

Molecular Dynamic Simulations of Ionic Liquids: A Reliable Description of Structure, Thermodynamics and Dynamics

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The parameterization of a new force-field and its validation for the liquid description of five imidazolium-based ionic liquids [C_nmim][NTf₂] (n = 1, 2, 4, 6, 8) are described. The proposed force-field is derived to reproduce densities, self-diffusion coefficients for cations and ions as well as NMR rotational correlation times for cations and water molecules in [C₂mim][NTf₂]. The temperature dependence and the cation chain-length dependence of these properties is described well. Very good agreement between simulated and experimental values for the heats of vaporization,

shear viscosities and NMR rotational correlation times is also achieved. All properties are crucial for understanding the nature and interaction of ionic liquids. The good performance of the new force-field suggests that the Lennard–Jones interactions previously were strongly overestimated. The given force-field now allows us to investigate other important properties of this class of ionic liquids such as the micro segregation of ionic liquids, ion pair formation, lifetimes of ion pairs and the solvent dependency of these properties.

1. Introduction

Ionic liquids (ILs) are a new class of solvents for use in environmentally benign industrial processes, and are seen as an alternative to toxic, volatile organic compounds.^[1–3] They are liquids below 100 °C, and are composed of an organic cation and organic or inorganic anion. A combination of different anions and cations in ILs will lead to an infinitely large number of compounds with varied physical and chemical properties. One can thus judiciously select from a multitude of ionic liquids, the one that optimally suits a specific chemical reaction. A number of simulation studies of ionic liquids have been carried out in recent years due to the numerous potential applications of these materials. Most simulation studies of ionic liquids have concentrated on ionic liquids with imidazolium cations.^[4–16] These simulations have provided insight into ionic liquid structures and dynamics as well as interaction of ionic liquids with organic solvents. However, a crucial validation of the force-fields lead to dynamic and thermodynamic properties which are significantly off the measured values.^[17,18]


For a rational design of ionic liquids it is important to understand their nature and interactions. In principle molecular dynamics (MD) simulations can be a powerful tool to derive structural, dynamic and thermodynamic properties of such liquids. The crucial point is the derivation of reliable force-fields which describes the interactions between ions in an appropriate way. For H-bonded liquids such as water and alcohols this is usually done by fitting charges and Lennard–Jones parameters against experimentally well known properties. Force-fields are parameterized to be in agreement with pair correlation functions from neutron or X-ray structure factors, self-diffusion coefficients from NMR and heats of vaporization from vapor pressure measurements.^[19,20] Until recently these properties were not available at all or are not easy to measure with suffi-

cient accuracy for ionic liquids. For that reason the first force-fields were parameterized purely by ab initio calculations and only validated against the liquid density.^[4–7] The measured density and the MD density differed by about 3 %, and the self-diffusion coefficients yielded values an order of magnitude smaller than the measured values.^[21] Additionally the obtained heats of vaporization are between 20 and 50 % too large compared to the most reliable experimental data available today.^[22–25] Obviously the interaction in this force-field is strongly overestimated leading to restricted dynamics and too large values for the heats of vaporization. One should note that even today only a very few reliable thermodynamic properties such as heats of vaporization for ionic liquids are available. Recent experimental values obtained from surface tensions,^[22] Knudsen effusion method,^[22] mass spectrometry,^[23] combustion,^[24] and microcalorimetry^[25] strongly differ. Differen-

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ces up to 50 kJ mol^{-1} make them useless for deriving new force-fields. Thus we parameterized a refined force-field against the liquid density, very accurately measured self-diffusion coefficients of cations and anions in $[\text{C}_2\text{mim}][\text{NTf}_2]$ at 303 K ^[21] as well as NMR rotational correlation times for imidazolium cations in $[\text{C}_2\text{mim}][\text{NTf}_2]$ and for water in $[\text{C}_2\text{mim}][\text{NTf}_2]$ at the same temperature. The reliability of the new force-field is thus validated for temperature behavior and the chain length dependence of these and other dynamic and thermodynamic properties. The heats of vaporization for the ILs $[\text{C}_2\text{mim}][\text{NTf}_2]$ perfectly reproduce the measured data obtained from the Knudsen effusion method,^[22] mass spectroscopy,^[23] and the transpiration method.^[24] Moreover dynamic properties such as rotational correlation times from NMR measurements as well as shear viscosities are perfectly described as a function of temperature and chain length of the cation. Herein we present the first reliable force-field for investigating ionic liquids containing alkylimidazolium cations, C_nmim^+ , and NTf_2^- anion. This allows investigating in detail the structural and dynamical properties such as the heterogeneity of ionic liquids, ion pair formation, and the validity of the Einstein–Debye relation.

