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ABSTRACT
Some examples of the use of Molecular Dynamics Simulation to study solutions of small molecules in ionic liquids are discussed. It is shown that electrostatic forces, while not the dominant solute-solvent interaction, determine the local solute environment. The solubility of aromatics and the changes in the spectra of low frequency intermolecular vibrations in two related ionic liquids (one dicationic and one monocationic) are compared with experimental results and related to the local environment.

KEYWORDS
ionic liquids, atomistic simulation, solvation

1. Introduction

I have been using atomistic computer simulation with the method of Molecular Dynamics since the 1980s to study the behaviour of various materials at the molecular level. In recent years my main interest has been in ionic liquids including their local structure and their properties as solvents as well as their behaviour at surfaces. Ionic Liquids are essentially molten salts which are liquid at or near room temperature. Unlike molten sodium chloride, they have bulky organic cations (or anions) and dispersion interactions are relatively more important than electrostatics compared to molten sodium chloride. Examples include alkyl ammonium and phosphonium salts, but my work has used imidazolium salts. Figure 1 shows an example, the butyl methyl imidazolium cation, often abbreviated as [bmim]$^+$ or [C$_4$C$_1$im]$^+$.

![Figure 1. The [bmim]$^+$ cation](image)

In order to perform a molecular dynamics simulation it is necessary to specify the temperature (or energy) and density (or pressure) and to supply an intermolecular potential. The
choice of the latter is always a compromise between accuracy and speed and the best choice may depend on the system and properties being simulated. For example many characteristics of simple liquids can be found using hard sphere or Lennard-Jones potentials, but for ionic liquids we expect the inclusion of both charges and molecular shapes to be important. Most simulations of ionic liquids have been made using models with charges distributed on different atomic sites and spherical non-electrostatic interactions between sites (often Lennard-Jones in form) [1, 2]. Sometimes united atom representations have been used for methyl or methylene groups. [1, 3]. One might anticipate that polarisability is also an important aspect of ionic liquids. Polarisability significantly increases the cost, but is increasingly being included in ionic liquid simulations [4–8].

2. Ionic liquids as solvents

In many applications ionic liquids are used as solvents for chemical reactions [9, 10], or in electrochemistry [11]. Atomistic simulations give information about the local environment of solute molecules in such solutions. I shall discuss two examples. The first example is benzene and other aromatic compounds. The second is CS$_2$, a small polarisable molecule whose lowest moment is a quadrupole moment.

2.1. Aromatic compounds in Ionic Liquids

One puzzle in the early 2000s was why aromatic compounds were, in general, more soluble in ionic liquids than aliphatic compounds. In order to investigate this phenomenon we performed two sets of investigations. In one set we measured the change in free energy between solutions of benzene and a hypothetical uncharged benzene (a proxy for an aliphatic compound). Although benzene has no charge or dipole moment, it does have a significant quadrupole moment [12]. This can be modelled by charges of $\frac{1}{2}e$ on the carbon and $\frac{1}{2}e$ on the hydrogen atomic sites in addition to Buckingham potentials between sites in different molecules [13]. The required change in chemical potential of the solute is found by thermodynamic integration to be

$$
\mu_q - \mu_0 = \int_0^{q=0.15} < \frac{\partial H}{\partial q} > dq
$$

(1)

where

$$
< \frac{\partial H}{\partial q} > = < \frac{U^C}{q} > /q
$$

(2)

and $< U^C >_q$ is the average electrostatic part of the benzene-solvent interaction energy when the charge on the benzene C sites is q. We found [14] that the chemical potential difference between charged and uncharged C$_6$H$_6$ is $-22 \pm 2$kJ/mol in [dmim][Cl] (dimethylimidazolium chloride) and $-12 \pm 2$kJ/mole in [dmim][PF$_6$] at 400K. At this temperature the value of kT is approximately 3.6kJ/mol. We concluded that the stabilisation of aromatic compounds in ionic liquids is primarily due to electrostatic interactions. This is confirmed by examining the local structure around the dissolved molecules, C$_6$H$_6$, 1,3,5-C$_6$H$_3$F$_3$, and C$_6$F$_6$ which have quadrupole moments equal to -2.9, 0.32 and +3.2 in units of $10^{-39}$Cm$^2$.

