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Liquid–vapor equilibrium and critical parameters of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate from molecular dynamics simulations

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ABSTRACT

The liquid–vapor equilibrium properties of the room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, often abbreviated as [bmim][PF_6] or [C_4mim][PF_6], have been determined using a classical all-atom force field in molecular dynamics simulations. Extending our earlier work, the behavior at elevated temperatures (875–1075 K) was studied to obtain the following refined estimates of the critical parameters: $T_c = 1105 \pm 25$ K, $\rho_c = 227 \pm 19$ kg m^{-3}, and $P_c = 3.1 \pm 1.4$ bar. In the above-mentioned temperature range, the vapor pressure can be calculated directly with reasonable accuracy, giving us indirect access also to the enthalpy of vaporization. From these new data, several corresponding-states properties, which are believed to be generic for ionic liquids and which do not depend too sensitively on any specific potential model, can be obtained in addition to Guggenheim's reduced surface tension which we reported previously. The critical compressibility factor is found to be $Z_c \approx 0.04 \pm 0.02$, Guggenheim's ratio $\Delta_{vap}H^{app}/(RT_c) \approx 9.9 \pm 0.5$, the relative normal boiling point $T_b/T_c = 0.90 \pm 0.05$, and Trouton's constant $\Delta_{vap}S(T_b) \approx 71 \pm 11$ J mol^{-1} K^{-1}. The implications of these findings are discussed.

1. Introduction

The past decade has seen a rapidly increasing interest in the physicochemical properties of room temperature ionic liquids (RTILs) due to their remarkable potential as green solvents and catalysts in synthesis and extraction as well as in electrochemical processes [1–3]. In all of these potential applications, the properties at liquid–vapor equilibrium, such as the densities of coexisting liquid and vapor phases, the surface tension, and the vapor pressure, are of importance.

From a theoretical point of view, RTILs are an interesting and challenging intermediate between simple fluids, whose behavior is determined by short-range dispersion forces, and molten salts, such as alkali halides, in which long-range Coulomb interactions dominate the omnipresent dispersion interactions. Complications in the theoretical description are added by the non-spherical shape of ions, internal degrees of freedom, domain formation and possibly hydrogen bonding, which imply highly directional interactions [4,5].

With regard to the applications, it is an advantage that RTILs can be tailored to the requirements of their specific task, e.g., by combining different anions and cations or by varying side chains. In this way, a vast number (millions) of different RTILs can be synthetized. It is, of course, not possible to measure the thermophysical properties of all these RTILs. For this reason, identifying the generic features of RTILs is important, for example, for the development of corresponding-states approaches. Many of these methods use the critical point as a reference to scale thermodynamic variables (thereby introducing reduced variables) [6]. For this purpose, reliable estimates of the critical parameters are needed. Due to the thermal decomposition of ionic liquids (many of which contain organic constituents) at elevated temperatures, the critical point is hypothetical and cannot be accessed experimentally. Nevertheless, even a hypothetical critical point influences (in fact, to a large degree determines) the behavior at or near room temperature. One must therefore refer to extrapolation schemes established for simple fluids, e.g., Guggenheim's and Eötvös' expressions for the temperature dependence of the surface tension (see below), and rely on these approaches to be valid for ionic fluids as well [7]. Alternatively, one may use molecular potential models, so-called classical force fields, in which bond breaking is not possible, so that the thermodynamic behavior can be studied even at elevated temperatures [8]. In this case, one must rely on the hope that a model which reproduces the properties of the fluid at experimentally accessible temperatures will continue to yield reasonable results all the way to the critical point. In many cases, there are several force fields available, which perform equally well at low temperatures and which may be used for this purpose.

The RTIL studied here, 1-butyl-3-methylimidazolium hexafluorophosphate, abbreviated as [bmim][PF_6], is reported to decompose thermally at temperatures exceeding 410 K [9–11]. To study the

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(hypothetical) behavior at higher temperatures, a force field (FF) which describes the properties at or near 300 K accurately is needed. Several all-atom FFs are available for this purpose: Canongia Lopes et al. developed an OPLS-type FF [12], which was later refined by Bhargava and Balasubramanian [13] to yield better results for the liquid density, the surface tension and the diffusion coefficient. Recently, Hernandez et al. employed a Dreiding potential model to compute the liquid–vapor equilibrium densities [14].

In our previous work on [bmim][PF_6] [8], we used the FF of Bhargava and Balasubramanian to calculate the densities of the coexisting liquid and vapor phases as well as the surface tension in a temperature range of 300–800 K; extrapolating the surface-tension data to zero, we obtained an estimate of the critical temperature of $T_c = 1100 \pm 100$ K for this particular FF. Extrapolation of experimental data (necessarily over a very large temperature interval) yielded similar values [8]. The recent work of Hernandez et al. [14], who used a Dreiding FF and deduced T_c from the width of the coexistence curve, however, indicated a higher value of $T_c = 1280$ K, which is outside the range of uncertainty we attributed to our estimate. It is, therefore, of interest to find out whether this discrepancy is caused by using a different FF, a different extrapolation method to obtain the critical temperature, or other, less obvious reasons. In addition, Hernandez et al. [14] pointed out that in our previous work, there is a large difference (exceeding an order of magnitude) between the vapor density at 800 K that is obtained using the Gromacs simulation package and the one resulting from carrying out the simulations using the YASP package for the same FF [8]. We take the opportunity to address this issue as well.