Up to now ionic liquids were modeled by the all-atom molecular force-field proposed by Lopes and co-workers.^[6–9] This force-field is based on the OPLS-AA/AMBER framework and developed specifically for ionic liquids. The model was parameterized against ab initio calculations of the torsion energy profiles in imidazolium cations, therefore yielding an accurate description of the conformational characteristics of these ions. Thereafter the molecular force-field was validated against experimental densities. The authors felt that an accuracy of $\pm 3\%$ in liquid densities is reasonable and justified by the generality of the present model. When compared to dynamical and thermodynamical properties such as self-diffusion coefficients and heats of vaporization, this model fails. The stimulated self-diffusion coefficients were an order of magnitude smaller than the measured values. This finding is in accordance with modeled heats of vaporization, which are 50 kJ mol^{-1} higher than the most reliable measured data. The failures of this model for describing the density and the diffusion coefficients of ionic liquids are shown in Figure 1. Our MD simulations using this force-field show that the interactions between anions and cations are tremendously overestimated.

Computational Methods

MD Simulation Details

Classical molecular dynamic simulations of liquid $[\text{C}_n\text{mim}][\text{NTf}_2]$ with $n=1,2,4,6,8$ were carried out mostly in the isobaric-isothermal (NPT) ensemble. For the viscosity simulations the canonical ensemble (NVT) is used because the Green-Kubo-equations are only defined for constant volumes. The simulated systems consist of 173 ion pairs at 1 bar. The simulations were carried out using the Gromacs-MD package for temperatures 273, 303, 343 and 383 K.^[26,27] Electrostatic interactions were computed using the particle mesh Ewald summation method with a real space cutoff of 1.2 nm and a mesh spacing of ap-

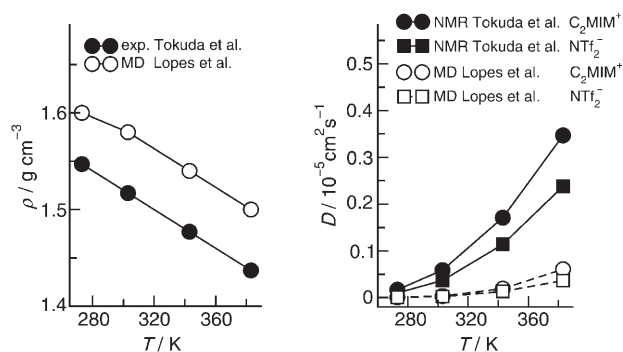


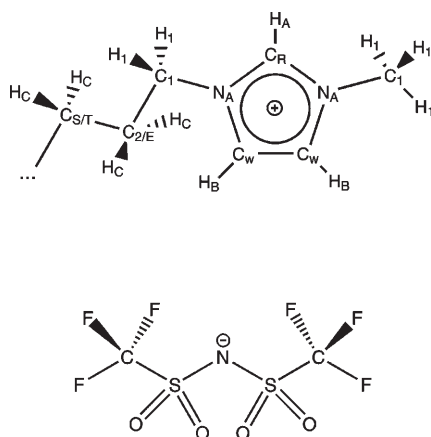
Figure 1. a) Comparison of measured (filled symbols) and simulated (open symbols) densities of $[\text{C}_2\text{mim}][\text{NTf}_2]$ as a function of temperature. The simulations were performed using the force-field by Lopes et al.^[6] The simulated densities are about 3% higher compared to the experimental values.^[36] b) Comparison of measured (filled symbols) and simulated (open symbols) self-diffusion coefficients of C_2mim^+ (open symbols) and NTf_2^- in $[\text{C}_2\text{mim}][\text{NTf}_2]$ as a function of temperature. The simulations were performed using the force-field by Lopes et al.^[6] The simulated diffusion coefficients are an order of magnitude smaller than the measured values by Tokuda et al.^[21]