Figure 2 shows the local environments of the benzene and uncharged benzene solutes in solution in [dmim][Cl]. The uncharged benzene-like molecule has very little charge localisation in its vicinity compared to quadrupolar benzene. In the latter case the cation density above and below the aromatic ring compared to that in the bulk is greatly increased (note that the contours are expressed as ratios of the local concentration to the bulk concentration). The distribution around benzene shows a negative charge density due to anions around the plane of the molecule near the positively charged hydrogen sites. Examination of the energetics shows
that the benzene-cation interaction energy is actually increased (less favourable) on charging the molecule, although the benzene-anion energy decreases. The high concentration of cations above and below the benzene ring is due to the cation-anion interactions in the liquid. One can think of it as the benzene increasing the concentration of anions in the plane of the ring which then hold the cations above and below the rings. Cation-anion interactions are important to the properties of ionic liquids as solvents. Although there is much less layering above and below the uncharged benzene, the shape of the neutral molecule influences the local structure in the liquid.

2.2. \( \text{CS}_2 \)

Like the work on aromatic solutes, my more recent work on \( \text{CS}_2 \) arose from discussions with an experimental scientist. Professor Quitevis has been using RIKES spectroscopy (Optical Kerr Effect) for many years to investigate the motion in liquids and in the last ten years he has been particularly interested in ionic liquids [15–19]. He asked whether I would do some simulations of solutions of \( \text{CS}_2 \) in various ionic liquids to complement his experiments. In order to model a solution of \( \text{CS}_2 \) in an ionic liquid it was first necessary to have a good model for its electrostatic field. The sulfur atom in a \( \text{CS} \) bond is anisotropic. In a local site-based model point charges are insufficient and both local dipoles and, in particular, local quadrupoles are necessary [20]. As our molecular dyanamics programs are designed for site charges rather than site multipoles, Anthony Stone developed a model with auxiliary charges on sites on each side of the S atom, along the molecular axis. Figure 3 shows the electrostatic field around a \( \text{CS}_2 \) molecule (left) and the difference between this and two point charge models (centre and right). The centre figure shows the result from the best model with charges on the three sites, while the right hand figure shows the improvement obtained by adding additional charges on either side of the S sites making a 7-site model [21]. However this is a case where the polarisability may be important and site polarisabilities were calculated with Misquitta and Stone’s CamCASP program [22]. A good representation of the polarisability was found to be an axial polarisability on the C atom, \( \alpha_{zz}^C = 7.77 \text{Å}^3 \), and isotropic polarisabilities on each of the S sites, \( \alpha^S = 2.62 \text{Å}^3 \).

We compared simulations with each of the three models, an uncharged model [23], the model with 7 site charges and the same short range intermolecular force field, and the model with 7 site charges and polarisability. In all three cases the interaction energy of \( \text{CS}_2 \) with the surroundings in a dilute solution in [dmin][NTf₂] was dominated by the (negative) Lennard-Jones energy. The electrostatic energy was more negative for the polarisable model than for the 7 site model, but still only one fifth of the total interaction energy. Figure 4, shows the local concentrations of \( \text{CS}_2 \) around the cations for three models, namely uncharged (top), charged-unpolarised (middle) and charged-polarisable (bottom). There is very little localisation of the solvent around the uncharged model. The charged and charged polarisable models both show very similar distributions, showing that electrostatics is important in determining the local structure around a solute molecule, but this degree of polarisability has little effect on the local

Figure 2. Average difference in cation and anion concentration in planes perpendicular to the rings for benzene (left) and uncharged benzene (right) dissolved in [dmin][Cl]. The symmetry axes of the molecules are vertical in these figures. Figure reproduced from reference [14].
One advantage of a polarisable model is that it provides a method of probing the local electric fields in the liquid. The j'th component of the induced dipole $\mu_j$ at a site is proportional to the field component $E_i$ at that site as

$$E_i = \frac{\mu_j}{\alpha_{ji}}$$

where $\alpha_{ji}$ is the $j,i$ component of the site polarisability tensor.

In our polarisable model of CS$_2$ the S polarisability is isotropic and the C polarisability is axial. Due to symmetry the average electric field must be zero at each site, although there are fluctuations in its value. In the [dmim][NTf$_2$] and [bmim][NTF$_2$] solutions we found that the root mean square (rms) value of the field components at each site was 0.13 pm$0.02$ V/Å perpendicular to the axis and 0.24±0.02 V/Å along the axis [21]. The fields tend to be largest along the molecular axes. As expected the rms electric field components are smaller by a factor of four or so in neat CS$_2$.

