

PREDICTION OF DENSITIES OF IMIDAZOLIUM BASED IONIC LIQUIDS USING MOLECULAR SIMULATION

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Abstract

Ionic liquids have recently emerged as effective and desirable alternative solvents. Their use is greatly favored because they are green solvents due to their low vapor pressure, non-flammability and chemical stability. A great variety of ionic liquids is potentially available and thus the design of task-specific ionic liquids is gaining importance. Solvent design and pre-screening of candidates by molecular modeling tools is an attractive way of streamlining this development. In this work, the density of some imidazolium based ionic liquids is investigated using commercially available software tools. It was found that the density of some imidazolium based ionic liquids can be calculated with satisfactory accuracy for a number of anions; however, further development of force field parameters is needed to study some other common ionic liquids.

I. Introduction

Ionic liquids are environmentally-friendly solvents representing a novel medium to perform well-established reactions or to develop new ones. Their structure is comprised entirely of ions and their melting points are below the boiling point of water. Favorable properties include non-volatility, non-flammability, chemical stability, and often thermal stability as well. One

of the greatest advantages of ionic liquids is their remarkable versatility: with different combinations of cations and anions, approximately 10^{18} different ionic liquids are possible [1]. In spite of the growing interest in this area, only a few ionic liquids have been characterized even by such basic properties as density, conductivity, melting point, and so on. Interactions with other substances, including inorganic, polar and non-polar organic and polymeric compounds can be finely tuned by selecting the proper cation–anion pair. The potential ability to engineer task-specific ionic liquids with pre-determined physical and chemical properties offers attractive prospects to facilitate the development of novel green chemical processes.

Computational chemistry has been successfully used to pre-screen candidate compounds, especially in the pharmaceutical industry. In-silico simulations of sufficient predictive accuracy could greatly aid the molecular design of task specific ionic liquids by reducing the number of experiments to be carried out by eliminating unsuitable candidate compounds. In this work, exploratory simulations are presented for the densities of imidazolium-based ionic liquids with varying alkyl chain length and for three different anions since density can be a technologically important property for example in drilling fluids or phase separation.

Computer simulations of ionic liquids have been reported in increasing numbers during the past few years. Some of the modeling work have been focused on the development of force field parameters, specific to an ionic liquid or an ionic liquid family [2]-[8]. Structural, dynamical, electric and thermodynamic properties of several pure ionic liquids have been simulated [9]-[11] using these force field tools. More recently, an ab initio molecular dynamics study has also been published [12], pushing the capabilities of computational chemistry to its current limits.

II. Computational methods

Since ionic liquids carry explicit charges on both the cationic and anionic components, the partial charges assigned to the individual atoms in the force field simulations strongly affect the quality of the calculations. In the current studies, the atomic charges were determined from density functional calculations in order to achieve good accuracy. The details of the protocol

followed will be published elsewhere [13].

Model systems for bulk ionic liquids were constructed as amorphous three dimensional periodic boxes using the Amorphous Cell Tools in Materials Studio by Accelrys. In order to build proper model systems, the density of the bulk phase must be determined. Room temperature densities were calculated here from simulation studies and tested against experimental data where available. The simulation cells, containing 10 cations and 10 anions, were equilibrated first using velocity scaling in a 20 ps molecular dynamics run using the NPT ensemble (keeping the particle number, pressure and temperature controlled while relaxing the cell parameters). This was followed by a 100 ps molecular dynamics production run to obtain the average density using the Berendsen barostat and the Andersen thermostat. At least five simulations were performed in order to obtain statistical averages and standard deviations. All simulations were executed at 298K (room temperature conditions). As a test case, a larger amorphous box containing 50 cations and 50 anions was also created and the same protocol was followed. Results were not significantly different from the smaller box simulations so all results reported here were obtained with those for the sake of efficiency.

III. Results

In order to assess the applicability of the commercial software packages that are available for this application, the Compass force field was chosen as currently implemented in the Discover molecular simulation engine in Materials Studio 4.0. To test the accuracy of densities calculated in atomistic simulations, benchmark calculations were performed for a few experimentally well-characterized organic solvents with some structural similarity to the imidazolium cation. The results of those simulations (which followed the protocol described above) are presented in Table 1.