proximately 0.12 nm and fourth order interpolations.^[28] Temperature and pressure control was achieved using a Nosé-Hoover thermostat^[29,30] and the Rahman-Parrinello barostat^[31,32] with coupling times $\tau_T=0.5 \text{ ps}$ and $\tau_P=2.0 \text{ ps}$, respectively. Since ionic liquids exhibit slow microscopic dynamics, equilibrium runs took 2 ns and were followed by trajectories of 10 ns long with 2 fs time steps.

The heats of vaporization ($\Delta_{\text{vap}}H$) were obtained from the calculated internal energies of the liquid ILs and the vacuum ion pairs at 298 K. It was assumed that the vapor phase is formed by isolated, neutrally charged contact ion pairs, which were simulated in vacuum without periodic boundary conditions and with translation and rotation degrees of freedom switched off. The transport properties such as the self-diffusion coefficients (D) and the shear viscosities (η) were calculated using the Einstein relation and the Green–Kubo relation, respectively. The rotational correlation times (τ) were calculated from the time autocorrelation function for the C(2)–H vector reorientation of the IL cations to be in agreement with measured rotational correlation times for this axis obtained from NMR relation time measurements.^[33] (This vector coincides with the $\text{C}_R\text{--H}_A$ bond given in Scheme 1.) All equations which are used to determine these thermodynamic and dynamic properties are given in the text.

Refinement of the Force-Field

We took the force-field for $[\text{C}_2\text{mim}][\text{NTf}_2]$ developed by Lopes and co-workers and refined it in such a way that the simulated properties mostly agree with experimental densities,^[6] accurately measured self-diffusion coefficients for cations and anions in neat $[\text{C}_2\text{mim}][\text{NTf}_2]$ ^[21] and NMR rotational correlation times for the cations in $[\text{C}_2\text{mim}][\text{NTf}_2]$ and water molecules in a 1 w% solution of water in $[\text{C}_2\text{mim}][\text{NTf}_2]$ at 303 K.^[33] For this purpose the TIP4P-Ew water model was employed.^[34] This kind of parameterization seems to be unusual but has significant



Scheme 1. Adopted nomenclature for the interaction sites of 1-alkyl-3-methylimidazolium ($C_n\text{mim}^+$) cation and bis[(trifluoromethyl)sulfonyl]amide (NTf_2^-).

benefits. The diffusion coefficients can be fitted separately to cations and anions no matter whether the ions exist as single particles, ion pairs or in larger aggregates. The same is true for the NMR rotational correlation times. Unfortunately these reorientation dynamics are available only for the C–H(2) vector of the imidazolium cations ($C_R\text{--}H_A$ vector in Scheme 1). Thus we used NMR reorientational correlation times of water in $[C_2\text{mim}][\text{NTf}_2]$ to fit the anion parameters. This unusual procedure is based on recent experimental findings showing that the structure and dynamics of single water molecules are sensitive probes for anion properties.^[35] We show that the single water behavior is mainly determined by anions in the ionic liquid; thus the water dynamics may serve as a good indicator for anion properties and can be used for deriving force-field parameters. The nonbonded interactions in the system are represented by a sum of pair-wise additive interatomic Lennard–Jones and Coulombic potentials shown in Equation (1), which represents the interaction energy between the ions.

$$U = \sum_{i=1}^{N-1} \sum_{j>1}^N [U^{\text{LJ}}(r_{ij}) + U^{\text{Coul}}(r_{ij})] \quad (1)$$

$$\text{where } U^{\text{LJ}}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \text{ and } U^{\text{Coul}}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}.$$

We kept the Coulombic term, U^{Coul} , unchanged and only modified the Lennard–Jones parameters in U^{LJ} . The new LJ-parameters are all given in Table 1. The nomenclature for the interaction sites is shown in Scheme 1. At this stage the change of LJ-parameters seems to be somewhat arbitrary. The procedure is justified by the obtained results. In particular the correct increase of heats of vaporization with increasing chain length of the cations can be only achieved by properly adjusting the van der Waals interactions. Testing for the properties of pure ionic liquids showed that the old scheme was inadequate and significant adjustments to the Lennard–Jones parameters are required.

