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Vapor–liquid equilibria in the binary mixtures of N-butylpyridinium hexafluorophophate and bis(trifluoromethanesulfonyl)imide ionic liquids with acetone: Molecular dynamics simulations

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ABSTRACT

Vapor–liquid equilibria of the N-butylpyridinium hexafluorophosphate [BPY][PF_6]-acetone and N-butylpyridinium bis(trifluoromethanesulfonyl)imide [BPY][TFSI]-acetone mixtures at 310–350 K were investigated using molecular dynamics (MD) simulations. A detailed analysis of the thermodynamic and dynamics properties is presented. The Raoult's law in conjunction with the van't Hoff parameter suggests a somewhat smaller boiling temperature increase then it is actually observed. The effect of both [BPY][PF_6] and [BPY][TFSI] on the acetone phase behavior is similar. Neither free ions nor ion pairs were detected in the vapor phase. Ionic motion at the interface is much less correlated than in the bulk phase. The vapor–liquid interfaces of the investigated mixtures are deemed interesting for the applications of versatile ion-molecular mixtures.

1. Introduction

Room-temperature ionic liquids (RTILs) are widely explored in pure and applied science due to their unprecedented tunability [1–6]. Different RTILs exhibit different sets of physicochemical properties making some of them suitable for particular applications. Most RTILs are robust solvents, which are able to solvate both polar and nonpolar solutes [7–11]. In addition, a liquid state is maintained over a wide temperature range, whereas many RTILs decompose prior to reaching their normal boiling and critical points on the phase diagram. Wide electrochemical windows in conjunction with relatively high ionic conductivities promote applications of RTILs as electrolytes in supercapacitors and lithium-ion batteries [12–14]. Competitive gas capture [15–18] can be achieved by the amine-group functionalized cations and peculiar coordination centers of RTILs, such as an intrinsically acidic hydrogen atom in the imidazole ring, which is able to engender a weak hydrogen bond with the carbon dioxide molecule. Low volatility of many RTILs contributes to their low toxicity for living beings. RTILs are actively employed to separate azeotropic and close-boiling substances [19–22]. In all of these existing and potential applications, the properties at vapor–liquid equilibrium, such as saturated vapor pressure, density of vapor, density of liquid, and surface tension, deserve certain attention.

RTILs differ from conventional ionic compounds by non-sphericity of their ions (exceptions are halogen anions, tetraalkylammonium and tetraalkylphosphonium cations), intramolecular flexibility, participation in hydrogen bonding and formation of ionic domains in the condensed phases. Peculiar intermolecular interactions play a major role in determining phase behavior of RTILs. RTILs, furthermore, differ from conventional molecular solvents — such as water, alcohols, acetone, nitriles, amides, organic carbonates and so on — by a greater role of electrostatic interactions and bulkier particles. The enumerated features complicate theoretically and computationally efficient description of pure RTILs and ion-molecular systems, which are formed in practically important mixtures. For instance, addition of polar molecular co-solvents is widely used to decrease a genuinely high shear viscosity of RTILs and increase their ionic transport [23–33].

Vapor–liquid equilibria of RTILs and their mixtures [34–43] have been a subject of recent research, although less intensive than that of electrochemical and solvation properties, as well as reaction media characteristics. Roemich and coworkers [38]