The close agreement between the computed and experimental density values shown in the table demonstrates that this simple model can predict densities of neutral solvents with very good accuracy and reproducibility using a relatively small number of molecules.

Results for some ionic liquids containing the 1-R,3-methylimidazolium

	D_{cal} (g/cm ³)	s (g/cm ³)	D_{exp} (g/cm ³)
pyridine	0.972	0.0017	0.982
alanine	1.022	0.0043	1.022
methyl imidazole	1.022	0.0016	1.036

Table 1: Calculated (D_{cal}) and experimental (D_{exp})[14] densities of some organic solvents along with the standard deviation (s) of the calculations

cation are presented in Table 2 with available experimental and other calculated values.

It can be seen from the table that the calculated densities are in good agreement with the experimental values where they are available. Accuracy is better for the bulkier anions than for the chloride counterion although trends are correctly reproduced for the chloride systems as well.

The density decreases with increasing alkyl chain length for the bulky anions CF_3COO^- and PF_6^- , while it changes to a much lesser extent for the Cl^- anion. Similar behavior was observed experimentally for the bulky $(CF_3SO_2)_2N$ anion by Tokuda et al. [18] using the same family of cations. The selection of the anion appears to be even more significant: densities can be engineered in the 0.9-1.5 g/cm³ range even with this very limited selection.

IV. Discussion

Calculated room temperature densities of the imidazolium based ionic liquids considered here were in good agreement with experimental values. Both absolute values and general trends were correctly reproduced when cations and anions were changed systematically. Based on these results, the commercially available Compass force field implemented in Materials Studio can be used in simulations to predict densities of ionic liquids. However, partial charges on atoms must be determined at a higher level of theory, such as our choice to use density functional calculations to obtain electrostatic potential derived atomic charges. It must be noted that some other commercially used anions such as larger halogens and polyvalent sulfur con-

Cation	Anion	D^a (g/cm ³)	s^a (g/cm ³)	D (g/cm ³)
[emim]	Cl ⁻	0.9523	0.0097	1.12 ^b
	CF ₃ COO ⁻	1.2985	0.0104	-
	PF ₆ ⁻	1.4812	0.0085	1.45 ^b , 1.54 ^c
[bmim]	Cl ⁻	0.9205	0.0058	1.05 ^b , 1.08 ^c
	CF ₃ COO ⁻	1.2414	0.0030	1.22 ^e
	PF ₆ ⁻	1.3795	0.0035	1.34 ^b , 1.36 ^d
[C ₆ mim]	Cl ⁻	0.9067	0.0077	1.00 ^b , 1.03 ^c
	CF ₃ COO ⁻	1.1734	0.0030	-
	PF ₆ ⁻	1.2847	0.0027	1.027 ^b , 1.36 ^d

a: this work

b: Reference 7 (calculated)

c: Reference 15 (experimental)

d: Reference 16 (experimental)

e: Reference 17 (experimental)

Table 2: Calculated densities and standard deviation of densities of ionic liquids comprised of the 1-R-3-methylimidazolium cations (R-ethyl, butyl, and hexyl) and different anions along with available experimental and other calculated values

taining anions currently could not be included in the simulations with this software package due to the incompleteness of the set of the necessary force field parameters.

V. Conclusions

It was found in these studies that the commercially available Compass force field as implemented in Materials Studio by Accelrys is capable of accurately predicting the room temperature densities of imidazolium based ionic liquids. However, further development in the force field parameters will be needed in order to be able to simulate a wider range of ionic liquids and to resolve some discrepancies for anions such as PF₆⁻.

The slow relaxation of ionic liquids in molecular dynamics runs makes this area especially challenging for atomistic simulations. Time scales could

possibly be extended by changing to coarse grain simulations at the meso-scale. However, the derivation of the necessary interaction parameters for that level of simulations will require further atomistic level studies. Future work in this area may include an effort to develop those parameters, as well as extending the current studies for higher temperatures and three component systems as well as other ionic liquid families.

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