Atoms	q/e	$\sigma/\text{\AA}$	$\epsilon/\text{kJmol}^{-1}$	Source
C_1	−0.17	3.50	0.27614	ref. [6]
C_2	0.01	3.50	0.27614	ref. [6]
C_E	−0.05	3.50	0.27614	ref. [6]
C_R	−0.11	2.13	0.43932	this work
C_S	−0.12	3.50	0.27614	ref. [6]
C_T	−0.18	3.50	0.27614	ref. [6]
C_W	−0.13	3.0175	0.20501	this work
H_A	0.21	1.452	0.18828	this work
H_B	0.21	2.057	0.0879	this work
H_C	0.06	2.5	0.12552	ref. [6]
H_1	0.13	2.5	0.12552	ref. [6]
N_A	0.15	3.25	0.71128	ref. [6]
F	−0.16	2.655	0.06651	this work
C	0.35	3.150	0.08282	this work
S	1.02	4.0825	0.31372	this work
O	−0.53	3.4632	0.26353	this work
N	−0.66	3.2500	0.21333	this work

2. Results and Discussion

2.1 Self-Diffusion Coefficients

The simulated densities and self-diffusion coefficients using the new force-field are shown in Figure 2. Over the whole temperature range the densities as well as the diffusion coefficients of

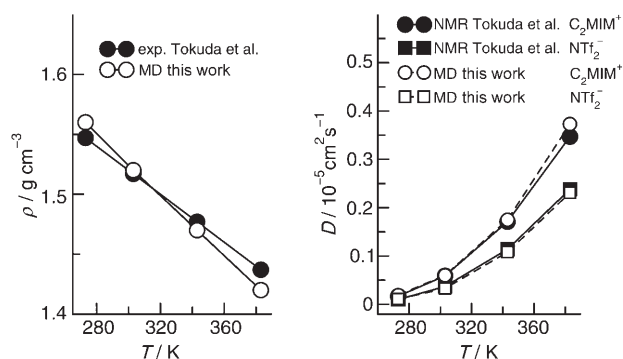


Figure 2. a) Comparison of measured (filled symbols) and simulated (open symbols) densities of $[C_2\text{MIM}][\text{NTf}_2]$ as a function of temperature. The simulations were performed using the refined force-field in this work. Over the whole temperature range the simulated densities are about $\pm 0.2\%$ within the experimental values.^[36] b) Comparison of measured (filled symbols) and simulated (open symbols) self-diffusion coefficients of $C_2\text{mim}^+$ (circles) and NTf_2^- (squares) in $[C_2\text{MIM}][\text{NTf}_2]$ as a function of temperature. The simulations were performed using the refined force-field. The simulated diffusion coefficients fit the measured values by Tokuda et al.^[21] within $\pm 1.7\%$ over the whole temperature range. The force was derived by fitting the above given properties to measured values at 303 K.

$[C_2\text{mim}][\text{NTf}_2]$ only differ about $\pm 0.2\%$ and $\pm 1.7\%$, respectively. This agreement is very satisfying. The self-diffusion coefficients D_i were calculated using the Einstein relation in Equation (2)

$$D_i = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle [\vec{r}_i(t) - \vec{r}_i(0)]^2 \rangle \quad (2)$$

Table 2. MD simulated and NMR measured self-diffusion coefficients of $C_n\text{mim}^+$ and NTf_2^- in ionic liquids $[C_n\text{mim}][\text{NTf}_2]$ (in $10^{-5} \text{ cm}^2 \text{ s}^{-1}$) at 303 K as a function of alkyl chain length. The experimental data were obtained by Tokuda et al.^[21]

