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## **Molecular Simulation**

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### **Molecular modelling simulations to predict density and solubility parameters of ionic liquids**

Bela Derecskei<sup>a</sup>; Agnes Derecskei-Kovacs<sup>a</sup>

<sup>a</sup> Millennium Inorganic Chemicals, A Cristal Company, Research Center, Baltimore, USA

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## Molecular modelling simulations to predict density and solubility parameters of ionic liquids

Bela Derecskei\* and Agnes Derecskei-Kovacs

Millennium Inorganic Chemicals, A Cristal Company, Research Center, Baltimore, USA

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Molecular modelling simulations are one of the most convenient tools to predict solvent properties of ionic liquids, which are otherwise difficult to predict or measure by experimental means. Ionic liquids have emerged as effective and desirable alternative solvents during the last decade. Their use is greatly favoured because of their ‘green’ characteristics: low vapour pressure, non-flammability and chemical stability. An enormous variety of ionic liquids are potentially available and thus the design of task-specific ionic liquids is gaining importance. Traditional solvents are often evaluated based on their multi-component solubility parameters to assess their compatibility with different solutes. The analogous parameter values for ionic liquids are also useful, though their availability is often limited. Consequently, solvent design and pre-screening of candidates by molecular modelling tools are attractive alternatives. In this work, the density and two-component solubility parameter of a variety of ionic liquids were investigated using atomistic level molecular modelling and the commercially available Materials Studio<sup>®</sup> software package. The ionic liquids chosen consisted of ethyl, butyl and hexyl imidazolium cations in conjunction with four anions ( $\text{Cl}^-$ ,  $[(\text{CN})_2\text{N}]^-$ ,  $[\text{CF}_3\text{CO}_2]^-$  and  $[\text{Tf}_2\text{N}]^-$ ). The goal was to develop appropriate computational protocols and carry out calculations, which are able to predict densities and two-component solubility parameters for these ionic liquids, as well as to evaluate the usefulness and accuracy of the currently available commercial molecular modelling software for these applications. It was found that the density of ionic liquids comprised of all possible combinations of these cations and anions could be calculated with satisfactory accuracy with the exception of systems containing the  $\text{Cl}^-$  anion. A Hess cycle-based protocol was developed to correct cohesive energy densities and solubility parameters as calculated in Materials Studio to take into account ion pair interactions to successfully reproduce the experimental results. It was found that both the cation and the anion of the ionic liquid had a strong impact on the components of the solubility parameter.

**Keywords:** ionic liquids; solubility parameters; molecular simulation

### 1. 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. Favourable 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, they can generate an astronomical number of different ionic liquids [1]. In spite of the growing interest in this area, only a few ionic liquids have been characterised 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 predetermined physical and chemical properties is an attractive prospect for facilitating 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, reducing the number of experiments to be carried out by eliminating unsuitable candidate compounds.

Mutual compatibility between a solute and a pool of candidate solvents is an important scientific and commercial issue and it is largely determined by the individual components. The basic idea of ‘like dissolves like’ was quantified through the introduction of the Hildebrand solubility parameter and further refined by Hansen [2] who introduced the multi-component solubility parameters. In previous work [3], we used the commercially available Materials Studio<sup>®</sup> program package to calculate the solubility parameters for some cellulose derivatives in an ongoing effort to study the compatibility of some ionic liquids with these commercially important raw materials. In the current work, results of exploratory simulations are presented for the densities and two-component solubility

\*Corresponding author. Email: bela.derecskei@cristalglobal.com

parameters of imidazolium-based ionic liquids with varying alkyl chain length and for four different anions. Density can be a technologically important property, for example, in drilling fluids or phase separation, while the dispersive and electrostatic contributions to the solubility parameter are useful when assessing the compatibility of solvents with different solutes.

Computer simulations of ionic liquids have been reported in increasing numbers during the past few years. Some of the modelling work has been focused on the development of force field parameters, specific to an ionic liquid or an ionic liquid family [4–10]. Structural, dynamical, electric and thermodynamic properties of several pure ionic liquids have been simulated [10–12] using these force field tools and the solvation of small solutes in ionic liquids has also been investigated [13–18]. More recently, *ab initio* molecular dynamics studies have also been published [19], pushing the capabilities of computational chemistry to its current limits.

## 2. 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 (see the Appendix for an illustration). In this work, atomic charges were determined from density functional theory calculations in order to achieve good accuracy. First, all species were constructed using the Builder module in Materials Studio 4.2 by Accelrys and a +1 or –1 overall charge was assigned to the ionic species. Full geometry optimisations were performed using the gradient-corrected density functional PW91, in conjunction with a polarised double numeric basis set in the all-electron approximation using Dmol<sup>3</sup> in Materials Studio [20]. Electrostatic potential-derived charges were then calculated and assigned to all atoms. The charges were kept unchanged during the subsequent molecular dynamics simulations.

