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Densities and dynamic viscosities of ionic liquids having 1-butyl-3-methylimidazolium cation with different anions and *bis*(trifluoromethylsulfonyl)imide anion with different cations in the temperature range (283.15 to 363.15) K

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ABSTRACT

Ionic liquids have been regarded as promising alternatives to conventional volatile organic solvents. For effective employment of ionic liquids as solvents in various industrial set-ups, the knowledge of their common physical properties is essential. Densities and dynamic viscosities of seven common and popular ionic liquids in the temperature range (283.15 to 363.15) K at 10 K interval are presented. In order to assess the role of the structure of the ionic liquid cation and anion, the selected ionic liquids are comprised of two groups. First group of four ionic liquids is constituted of same 1-butyl-3-methylimidazolium ([bmim$^+$]) cation and hexafluorophosphate [PF_6^-], ethylsulfate [$CH_3CH_2OSO_3^-$], trifluoromethysulfonate [$CF_3SO_3^-$], and bis(trifluoromethylsulfonyl)imide [$(CF_3SO_2)_2N^-$] anions, and the second group of four ionic liquids is constituted of same [$(CF_3SO_2)_2N^-$] anion and 1-methyl-1-propylpiperidinium [pmpip$^+$], *N*,*N*,*N*-trimethylethanolammonium [choline$^+$], 1-ethyl-3-methylimidazolium [emim$^+$], and [bmim$^+$] cations. Decrease in density with increasing temperature is found to follow a simple linear expression for all ionic liquids. Anion of the ionic liquid appears to control the density more than the cation. Density and its temperature dependence depend on the number of fluorine atoms present in the anion of the ionic liquid followed by the molar mass. The temperature dependence of the dynamic viscosity of the ionic liquids is found to be better described by a Vogel–Ful cher–Tamman (VFT) model as opposed to an Arrhenius expression. The two ionic liquids with aromatic imidazolium cations have relatively lower dynamic viscosities as compared to the two with non-aromatic cations.

1. Introduction

Among the alternatives to currently used solvents, major interest has been garnered by the ionic liquids due to their unique and tunable physicochemical properties. Among the key properties of ionic liquids, negligible vapor pressure, good thermal stability, high solubility, and non-flammability are the most noteworthy [1–6]. Because of their several remarkable features, ionic liquids have become solvents of curiosity by academicians and industrialists alike. Recognizing the inherent application potentials of ionic liquids, researchers have intensively explored and reported on the physical properties of ionic liquids [7–13]. Knowledge regarding key fundamental physicochemical properties of ionic liquids and the relation to the structure of the ionic liquids is still lacking in literature. Among the important physicochemical properties, density and dynamic viscosity play key role in both academia and industries. Various pharmaceutical and biotechnological industries and chemical engineering processes require knowledge of density and dynamic viscosity and their temperature dependence as essential piece of information. Density and dynamic viscosity are routinely used properties in both industrial and academic research as well. Furthermore, density and dynamic viscosity are essential parameters that help develop a solubilizing milieu and play a major part in chemical transformations in solution [14,15].

In this paper, we report temperature-dependent densities and dynamic viscosities of two sets of ionic liquids in the temperature range (283.15 to 363.15) K at 10 K intervals. While the first set is constituted of four ionic liquids having same 1-butyl-3-methylimidazolium ([bmim$^+$]) cation and hexafluorophosphate [PF_6^-], ethylsulfate [$CH_3CH_2OSO_3^-$], trifluoromethysulfonate [$CF_3SO_3^-$],

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and bis(trifluoromethylsulfonyl)imide [$(CF_3SO_2)_2N^-$] anions, ionic liquids in the second set have the same anion [$(CF_3SO_2)_2N^-$] and 1-methyl-1-propylpiperidinium [$pmpip^+$], *N,N,N*-trimethylethanolammonium [$choline^+$], 1-ethyl-3-methylimidazolium [$emim^+$], and [$bmim^+$] cations (Fig. 1 shows structures of the ionic liquids used). The ionic liquids selected encompass widely varying structures and physicochemical properties. [$bmim^+$] ionic liquids with [PF_6^-] and [$(CF_3SO_2)_2N^-$] show low water-miscibility while those with [$CH_3CH_2OSO_3^-$] and [$CF_3SO_3^-$] are completely water-miscible. While [$CH_3CH_2OSO_3^-$] ionic liquids with [$bmim^+$] and [$emim^+$] have aromatic cations with different alkyl chains, [$pmpip^+$] and [$choline^+$] have non-aromatic cations. Presence of –OH functionality on [$choline^+$] affords further diversity to selected ionic liquids. We believe this selection of ionic liquids may afford information on the structural aspects of cation and anion of the ionic liquids on density and dynamic viscosity and their temperature dependence.