	$C_n\text{mim}^+$	$C_n\text{mim}^{+ [21]}$	NTf_2^-	$\text{NTf}_2^{- [21]}$
$[\text{C}_1\text{mim}][\text{NTf}_2]$	0.063	0.059	0.0324	0.0318
$[\text{C}_2\text{mim}][\text{NTf}_2]$	0.060	0.059	0.023	0.037
$[\text{C}_4\text{mim}][\text{NTf}_2]$	0.030	0.0337	0.022	0.0269
$[\text{C}_6\text{mim}][\text{NTf}_2]$	0.013	0.0211	0.012	0.0193
$[\text{C}_8\text{mim}][\text{NTf}_2]$	0.005	0.0148	0.0048	0.0148

where $[\vec{r}_i(t) - \vec{r}_i(0)]^2$ is the mean-square displacement of the molecule center of mass for species i during time t and the broken brackets denote an ensemble average. An example for mean square displacements versus time for deriving self-diffusion coefficients of ions in $[\text{C}_2\text{mim}][\text{NTf}_2]$ is given in the Supporting Information.

A reliable check for the quality of the new force-field obtained for $[\text{C}_2\text{mim}][\text{NTf}_2]$ is to simulate the self-diffusion coefficients for all ionic liquids $[C_n\text{mim}][\text{NTf}_2]$ with $n = 1, 2, 4, 6$ and 8. In Table 2 the simulated self-diffusion coefficients for cations and anions are given compared to the measured properties by Tokuda and co-workers.^[21] The agreement is nearly perfect. The slight change from $[\text{C}_1\text{mim}][\text{NTf}_2]$ to $[\text{C}_2\text{mim}][\text{NTf}_2]$ is reproduced as well as the continuously decreasing self-diffusion coefficients with chain length of the cation. In particular the merging of the cation and anion self-diffusion coefficients with increasing chain length is simulated well (Figure 3). It is the merit of MD simulations that this effect can be explained on a molecular basis. With increasing chain length the cohesive energy is increasing resulting in a decrease of self-diffusion coefficients for cations and anions. Also important is the steric hindrance caused by the alkyl side chains which slows down

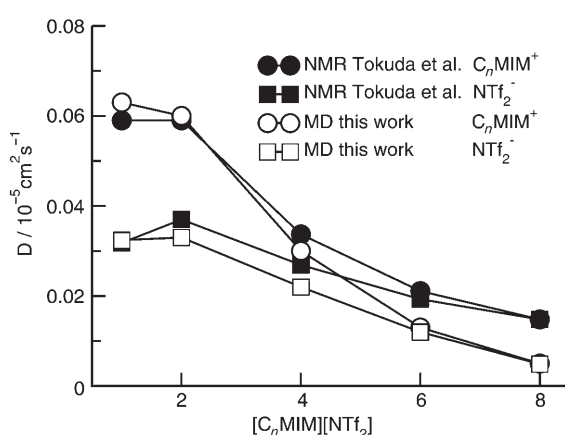


Figure 3. Self-diffusion coefficients of $C_n\text{mim}^+$ and NTf_2^- in $[C_n\text{MIM}][\text{NTf}_2]$ at 303 K as a function of alkyl chain length n . The simulated values (open symbols) are compared to experimental findings (filled symbols).^[21,35] It is nicely seen that the self-diffusion coefficients are significantly different for cations (circles) and anions (squares) for small chain lengths of the cation and seem to merge for higher n .

the dynamics. As a consequence the diffusion of the cation strongly decreases with increasing chain length.

2.2 Heats of Vaporization

Using this refined force-field we simulated further dynamic and thermodynamic properties for this class of ionic liquids. The heat of vaporization $\Delta_{\text{vap}}H(T) = \Delta_1^g H_m^0(T)$ has been computed from the differences between the molar internal energy of the gas and the liquid phases $\Delta_1^g U_{c,m}(T)$ and RT by using Equation (3).

$$\Delta_1^g H_m^0(T) = \Delta_1^g U_{c,m}(T) + RT \quad (3)$$

where R represents the gas constant. The simulated values for $\Delta_{\text{vap}}H(298 \text{ K})$ are shown in Figure 4. The increase from $132.5 \text{ kJ mol}^{-1}$ for $[\text{C}_1\text{mim}][\text{NTf}_2]$ up to $154.3 \text{ kJ mol}^{-1}$ for $[\text{C}_8\text{mim}][\text{NTf}_2]$, is in very good agreement with experimental