Model systems for bulk ionic liquids were constructed as amorphous three-dimensional periodic boxes using the Amorphous Cell Tool in Materials Studio. In order to build proper model systems, the density of the bulk phase must be specified. Since room temperature densities are not presently available for all of the ionic liquids considered here, values were determined via simulation for all of the systems and compared against the available data. The simulation cells contained 20 cations and 20 anions. They were equilibrated first in a 100 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 for mean density using the Berendsen barostat and the Andersen thermostat. Electrostatic and van der Waals terms were

determined by the Ewald summation method at the 0.001 kcal/mol accuracy using a 6 Å cut-off value and 0.5 Å buffer width. (Additional details about how the model was built are given in the Appendix.) Three to five amorphous boxes were created and simulated in order to obtain statistical averages and to determine the overall SDs. All simulations were run at 298 K.

The cohesive energy is the amount of internal energy per mole of a substance in the condensed state arising from all of the intermolecular interactions that hold the substance together. A related quantity, the cohesive energy density (the cohesive energy divided by the molar volume of the material) is commonly used in the computation of the energy of mixing. The solubility parameter is the square root of the cohesive energy density. Since both dispersion and electrostatic forces contribute to the interaction energies, the solubility parameter will also have dispersive and electrostatic components. These (and hydrogen bonding contributions) are frequently used to quickly assess the compatibility of solvents and solutes: similar solubility parameter components imply good compatibility (for a more detailed evaluation, see, for example, [21]). In the simulation of cohesive energy densities and solubility parameters, three to five amorphous boxes were constructed at the average of the previously calculated densities. After a 100 ps long equilibration run, 100 ps NVT molecular dynamics simulations were performed, sampling the conformer space with 1 ps frequency. The resulting trajectories were then used in the cohesive energy density and solubility parameter calculations. The calculation as performed in Materials Studio was designed for molecular solvents and the results must be corrected to reflect that ionic liquids will evaporate in the form of neutral ion pairs. The interaction energy of the gas phase ion pair had to be applied as a correction factor to the total solubility parameter as well as its components based on the Hess principle. The interaction energies were calculated at the optimal gas phase ion pair geometry (determined at the PW91/DNP level) using the same force field as the molecular dynamics simulations.

## 3. Results and discussion

### 3.1 Density functional level characterisation of the 1-*R*-3-methylimidazolium, *R* = ethyl, butyl and hexyl [RMIM] ions

Figure 1(a)–(c) shows the electrostatic potential field around the 1-ethyl-3-methylimidazolium [EMIM], 1-butyl-3-methylimidazolium [BMIM] and 1-hexyl-3-methylimidazolium [C<sub>6</sub>MIM] cations as a result of density functional calculations described above.

It can be seen from the sequence of structures that the charge density above the five-membered ring decreases as the chain length of the alkyl substituent increases. This change in the electrostatic properties coupled with the