In this work, we repeat some of our earlier simulations, extend the temperature range to 1075 K, and use longer simulation runs in order to obtain more reliable results. In addition, we calculate properties that could not be obtained before due to the limited temperature range. We calculate the vapor pressure at different elevated temperatures and use these data to derive the enthalpy of vaporization. Furthermore, we estimate the correlation length from the thickness of the liquid–vapor interface. Subsequently, we calculate several corresponding-states properties and compare them to those of generic ionic and non-ionic model fluids [15] and to the results for molecular models of RTILs evaluated by means of Monte Carlo simulation [16–19] to test the applicability of different methodologies.

The remainder of the paper is organized as follows: In Section 2, we briefly outline the main features of the potential model used here, describe the simulation details, and explain how thermodynamic properties and critical parameters are calculated. The results obtained directly from the MD simulations are presented in Section 3. Critical parameters and corresponding-states properties are then derived from these data. A discussion of the main findings in comparison with the results of other simulation approaches as well as those derived from experimental data concludes the paper in Section 4.

2. Methodology

2.1. Potential model (force field)

To calculate the thermophysical properties of [bmim][PF_6] at liquid–vapor coexistence from simulations, a suitable model is required. Such a model potential determines the interactions among the particles comprising the system and is needed to compute the forces in the propagation of Newton's equations of motion in a classical molecular dynamics simulation. From the resulting trajectories, the thermodynamic properties can be calculated. Given the fact that the potential model is used to compute the forces among the particles, it is often referred to as the “force field” (FF). Here, following our earlier work on [bmim][PF_6] [8], we employ the all-atom FF of Bhargava and Balasubramanian [13]. It represents a refinement of the OPLS-FF proposed by Canongia Lopes et al. [12] in the sense that, by re-adjusting the partial charges, it leads to a better agreement of the liquid density, the diffusion coefficient, and the surface tension with experimental data [13] than the original force field. The main difference between the two FFs is that the ionic charges are reduced from $\pm 1e$ to $\pm 0.8e$ in the refined version, where e denotes the elementary charge.

Here, as before [8], we further modify the FF of Bhargava and Balasubramanian in three respects, none of which is expected to alter the results significantly: To save computational resources, all bond lengths are fixed by imposing holonomic bond constraints; doing so allows us to use a single and comparatively large time step. To be compatible with our earlier work, the cutoff distance for long-range Lennard-Jones interactions is set to 1.2 nm (instead of the 1.3 nm used by Bhargava and Balasubramanian). As usual in OPLS-AA FFs, the intramolecular 1–4 non-bonded interactions are scaled by a factor of 1/2, whereas Bhargava and Balasubramanian did not include this contribution at all.

The input file for the FF was built completely anew to double-check the results of our previous work. On this occasion, we note the correction of three minor typos in the FF used in our earlier work [8]: In the expression for the torsional energies, three dihedral H–C–C–H angles in the butyl side chain had mistakenly been assigned the C–C–C–H value of $V_3\,/\,2 = 0.76565$ kJ mol^{-1} instead of the correct 0.66525 kJ mol^{-1} [12,20]. As is expected and, in fact, shown by the results presented below, absolutely no difference in the thermophysical properties is observed between the earlier simulations and the ones using the corrected FF.

2.2. Simulation details

All molecular dynamics simulations reported here were carried out using version 4.5.3 of the simulation package Gromacs [21]. Compared to our previous work [8], we obtain data for the liquid–vapor equilibrium of the ionic liquid [bmim][PF_6] in an extended temperature range (300–1075 K) and, in almost all cases, from longer simulation runs of 20 ns. Only at low temperatures ($T < 600$ K), 15 ns is found to suffice.

In these simulations, the constraints of fixed bond lengths were enforced using the LINCS algorithm available in Gromacs [22]. To evaluate the Lennard-Jones interactions between non-bonded atoms, standard Lorentz–Berthelot mixing rules were applied. The long-range cutoff for Lennard-Jones interactions was 1.2 nm; the same range was used to switch from evaluating the Coulomb interaction in real space to Ewald summation in reciprocal space. Long-range electrostatic interactions were accounted for in this way by the particle-mesh Ewald summation [23,24]. Long-range dispersion corrections were applied to the energy, but not to the pressure.

In our previous work, a time step of 2 fs had been employed [8]. For temperatures beyond 800 K, this time step turns out to be too large due to the rapid motion of atoms. Therefore, we reduced the time step to 1 fs for all simulations reported here. Instead of the Berendsen thermostat [25] used in our earlier study, we employed a Nosé–Hoover thermostat [26,27] here.

To impose the condition of two-phase coexistence at constant temperature T, the simulations for a given number of particles N were carried out keeping the volume V constant, such that the overall density was in between the bulk liquid and vapor densities (NVT conditions). The tetragonal simulation cell contained 512 ion pairs and had lateral (x and y) dimensions of $L_x = L_y = 4.46$ nm in all cases, but the dimension in the direction perpendicular (z) to the interface(s), L_z, depended on T. In order to be able to use periodic boundary conditions in all three dimensions, two interfaces are present in the simulation cell. The higher the temperature, the larger L_z has to be chosen to accommodate interfaces of increasing thickness. For temperatures below 700 K, we set $L_z = 25$ nm; for 700 K ≤ T ≤ 850 K, we employed $L_z = 30$ nm; $L_z = 35$ nm was selected for 875 K ≤ T ≤ 1000 K, $L_z = 40$ nm for 1025 K and 1050 K, and $L_z = 50$ nm for 1075 K.