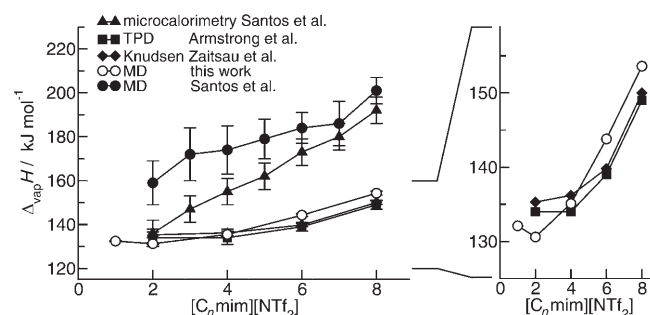


Figure 4. Molar enthalpies of vaporization of $[C_n\text{MIM}][\text{NTf}_2]$ versus alkyl chain length from the Knudsen effusion method by Zaitsau et al.^[22] (◆), the TPD method by Armstrong et al.^[23] (■), microcalorimetric measurements by Santos et al.^[25] (▲), molecular dynamics simulations by Santos et al.^[25] (○), and MD simulations using the refined force field in this work (○).

values from the Knudsen effusion method,^[22] surface tension^[22] and combustion measurements,^[24] and mass spectrometry.^[23] Obviously the refined force-field is capable to describe correctly the internal energy of the liquid and the interaction of ion pairs. The good agreement with measured heats of vaporization and their slight increase with increasing chain length of the cations allows some careful judgment of $\Delta_{\text{vap}}H(298 \text{ K})$ values obtained from other experimental methods such as microcalorimetry.^[25] As seen in Figure 4 these heats of vaporization are significantly higher for ionic liquids $[C_n\text{mim}][\text{NTf}_2]$ than those obtained from all other experimental methods. The MD simulations by Santos and co-workers^[25] using the force-field by Lopes and co-workers^[6] give even higher heats of vaporization and strongly overestimate this property. This can be seen in Table 3 where the heats of vaporization for $[\text{C}_8\text{mim}][\text{NTf}_2]$ are between 149 and 150 kJ mol^{-1} obtained from the Knudsen, TPD and surface tension measurements, compared to $154.3 \text{ kJ mol}^{-1}$ from our MD simulations.^[22,23] This is in stark contrast to the microcalorimetry measurements and the MD simulations by Santos and co-workers which yield values for the heats of vaporization for $[\text{C}_8\text{mim}][\text{NTf}_2]$ of about 192 and

Table 3. Estimated values of enthalpies of vaporization, $\Delta_{\text{vap}}H(298)$ in kJ mol^{-1} of ionic liquids $[\text{C}_n\text{mim}][\text{NTf}_2]$ obtained by various experimental methods compared to results from MD simulations.

Ionic liquid	Knudsen ^[22]	Surface tension ^[22]	TPD ^[23]	Microcalorimetry ^[25]	MD simulations ^[25]	Transpiration ^[24]	MD simulations in this work
$[\text{C}_1\text{mim}][\text{NTf}_2]$							132.1 ± 0.3
$[\text{C}_2\text{mim}][\text{NTf}_2]$	135.3	136.1	134	136	159 ± 10	136.7 ± 3.4	130.6 ± 0.4
$[\text{C}_4\text{mim}][\text{NTf}_2]$	136.2	134.6	134	155	174 ± 11		135.1 ± 0.6
$[\text{C}_6\text{mim}][\text{NTf}_2]$	139.8	141.6	139	173	184 ± 7		143.8 ± 0.6
$[\text{C}_8\text{mim}][\text{NTf}_2]$	150.0	149	149	192	201 ± 6		153.6 ± 0.9

201 kJ mol^{-1} , respectively.^[25] Obviously these too high heats of vaporization and their too strong increase with alkyl chain length have their origin in overestimated Lennard–Jones interactions in the previous force-fields. If the LJ-parameters are significantly reduced as in the refined force-field, the absolute values as well as their increase with the chain length of the imidazolium cation are described correctly. This increase can be attributed to an increase of the van der Waals interactions in these highly structured liquids. A detailed analysis of the van der Waals and Coulomb interactions contributing to the heats of vaporization (see Santos et al.^[25]) will be given in a forthcoming paper.

