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Densities and excess volumes of binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with aromatic compound at $T = (298.15$ to $313.15)$ K

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Abstract

The density of two binary mixtures formed by 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF6] with aromatic compound (benzyl alcohol or benzaldehyde) has been determined over the full range of compositions at the temperature range from 298.15 K to 313.15 K and at atmospheric pressure using a vibrating-tube densimeter (DMA4500). Excess molar volumes (V_m^E) have been obtained from these experimental results, and been fitted by the fourth-order Redlich–Kister equation. Our results show V_m^E decreases slightly when temperature increases in the systems studied. The results have been interpreted in terms of ion–dipole interactions and structural factors of the ionic liquid and these organic molecular liquids.

Keywords: Ionic liquids; 1-Butyl-3-methylimidazolium hexafluorophosphate; Binary mixtures; Density; Excess molar volumes

1. Introduction

Room-temperature ionic liquids (ILs) are a class of organic salts that are comprised entirely of ions and are liquids at conditions around room temperature in their pure state. They are non-volatile, thermally stable and highly polar, are attracting growing interest as alternatives to conventional molecular liquids [1–8]. The ILs have been considered as solvents for reactions, as absorption media for gas separations, as the separating agent in extractive distillation, as heat transfer fluids, for processing biomass, and as the working fluid in a variety of electrochemical applications (batteries, capacitors, solar cells, *etc.*) [7–13]. Due to their unique physical and chemical properties, some of them have been used as lubricants [14] and in biocatalysis [15,16] with great advantages.

Despite their importance and interest, detailed knowledge of the physicochemical properties of ionic liquids has not been studied systematically. Particularly, properties of the mixtures of ionic liquids with organic molecular liquids that are paramount for the design of many technological processes are very limited [5,17–20], which greatly restrict their applications and further development. Thus, there is a need for thermophysical property data of ionic liquids. The 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF6]) is historically one of the most important and the most commonly investigated ionic liquids. Thermodynamic functions such as heat capacities, densities, and enthalpy changes for [bmim][PF6] have been reported at different temperatures [21–23]. However, the data on volumetric properties of ionic liquids are rather limited.

In recent yeas, the reaction of the benzenyl alcohol (or benzaldehyde) in the ionic liquid [bmim][PF6] is actively studied [24–30]. To the best of our knowledge, the excess molar volume, V_m^E, is a helpful parameter in the design of the technological processes of the reaction. Furthermore, there are no experimental data available in the literature for ([bmim][PF6] + benzyl alcohol, or benzaldehyde) over

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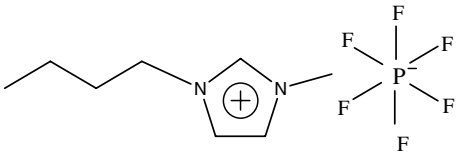

FIGURE 1. Molecular structure of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate.

the entire composition range at $T = (298.15$ to 313.15 K). This has stimulated the following work.

In this paper, we determined experimentally the density for the mixtures of the ionic liquid, 1-butyl-3-methylimidazolium hexaflurophosphate [bmim][PF6] (whose molecular structure is shown in figure 1) with benzenyl alcohol or benzaldehyde over the entire composition range at $T = (298.15$ to $313.15)$ K and at atmospheric pressure. The excess molar volumes, V_m^E, were reported for every system investigated. The results are discussed in terms of the ion–dipole interactions between the cation of the ionic liquid and the aromatic compounds, and their effect on the association between $[bmim]^+$ and $[PF6]^-$ of the ionic liquid.

2. Experimental

2.1. Materials

The ionic liquid, [bmim][PF6], was prepared and purified by using the procedures described by other workers [31,32]. It was washed several times with water to decrease the chloride content. It was determined that no precipitation of AgCl occurred by the addition of $AgNO_3$ to the wash water. The Cl^-content, measured with a Cl^--specific electrode using the standard addition method, was $48 \cdot 10^{-6}$ for [bmim][PF6]. To reduce the water content and volatile compounds to negligible values, vacuum (<1.0 kPa) and moderate temperature to 353 K were applied to the [bmim][PF6] samples for several days, always immediately prior to their use. The samples were analyzed by Karl Fisher titration and showed a mass% of water lower than $100 \cdot 10^{-6}$ for [bmim][PF6].

Other reagents, such as benzyl alcohol (AR, mass fraction >0.99) and benzaldehyde (AR, mass fraction >0.985)used in the experiments, were purchased from Shanghai Chemical Factory. Reagents were used without further purification. During the course of the experiments, the purity of the solvents was monitored by density measurements.

2.2. Apparatus and procedure

Mixtures were prepared by mass on the molality concentration scale. Every precaution was taken to minimise contamination by water. The densities of pure compounds and mixtures were measured by means of an Anton Paar DMA 4500 vibrating-tube densitometer with estimated accuracy of ± 0.05 kg · m^{-3}. In order to check the purity of the substances, their density were determined at $T = 298.15$ K and compared with the literature values [33–35]. As listed in table 1, the agreement is good. Gas chromatographic studies showed no evidence of appreciable impurities in reagents.

TABLE 1
Densities at $T = 298.15$ K of the pure components, and comparison with the literature

	ρ/(kg · m^{-3})	
	This work	Literature
Benzyl alcohol	1044.85	1041.46[a]
Benzaldehyde	1043.61	1044.37[b]
[bmim][PF6]	1369.74	1367.88[c]

[a] Reference [33].
[b] Reference [34], at $T = 293.15$ K.
[c] Reference [35].

All the measurements were made at several different thermostatted temperatures, where temperature stability was better than ± 0.002 K and the accuracy ± 0.01 K.

All samples were prepared by mass using a balance with the precision of $\pm 1 \cdot 10^{-4}$ g, and then partially degassed at the desired measurement temperature for 3 h by means of an ultrasonic heated bath to prevent the formation of gas bubbles in the densimeter capillary at higher temperatures. Attention was paid to the changes in the composition of the samples during weighing and partial degassing. To diminish this effect, the samples were weighed, degassed, and stored in vessels designed and recommended by Takenaka *et al.* [36]. Use of these vessels ensured that the composition calculated from weighed amounts of pure substances corresponded most accurately to the actual composition of the mixture sample without being necessary to take account the amount of substances in the vapour phase. The vessels are of a special shape, with a negligibly small vapour space left (<0.25 cm^3 compared to the total cell volume of 10 cm^3). They are tightly sealed with Teflon stoppers during the operations. To avoid formation of bubbles in the volatile liquid benzyl alcohol (or benzaldehyde) inside the vibrating tube of the densimeter, injection is carried in room temperature and slowly raised to desired temperatures. All molar quantities are based on the relative atomic mass table of 1986 issued by IUPAC [37].

The experimental uncertainty in the mole fraction composition is less than $\pm 5 \cdot 10^{-5}$, in density is approximately $\pm 1 \cdot 10^{-4}$ kg · m^{-3}, and in $V_m^E \pm 2 \cdot 10^{-4}$ cm^3 · mol^{-1}.

3. Results

The experimental density (ρ) for {[bmim][PF6] (1) + benzyl alcohol (2)} and {[bmim][PF6] (1) + benzaldehyde (2)} binary mixtures, as a function of [bmim][PF6] mole fraction (x) at the temperature range from $T = (298.15$ to $313.15)$ K are presented, respectively, in tables 2 and 3.

The V_m^E for binary mixtures of $\{x$[bmim][PF6] + $(1 - x)$(organic molecular liquids)$\}$ over the entire composition range was calculated from density data at the tem-