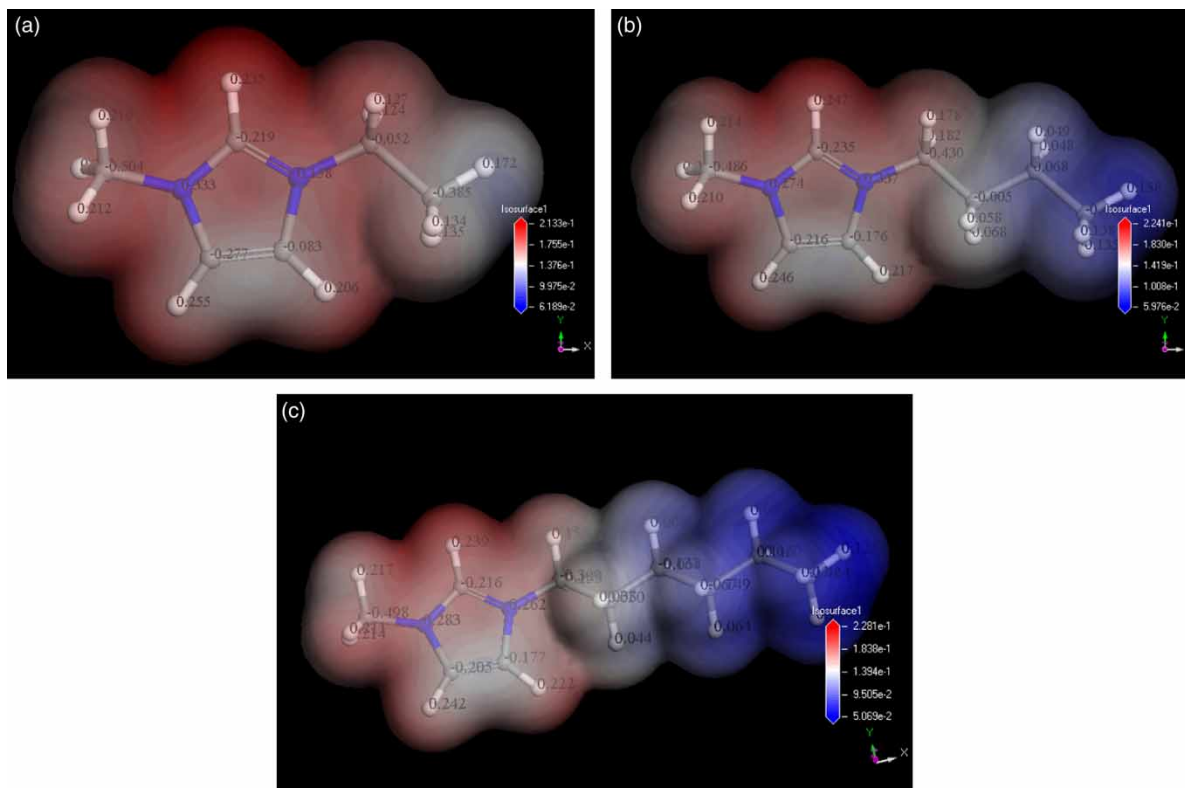


Figure 1. Electrostatic potential field around various cations as calculated at the PW91/DNP level. (a) EMIM, (b) BMIM, (c) C<sub>6</sub>MIM.

change in the steric nature of the cation will alter many of the physicochemical properties of related ionic liquids, including viscosity, melting point, density, conductivity and so on [22]. Point charges derived from the electrostatic potential depicted above were assigned to the cations. The anions were treated in a similar manner and these charges were used for the subsequent molecular dynamics simulations.

### 3.2 Densities

#### 3.2.1 Method validation using traditional solvents

In order to assess the applicability of the modules in Materials Studio 4.2, which are relevant for this application, the COMPASS force field [23] was chosen as currently implemented in the Forcite molecular simulation engine. To test the accuracy of densities calculated in these atomistic simulations, benchmark calculations were performed for some experimentally well-characterised traditional solvents either with some structural similarity to the imidazolium cation (pyridine, methylimidazole) or for some specifically selected value of the solubility parameter components as will be shown later (CS<sub>2</sub>, formamide). The results of the simulations (which used 20 solvent molecules and followed the protocol described above) are presented in Table 1.

The very good agreement between the computed and experimental density values shown in the table demonstrates that this simple model can predict densities of traditional solvents with good accuracy (<3%) using a relatively small number of molecules. As shown in the Appendix, using larger number of molecules in the simulation reduces the SD of the calculations but does not affect the average calculated density.

#### 3.2.2 Calculated densities of ionic liquids

Results for ionic liquids containing the 1-R,3-methylimidazolium cation (R = ethyl, butyl and hexyl) and some common anions such as chloride, trifluoroacetate, dicyanamide and bis(trifluoromethylsulfonyl)imide are

Table 1. Calculated ( $D_{\text{cal}}$ ) and experimental  $D_{\text{exp}}$  [24] densities of some organic solvents along with the SD ( $\sigma$ ) of calculations.

	$D_{\text{cal}}$ (g/cm <sup>3</sup> )	$\sigma$ (g/cm <sup>3</sup> )	$D_{\text{exp}}$ (g/cm <sup>3</sup> )
Pyridine	0.978	0.022	0.982
Carbon disulphide	1.313	0.035	1.313
Benzyl alcohol	1.037	0.019	1.05
Formamide	1.166	0.029	1.134
Methylimidazole	1.031	0.024	1.036

Table 2. Calculated densities and SD of densities of ionic liquids comprised of the RMIM cations (R-ethyl, butyl, and hexyl) and the chloride, trifluoroacetate, dicyanamide and bis(trifluoromethylsulphonyl)imide anions along with available experimental and other calculated values.