2.3 Viscosities

Another crucial property describing the nature of ionic liquids is the shear viscosity which can be calculated from the integral over time of the pressure tensor autocorrelation function following the Green-Kubo relation in Equation (4)

$$\eta = \frac{V}{kT} \int_0^\infty dt \langle P_{\alpha\beta}(0) \cdot P_{\alpha\beta}(t) \rangle \quad (4)$$

The brackets indicate that the average must be taken over all time origins $t=0$, V is the volume of the system, T is the temperature, and k is the Boltzmann constant. $P_{\alpha\beta}$ denotes the element $\alpha\beta$ of the pressure tensor. Unlike self-diffusion, the shear viscosity is a collective property, so it is not statistically improved by averaging over the number of particles in the system. Some statistical improvement in the calculated shear viscosity can be achieved by averaging over three independent terms of the pressure tensor, namely, P_{xy} , P_{yz} , P_{xz} . The elements of the pressure tensor are calculated during the simulation using the following expression [Eq. (5)]:

$$P_{\alpha\beta} = \frac{1}{V} \left[\sum_j m_j v_{\alpha j} v_{\beta j} + \frac{1}{2} \sum_{i \neq j} r_{\alpha ij} f_{\beta ij} \right] \quad (5)$$

where m_j is the mass of particle j and \vec{v}_j is its velocity, while r_{ij} and \vec{f}_{ij} represent, respectively, the distance and the force between particles i and j . The subscripts α and β refer to the corresponding components of the vector. An example for a running integral, Equation (3), corresponding to the shear viscosity for $[\text{C}_2\text{mim}][\text{NTf}_2]$ is given in the Supporting Information.

The simulated results are shown for $[\text{C}_2\text{mim}][\text{NTf}_2]$ as a function of temperature compared to experimental viscosities measured by Crosthwaite and co-workers in Figure 5.^[36] We find

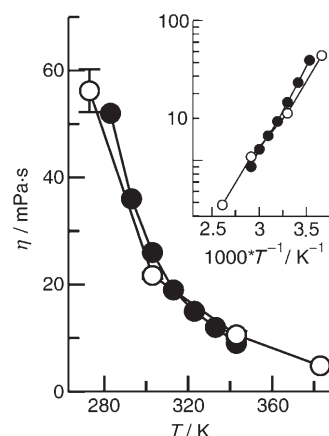


Figure 5. Shear viscosities of $[\text{C}_2\text{mim}][\text{NTf}_2]$ calculated from the Green-Kubo relation (open symbols) and from experiments (filled symbols) as a function of temperature.^[36] The inset shows the plot of $\log \eta$ vs $1000/T$, which indicates Arrhenius behavior of the viscosities.

good agreement over the whole temperature range. Plotting the $\ln \eta$ vs T^{-1} we obtain an activation energy of about 21.7 kJ mol^{-1} which is only slightly different from the experimental value. This is another proof for the quality of the refined force-field. Most of the existing force-fields of ionic liquids strongly overestimate the shear viscosities.^[37] However, equilibrium MD simulation is certainly not the most appropriate method to describe high viscous systems such as ionic liquids indicated by the stronger deviation between theory and experiment at low temperatures (see Figure 5). Fortunately the ILs $[\text{C}_n\text{mim}][\text{NTf}_2]$, which are considered in this work, exhibit relatively low viscosities probably caused by ion-pair formation. However, it would be interesting to see how this refined force-field performs in non-equilibrium molecular dynamics simulations which are known to be the most appropriate technique to simulate collective properties for highly viscous systems.^[38]

2.4 Reorientational Correlation Times

For $[\text{C}_2\text{mim}][\text{NTf}_2]$ we also simulated the rotational correlation time for the C(2)–H vector of the cation as a function of temperature. For the extreme narrowing case the rotational corre-

lation time (τ_2) is calculated from the integral of the time autocorrelation function of the form [Eq. (6)]

$$\tau_2 = \int_0^{\infty} dt \langle C_2(0) \cdot C_2(t) \rangle \text{ with } C_2(t) = \frac{\langle P_2[\theta(0)] P_2[\theta(t)] \rangle}{\langle P_2[\theta(0)]^2 \rangle} \quad (6)$$