### 2.3. RIKES spectroscopy

RIKES spectroscopy explores the intermolecular motion in liquids through the spectrum of fluctuations in the anisotropic polarisability of the sample. It is complementary to dielectric spectroscopy which measures the spectrum of fluctuations in the dipole moment of the sample; both spectroscopies probe intermolecular motion in the liquid. CS$_2$ is a small molecule with a large anisotropic susceptibility and, in solution, is particularly useful as a probe for the local environment of a solvent [24]. Although it is possible to obtain the RIKES spectra from simulations [25], it is expensive as a large matrix must be diagonalised at each step and, being a collective property rather than a molecular property the simulation must be run for $\sqrt{N}$ times as long to obtain the same signal to noise ratio as for a single molecule property. Here $N$ is the number of molecules in the molecular dynamics cell. However the low frequency molecular vibrational density of states provides another measure of intermolecular motion, and is cheaper to calculate being a single molecule property. Although we would not expect quantitative agreement between the vibrational density of states and the experimental RIKES spectra, we can expect that the effects of changes in the environment would be similar and that the simulation could help give a molecular explanation of these changes.

An example of the of the sort of comparisons that can be made is our recent work comparing the RIKES spectra and the librational density of states of CS$_2$ solutions in the related dication and monocation liquids [C$_8$(C$_1$im)$_2$][NTf$_2$] and [C$_4$C$_1$im][NTf$_2$]. Figure 5 shows the [C$_8$(C$_1$im)$_2$] cation; the monocation is formed by cutting the C$_8$ alkyl linker in half.

Figure 6 shows the spectra of solutions in these two liquids at various CS$_2$ concentrations. One sees that the peak in the RIKES spectrum is higher in frequency in the corresponding
Figure 4. Regions of high concentration of CS$_2$ molecules near a cation in [dmin][NTf2] solutions. Top: uncharged CS$_2$ (cutoff=1.2 bulk concentration); middle: non-polarisable, charged CS$_2$ (cutoff=1.5 bulk concentration); bottom: polarisable, charged CS$_2$ (cutoff=1.3 bulk concentration). Parts of figure taken from reference [21].
Figure 5. The dication \([C_4(C_1\text{im})_2]^+\) in a linear conformation. Methylene and methyl hydrogens are not shown. The monocation \([C_4C_1\text{im}]^+\) is made by breaking the central bond in the alkyl chain and replacing the free methylene groups by methyl groups.

Figure 6. RIKES spectra of CS\(_2\) solutions in a monocationic ionic liquid (left) and the corresponding dicationic liquid (right). The frequency scale on the x axis is in cm\(^{-1}\).

dication solution than in the monocation solution, and it is found that the first moments increase. When the molecule is cut and the liquid equilibrated at constant volume the pressure increases. We found that in this case the peak frequency and first moment of both the librational and translational densities of states of CS\(_2\) increase. This is in contrast to the experimental finding. However it was found that the spectra of the CS\(_2\) densities of states were sensitive to pressure as is shown in figure 7. On reducing the pressure to ambient the free volume increased and the peak frequency and first moments of the vibrational densities of states moved to lower values in agreement with experiment.

Examining the radial distribution functions shows that, on reducing the pressure, CS\(_2\) is likely to be slightly further on average from both cations and anions, especially from the anions. This supports the idea that the change is mainly due to an increase in the local free volume which allows the molecules more freedom of motion.

3. Conclusions

In these two examples of simulations of ionic liquid solutions I hope to have shown that simulation can inform experimental findings. Although electrostatics is not always the dominant interaction in ionic liquid solutions, it plays an essential role. The greater solubility of aromatics compared to aliphatics depends on solute-solvent electrostatic interactions, and the charge distribution and subsequent quadrupole of aromatic rings is the main cause of this difference. However the cation-anion interactions in the solvent also have an important secondary effect on the local structure in the liquid around the solute. The low frequency librational spectrum of CS\(_2\) differs in dication and monocation solutions mainly because of increased confinement in the former. This change can be correlated with changes in the RIKES spectra.

In order to study liquids and solutions one should consider computer simulation, spec-
troscopy and thermodynamic measurements as complementary. Each technique can inform the others.

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References