Cation	Anion	$D^a$ (g/cm <sup>3</sup> )	$\sigma^a$ (g/cm <sup>3</sup> )	$D$ (g/cm <sup>3</sup> )
[EMIM]	Cl <sup>-</sup>	0.961	0.012	1.12 <sup>b</sup>
	[CF <sub>3</sub> CO <sub>2</sub> ] <sup>-</sup>	1.336	0.017	–
	[(CN) <sub>2</sub> N] <sup>-</sup>	1.095	0.010	–
	[Tf <sub>2</sub> N] <sup>-</sup>	1.520	0.022	1.519 <sup>c</sup>
[BMIM]	Cl <sup>-</sup>	0.919	0.012	1.05 <sup>b</sup> , 1.08 <sup>d</sup>
	[CF <sub>3</sub> CO <sub>2</sub> ] <sup>-</sup>	1.233	0.015	1.22 <sup>e</sup>
	[(CN) <sub>2</sub> N] <sup>-</sup>	1.051	0.010	1.058 <sup>f</sup>
	[Tf <sub>2</sub> N] <sup>-</sup>	1.436	0.0185	1.436 <sup>c</sup>
[C <sub>6</sub> MIM]	Cl <sup>-</sup>	0.910	0.011	1.00 <sup>b</sup> , 1.03 <sup>d</sup>
	[CF <sub>3</sub> CO <sub>2</sub> ] <sup>-</sup>	1.175	0.013	–
	[(CN) <sub>2</sub> N] <sup>-</sup>	1.020	0.010	–
	[Tf <sub>2</sub> N] <sup>-</sup>	1.400	0.0189	1.373 <sup>c</sup>

<sup>a</sup>This work. <sup>b</sup>[9] (calculated). <sup>c</sup>[25] (experimental). <sup>d</sup>[http://ildb.merck.de/ionicliquids/ASP/IonicLiquidsRead\\_PrintDetails.asp](http://ildb.merck.de/ionicliquids/ASP/IonicLiquidsRead_PrintDetails.asp) (experimental). <sup>e</sup>[26] (experimental). <sup>f</sup>[27] (experimental).

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

Table 2 shows that the calculated densities are in very good agreement with the experimental values where those are available with the exception of all systems containing the chloride ion. The larger errors in density (> 10%) for Cl<sup>-</sup> cases most likely indicate that this implementation of COMPASS is not appropriate for the simulation of this family of ionic liquids<sup>1</sup>. It is expected, however, that all other calculated values are reasonable estimates for the room temperature densities of ionic liquids that are yet to be characterised experimentally (or with unpublished density measurements).

These results are shown graphically in Figure 2 in order to observe the trends introduced by changing the

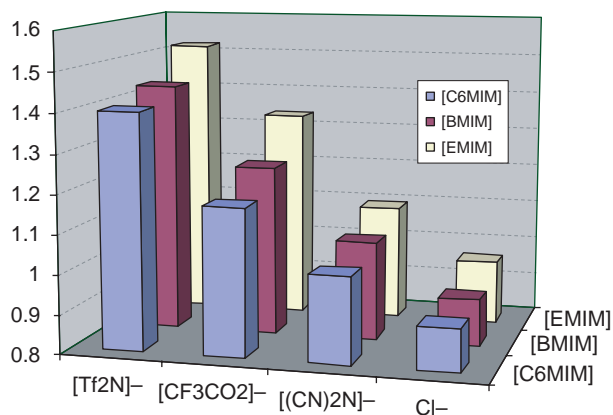


Figure 2. Cation and anion effects on the calculated room temperature density of some imidazolium-based ionic liquids.

anions and systematically increasing the side chain length in the [RMIM] cation.

Figure 2 shows that the density decreases with increasing alkyl chain length, and the extent of the change increases with the size of the anion. Similar behaviour was observed experimentally by Tokuda et al. [22] using the same family of cations. The selection of the anion appears to be even more significant: densities can be engineered to span the range of 0.9–1.5 g/cm<sup>3</sup> even with this very limited selection.

### 3.3 Cohesive energy densities and solubility parameters of ionic liquids

#### 3.3.1 Method validation using organic solvents

In order to assess the compatibility of solvent and solute, it is often necessary to examine the various contributions to the solubility parameter rather than the net value. Experimental tables often list at least three components: van der Waals (dispersive), Coulombic and H-bonding (the last two may be considered as electrostatic components). Since most commercial force fields do not contain a separate term for H-bonding, calculations yield a van der Waals,  $\delta_{vdw}$ , and an electrostatic,  $\delta_{ES}$ , component. For the sake of direct comparison with experiment, we calculated an equivalent electrostatic term from the Coulomb and H-bonding values using the formula:

$$\delta_{ES} = (\delta_C^2 + \delta_H^2)^{1/2},$$

where  $\delta_C$  and  $\delta_H$  are the Coulombic and H-bonding components of the solubility parameter, respectively.

