is qualitatively different than the trend expected in molecular liquids, where the increasing rotational averaging of solvent dipoles with increasing temperature leads to a decrease in electrostatic interactions that does not correlate with liquid density in a simple way.[44] While we realize it may be a considerable effort, we respectfully request that experimental researchers consider investigating the variation of π^* with temperature and density for an ionic liquid as a means of exploring this idea.

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