2. Experimental

2.1. Materials

Ionic liquids used are of the highest purity. Ionic liquid [choline][$(CF_3SO_2)_2N$] (99%) was purchased from Iolitec. Ionic liquids [bmim][PF_6], [bmim][CF_3SO_3], [pmpip][$(CF_3SO_2)_2N$], [bmim][$CH_3CH_2OSO_3$], [bmim][$(CF_3SO_2)_2N$] and [emim][$(CF_3SO_2)_2N$] were purchased from Covalent Associates, Inc., and they were of electrochemical grade (>99%). All ionic liquids were stored under argon in an Auto Secador desiccator cabinet. Before use, ionic liquids were rigorously dried under vacuum for at least 72 h. Karl-Fisher titrator was used next to assess water content of an ionic liquid prior to its use. Ionic liquid was dried further till the water content became less than or equal to 100 ppm. The description of the chemicals used together with their sources is provided in Table 1.

2.2. Methods

Densities (ρ) of the ionic liquids were measured using a Mettler Toledo, DE45 delta range density meter. The density measurement with the above–mentioned density meter was based on electromagnetically-induced oscillations of a U-shaped glass tube. The measurements were performed at 10 degree intervals in the temperature range (283.15 to 363.15) K. The standard deviation associated with the density measurement of ionic liquids in the entire temperature range of investigation is estimated to be ±0.005 g cm^{-3}. The dynamic viscosities (η) were measured with a Peltier-based (resolution of 0.01 K and accuracy <0.05 K) automated Anton Paar microviscometer (model AMVn) having calibrated glass capillaries of different diameters (1.6, 1.8, 3.0, and 4.0 mm). This instrument is based on the rolling-ball principle, where the steel ball rolls down the inside of inclined, sample-filled calibrated glass capillaries. The deviation in η of ionic liquids in the entire temperature range of investigation is estimated to be ±2%. Tables 2 and 3 present comparison of densities and dynamic viscosities, respectively, of the ionic liquids measured on our instrumentation with those available in literature [16–51].

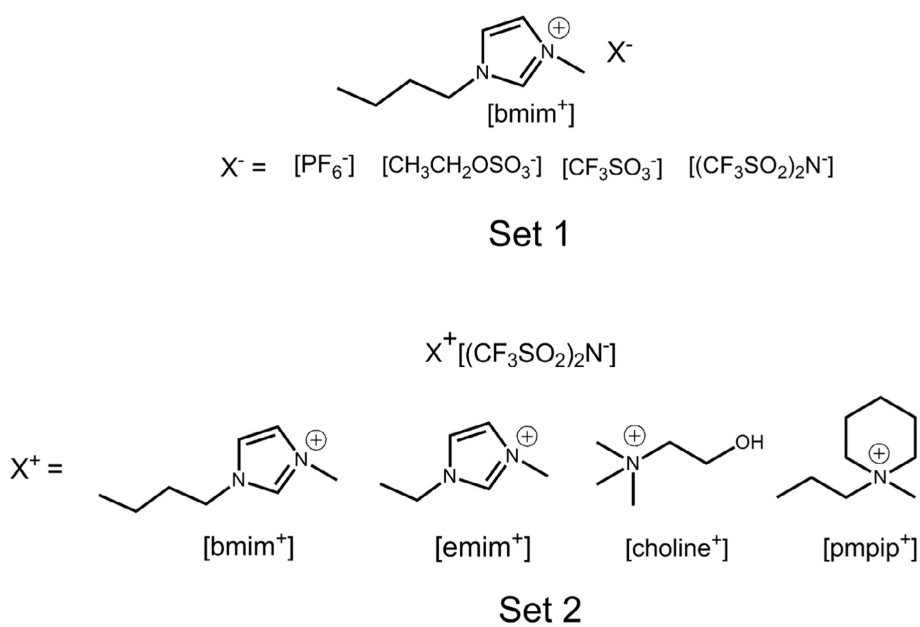

Fig. 1. Structure of the ionic liquids used.

Table 1
Description of the Chemicals Used in this Work. The Purity of the Studied Ionic Liquids are Shown in Certificate of Analysis given by Covalent Associates (see Supporting Information). Water contents are before and after each measurement.

Chemical	Molar Mass (g/mol)	Source	Purity (% mass)	Purification done	Water content (ppm)
[bmim][PF_6]	284.2	Covalent Associates	≥99	Vacuum-drying	<100
[bmim][$CH_3CH_2OSO_3$]	264.5	Covalent Associates	≥99	Vacuum-drying	<100
[bmim][CF_3SO_3]	288.3	Covalent Associates	≥99	Vacuum-drying	<100
[bmim][$(CF_3SO_2)_2N$]	419.4	Covalent Associates	≥99	Vacuum-drying	<100
[emim][$(CF_3SO_2)_2N$]	391.3	Covalent Associates	≥99	Vacuum-drying	<100
[pmpip][$(CF_3SO_2)_2N$]	422.4	Covalent Associates	≥99	Vacuum-drying	<100
[choline][$(CF_3SO_2)_2N$]	384.3	Iolitec	≥99	Vacuum-drying	<100