Table 3 contains our calculated values along with the experimental data for some molecular solvents (at the experimental densities).

Pyridine and methylimidazole were chosen for the validation calculations because they exhibit some structural similarity to the imidazolium cation, present in the ionic liquids under investigation. Carbon disulphide was chosen as a limiting case since it has a negligible electrostatic component, while formamide was chosen because it has both large dispersive and electrostatic

Table 3. Calculated (Calc.) and experimental [21] (Exp.) values of the different components of the solubility parameter of some molecular solvents.

	$\delta_{vdw}$		$\delta_{ES}$		$\delta_C$	$\delta_H$
	Calc.	Exp.	Calc.	Exp.	Exp.	Exp.
Pyridine	19.3	19.0	8.9	10.6	8.8	5.9
Carbon disulphide	20.3	20.5	3.8	0.6	0.0	0.6
Benzyl alcohol	18.8	18.4	16.4	15.1	6.3	13.7
Formamide	20.9	17.2	29.3	32.4	26.2	19.0
Methylimidazole	19.3	19.7	19.3	19.2	15.6	11.2



components. Benzyl alcohol exhibits an average behaviour.

It can be observed from Table 3 that the dispersive components were reproduced well with these simulations. Formamide had the largest deviation from the experiment. The electrostatic components had larger deviations, in general, with carbon disulphide exhibiting the worst agreement. However, the trend of the polar components was reproduced correctly. Simulated components of the solubility parameter for methylimidazole (which is structurally the closest to the cation component of the ionic liquids of interest) were the closest to the experimental values.

### 3.3.2 Solubility parameters of ionic liquids

The solubility parameters (total as well as the van der Waals and electrostatic components) for the family of ionic liquids studied are summarised in Table 4 (chloride-containing ionic liquids were omitted due to reasons explained above).

Experimental data were found only for the total solubility parameter of the  $[\text{Tf}_2\text{N}]^-$  series [26]. The Hildebrand solubility parameters as determined from intrinsic viscosity measurements in [26] are listed along with our calculated total solubility parameter values in Table 5.

Table 5 shows a good agreement between the calculated and experimental values. In addition to the total value determined experimentally, one can also analyse the contribution of the dispersive and electrostatic components as presented in Table 4. For all anions, the change in the dispersive component is moderate as the carbon chain length increases. Almost all variation in the total solubility parameter is due to the changes in the polar component, which decreases with increasing carbon chain length (which is most likely related to the trends in the charge density depicted in Figure 1). By contrast, the nature of the anion has an impact on both the dispersive and polar components. With these few anions, the

Table 4. Calculated solubility parameters of ionic liquids (components as well as total) comprised of the RMIM cation (a: R-ethyl, b: R = butyl and c: R = hexyl) and three different anions.

Cation	Anion	$\delta_{\text{vdW}}$	$\delta_{\text{ES}}$	$\delta_{\text{total}}$
[EMIM]	$[\text{CF}_3\text{CO}_2]^-$	25.3	24.6	34.9
	$[(\text{CN})_2\text{N}]^-$	23.7	20.8	35.1
	$[\text{Tf}_2\text{N}]^-$	21.9	17.8	28.9
[BMIM]	$[\text{CF}_3\text{CO}_2]^-$	23.8	21.3	31.6
	$[(\text{CN})_2\text{N}]^-$	24.2	20.4	34.0
	$[\text{Tf}_2\text{N}]^-$	21.1	16.0	26.1
[C <sub>6</sub> MIM]	$[\text{CF}_3\text{CO}_2]^-$	23.7	19.7	30.5
	$[(\text{CN})_2\text{N}]^-$	23.4	18.4	32.2
	$[\text{Tf}_2\text{N}]^-$	21.2	12.7	25.5

Table 5. The comparison of calculated and experimental values of the solubility parameter for some ionic liquids containing the imidazolium cation and the  $[\text{Tf}_2\text{N}]^-$  anion.

Cation	Anion	$\delta_{\text{total,Calc.}}^{\text{a}}$	$\delta_{\text{total,Exp.}}^{\text{b}}$
[EMIM]	$[\text{Tf}_2\text{N}]^-$	28.9	27.6
[BMIM]	$[\text{Tf}_2\text{N}]^-$	26.1	26.7
[C <sub>6</sub> MIM]	$[\text{Tf}_2\text{N}]^-$	25.5	25.6

<sup>a</sup> This work. <sup>b</sup> [26].

dispersive components can be engineered to be in between 21 and 25 and the polar components can be selected in the range of 13–25.