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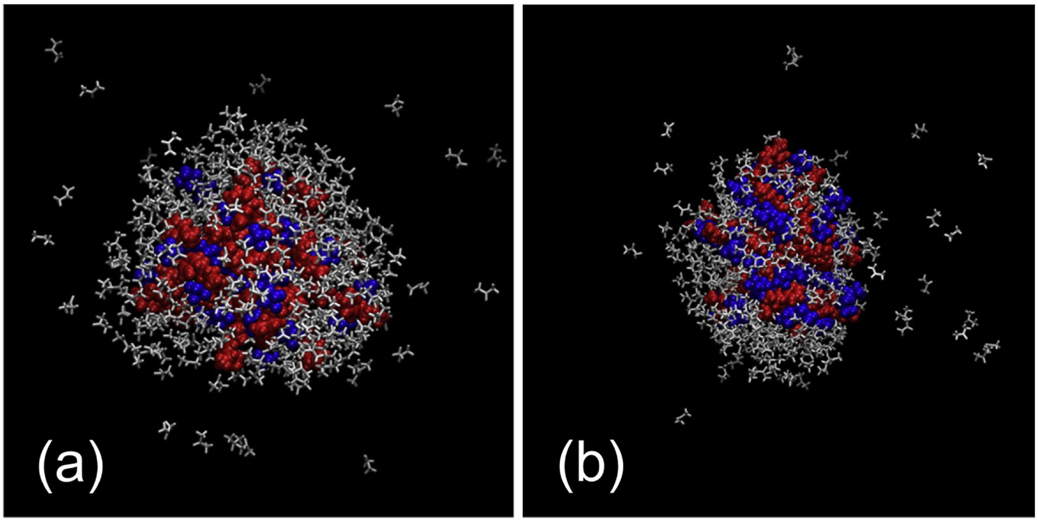

Fig.. 1Equilibrated immediate ion-molecular configurations of the simulated systems: (a) 10 mol% [BPY][PF_6] and (b) 10 mol% [BPY][TFSI] at 330 K: cations are red; anions are blue; co-solvent molecules are white. Most ACET molecules are located on the surface of the ion-molecular droplet. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
List of the simulated systems, their compositions, and temperatures.

#	RTIL	# Ion pairs	# Molecules	# Int. centers	x (RTIL), %	Temperature, K
1	–	0	475	4750	0	310
2		0	475	4750	0	320
3		0	475	4750	0	330
4	[BPY][PF_6]	45	405	5445	10	320
5		45	405	5445	10	330
6		45	405	5445	10	340
7		45	405	5445	10	350
8		75	300	5325	20	320
9		75	300	5325	20	330
10		75	300	5325	20	340
11		75	300	5325	20	350
12		105	245	5705	30	320
13		105	245	5705	30	330
14		105	245	5705	30	340
15		105	245	5705	30	350
16	[BPY][TFSI]	40	360	5160	10	320
17		40	360	5160	10	330
18		40	360	5160	10	340
19		40	360	5160	10	350
20		65	260	5135	20	320
21		65	260	5135	20	330
22		65	260	5135	20	340
23		65	260	5135	20	350
24		90	210	5610	30	320
25		90	210	5610	30	330
26		90	210	5610	30	340
27		90	210	5610	30	350

reported specific heat capacity, density, viscosity, thermophysical properties and vapor–liquid equilibria for the two hygroscopic RTILs, in particular 1-ethyl-3-methylimidazolium acetate and diethylmethylammonium methane sulfonate. According to the authors, both RTILs are fully miscible with water, possess negligible vapor pressure and may find an application in absorption cycles. The properties were reported in a whole concentration range between pure water and pure RTIL, for each RTIL. It was argued that both hygroscopic RTILs exhibit a similar behavior.

Lu and coworkers [35] employed the 1-butyl-3-methylimidazolium dibutylphosphate RTIL for separation of acetic acid from its mixtures with water. This RTIL showed a remarkable entrainer performance, since the boiling point difference for the water–acetic acid system increased from 17.88 K (at zero RTIL content) to 41.13 K (at ca. 59 w/w.%). Therefore, a new important application of RTILs was outlined. In turn, Ohmasa and coworkers [44] studied the capillary wave spectra on the surface of the 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide RTIL. The surface properties, such as surface excess entropy, surface tension, viscosity, were measured using the improved analysis method. It was concluded that the surface dipole moment density for this RTIL is much smaller as compared to that in 1-butyl-3-methylimidazolium hexafluorophosphate. An effect of the hexafluorophosphate anion will be in detail considered in the present work.

Ghatee and coworkers [45] skillfully used the capillary rise