$P_2[\theta]$ is the second Legendre polynomial of the angle between a certain molecule fixed vector and the z axis of the system frame. The angular bracket signifies an equilibrium average. An example for a time autocorrelation function corresponding to the reorientational correlations time of ions in $[C_2\text{mim}][\text{NTf}_2]$ is given in the Supporting Information. The obtained correlation times can be linearly related to NMR relaxation rates. In our case we focused on the axis along the C(2)–H bond of the imidazolium cation to be in agreement with the experimental situation. In the deuteron relaxation rates $1/T_{\text{CD}}$ the interaction between the main component of electric field gradient tensor eq_{zz} and the nuclear quadrupole moment eQ of the deuteron in C–D is measured. Fortunately, eq_{zz} occurs nearly along the C(2)–D bond and we obtain similar information from the NMR experiment and the MD simulation. The calculated τ values are compared to available experimental data obtained from NMR deuteron relaxation time measurements.^[33] The correlation times from MD and NMR describe the same rotational dynamics. Again we find reasonable agreement between simulation and experiment. As shown in Figure 6 the measured correlation times are slightly smaller than the simulated values. Here it should be noted that further drying of the IL samples could lead to an increase of the NMR correlation times and thus giving even better agreement. Also the temperature dependence is described well. The measured activation energy of about 27.9 kJ mol^{−1} is in excellent agreement with the measured value of 27.6 kJ mol^{−1}. Having reliable transport properties such as diffusion coefficients and viscosities as well as reorientational correlation times we can check the val-

idity of the Stokes-Einstein-Debye relation which is planned in forthcoming studies.

3. Conclusions

We presented the parameterization of a force-field and its validation for the liquid description of five ionic liquids $[C_n\text{mim}][\text{NTf}_2]$ ($n = 1, 2, 4, 6, 8$). The proposed force-field was derived to reproduce available experimental properties such as density, self-diffusion coefficients for cations and ions as well as NMR rotational correlation times for cations and water molecules in $[C_2\text{mim}][\text{NTf}_2]$ at 303 K. For that purpose the Lennard-Jones interactions were reduced significantly, whereas the charges remained unchanged. As a consequence the temperature dependence as well as the chain length dependence of these properties is well described. We have achieved very good agreement between simulated results and experimental findings for the heats of vaporization, shear viscosities and NMR rotational correlation times. All properties are crucial for understanding the nature and interaction of ionic liquids. The successful parameterization of the ILs encourages us to extend the procedure in order to include other important cations and anions and to investigate their influences on structure, hydrogen bonding, solvent-to-solute interactions, and other physical properties, both in the bulk liquid and in mixtures with other solvents. Our new force-field allows the detailed investigation of other important properties of this class of ionic liquids such as the micro segregation of ionic liquids, ion pair formation, lifetimes of ion pairs and the solvent dependency of these properties.

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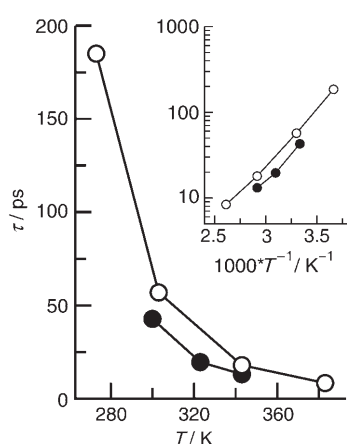


Figure 6. Rotational correlation times (τ) of $C_2\text{mim}^+$ in $[C_2\text{mim}][\text{NTf}_2]$ calculated from the time correlation function (symbols) and from NMR relaxation time experiments (filled symbols) as a function of temperature.^[33] The inset shows the plot of $\log \tau$ vs $1000/T$, which indicates Arrhenius behavior of the rotational correlation times.

Keywords: force-field calculations • ionic liquids • molecular dynamics • thermodynamics

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