## 4. Conclusions

Calculated room temperature densities of the imidazolium-based ionic liquids considered here were in good agreement with experimental values for a variety of anions but were poor for ionic liquids containing the chloride ion. Both the experimental values and the general trends were correctly reproduced when cations and anions were changed systematically. Based on these results, the commercially available COMPASS force field as 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 and assign electrostatic potential-derived atomic charges. It must be noted that some other anions that are present in commercially available ionic liquids (such as larger halogens and polyvalent sulphur- and phosphorous-containing anions) currently may not be included in simulations with this software package due to the incompleteness of the set of the necessary force field parameters.

The COMPASS force field was found to be able to predict the components of the solubility parameter for some traditional solvents and the total solubility parameter for the few ionic liquids where they were available from experimental studies. The cation selection affected mainly the electrostatic component while the anion selection had an impact on both the dispersive and electrostatic contributions. Future experimental studies are necessary to check the validity of these findings and many more ionic liquid families will have to be studied experimentally and in simulation studies to be able to select the proper solvent purely on the basis of the components of the solubility parameter.

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## Note

1. The underlying reason, most likely, is the inability of the force field to predict interaction energies between the cations and the chloride ion in a satisfactory fashion. In spite of seeing this discrepancy when comparing cation–anion interaction energies at the DFT and force field levels, we still attempted to carry out the simulations due to the frequent applications of chloride-containing ionic liquids. Unfortunately, after the density simulations, we had to give up this effort until some development in further releases of the software.

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## Appendix: Factors affecting the outcomes of the simulations

### 1. The effect of the system size

In order to test the sensitivity of the calculated densities to the size of the model unit cell, we created sets of five amorphous cells consisting of 10, 20 and 30 ion pairs each, using [BMIM][CN]<sub>2</sub>N as a test case. After following the protocol described earlier, the density data were evaluated using the Minitab 15 statistical program package. Results of the basic statistical analysis are shown in Figure 3(a)–(c).

Visual inspection of the distributions shows that the density data distribution is normal for all three cases. The SD becomes smaller with increasing system size. The mean density varies only moderately with the size of the simulation box: the smallest box (10 ion pairs) yielded a statistically different mean density (1.0906 g/cm<sup>3</sup>) than the two larger boxes (1.0951 and 1.0952 g/cm<sup>3</sup>), which were found to be statistically the same. The boxplot visualisation of the data set (see figure 4) illustrates this finding. It must be pointed out that even the density of the smallest simulation box is well within the range of technical grade (but not analytical grade) compounds, commonly used in most industries. Increasing the system size from 20 ion pairs to 30 did not introduce a significant improvement of the results; consequently, 20 ion pair amorphous boxes were used in all simulations described in this work to save computational time during the simulations without losing computational accuracy.

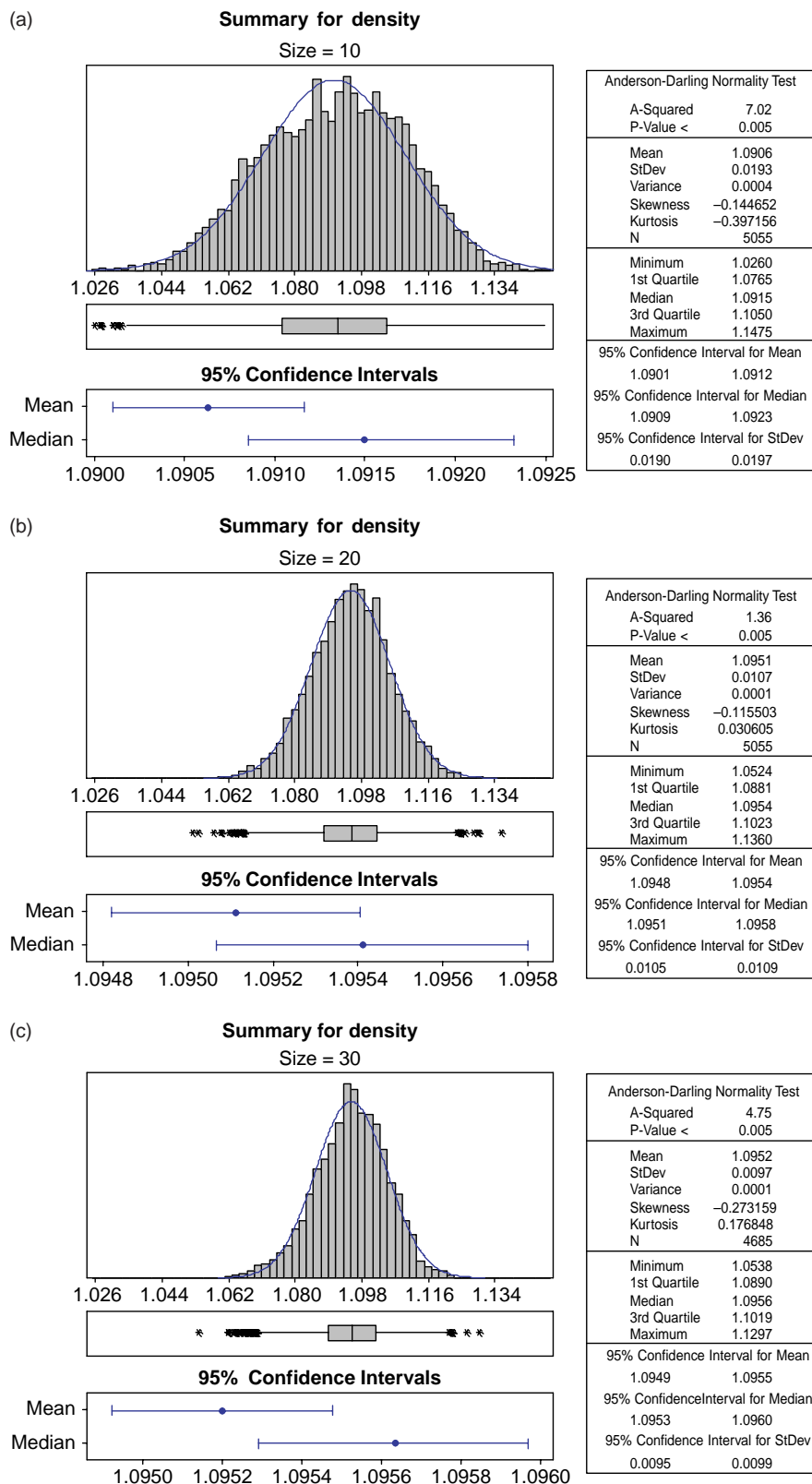


Figure 3. Results of basic statistics for the density distribution of the molecular dynamics simulation of the  $[\text{BMIM}][(\text{CN})_2\text{N}]^-$  ionic liquid simulation boxes containing (a) 10, (b) 20 and (c) 30 ion pairs.



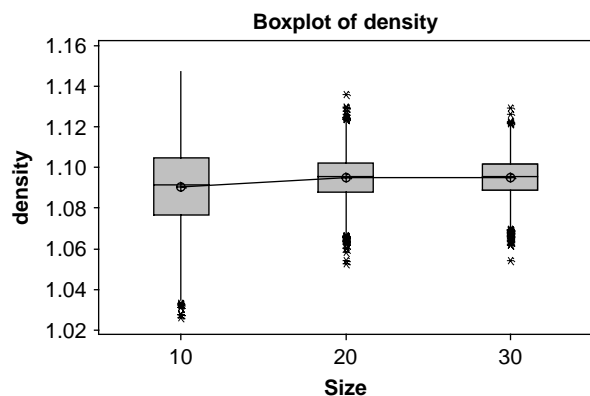


Figure 4. Boxplot representation of the density distribution of the molecular dynamics simulation of the  $[\text{BMIM}][(\text{CN})_2\text{N}]^-$  ionic liquid simulation boxes containing 10, 20 and 30 ion pairs showing the means and the middle quartiles.

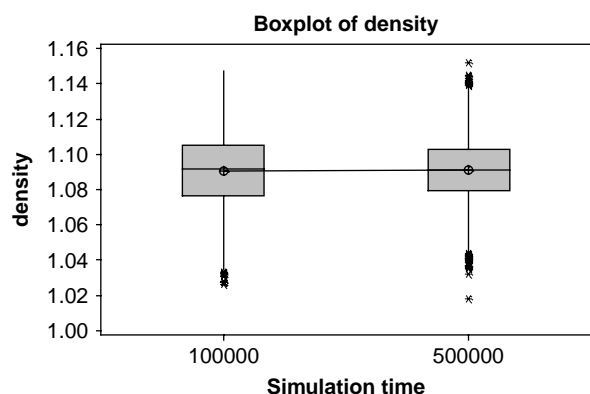


Figure 5. Boxplot representation of the density distribution of two molecular dynamics simulations of different lengths for a  $[\text{BMIM}][(\text{CN})_2\text{N}]^-$  ionic liquid simulation box containing 10 ion pairs showing the means and the middle quartiles.

## 2. The effect of the length of the simulation

Starting from the same five amorphous boxes (each containing 10 ion pairs and pre-equilibrated for 100,000 fs), we executed independent production runs of 100,000 and 500,000 fs. The inspection of the box plots (see figure 5) showed that increasing the length of simulation introduced almost no change in the mean density and only a very moderate change in the SD.

Since there was no additional advantage to be gained for the longer production runs, we used 100,000 fs in all simulations (following 100,000 fs pre-equilibration molecular dynamics runs).

## 3. The effect of the charge assignment

In order to investigate the role of the charge assignment, we performed benchmark studies on formamide which is a molecular solvent with large dispersive and electrostatic components of the solubility parameter. In two sets of calculations, we used atomic charges as assigned by COMPASS and as calculated from the electrostatic potential at the density functional level. The results along with the experimental values are in Table 6.

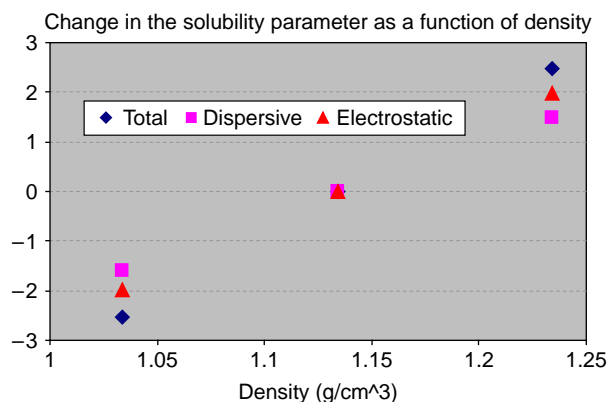


Figure 6. Changes in the calculated components of the solubility parameter of formamide as a function of density of the simulation box using the values at the experimental density as reference.

Table 6. The two components of the solubility parameter of formamide as determined in molecular dynamics simulations using charges assigned by the COMPASS force field and electrostatic potential-derived charges along with the experimental values.

	$D$ (g/cm <sup>3</sup> )	$\delta_{\text{vdW}}$	$\delta_{\text{ES}}$
COMPASS	1.160	21.5	28.2
DFT	1.166	20.9	29.3
Exp.	1.134	17.2	32.4

These data show that while the density changes only slightly when the force field-assigned charges are replaced by those determined at the density functional level, the components of the solubility parameters show some improvement. Similar studies on ionic liquids (not shown here) exhibit even larger differences. Analogous observations were made earlier [3] for oligomers mimicking some cellulose derivatives in the amorphous phase.

## 4. The effect of force field selection

Since there are several force fields available for use in the Forcite engine each having certain advantages and disadvantages, we also carried out a set of simulations using the Dreiding force field, which is somewhat less sophisticated than COMPASS. In order to decouple the effect of the force field from the effect of the charge assignment, we performed simulations both with using charges as determined from charge equilibration and at the DFT level. The results in Table 7 below for formamide along with

Table 7. The two components of the solubility parameter of formamide as determined in molecular dynamics simulations using the Dreiding force field with charges obtained by charge equilibration (charge eq.) and determined by density functional calculations (DFT) along with the experimental values.

	$D$ (g/cm <sup>3</sup> )	$\delta_{\text{vdW}}$	$\delta_{\text{ES}}$
Dreiding, charge eq.	1.102	8.9	31.6
Dreiding, DFT	1.021	7.7	29.7
Exp.	1.134	17.2	32.4

experimental values. Clearly, changing the force field from COMPASS to Dreiding had a large negative impact both on the calculated density and the dispersive component of the solubility parameter. Somewhat surprisingly, the electrostatic component of the solubility parameter showed some moderate improvement.

### 5. *The effect of density inaccuracies on the solubility parameters*

Based on the data in Tables 6 and 7, the densities determined from molecular simulations have some inaccuracies associated with the selection of the force field, assignment of charges and other details of the calculations. Since the calculated values of the solubility parameter also have the same computational inaccuracies, it seems to be worthwhile to investigate the extent

of error introduced by a known error in the density calculation. For these studies, we built three copies of amorphous boxes containing 20 formamide molecules at the experimental density and at 0.1 g/cm<sup>3</sup> higher and lower densities (about 9% change). The solubility parameters for all systems were then determined as usual. In this range, the components of the solubility parameters changed linearly with the density of the system and the differences relative to the value at the experimental density are shown in Figure 6.

It can be observed in Figure 6 that even an almost 10% inaccuracy in the density introduces only a  $< 2$  unit (about 7%) change in the solubility parameters. Formamide was chosen for this test because it has large van der Waals and electrostatic contributions both and it is expected that the other molecular solvents are even less sensitive to changes in the density.