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Surface tension measurements of imidazolium-based ionic liquids at liquid–vapor equilibrium

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Abstract

A series of high quality 1-alkyl-3-methylimidazolium-based ionic liquids are synthesized and used for studying their surface tension. The capillary rise method is used for measuring the surface tension of I^-, Cl^-, $PF_6{}^-$, and $BF_4{}^-$ salts in the temperature range 298–393 K. The capillary apparatus is evacuated and sealed under vacuum. The experimental results show that surface tension of these compounds depend systematically on temperature.

For ionic liquids containing a butyl alkyl chain, the contribution of the anion to the surface tension is found to be in the order of $I^- > Cl^- > PF_6{}^- > BF_4{}^-$. As the chain length of the alkyl group is increased, the surface tension decreases and approaches the surface tension of alkyl fluids of the same chain length.

The surface entropy decreases smoothly as the chain length increases while the surface energy decreases rather sharply. This resembles the behavior of normal liquids, molten salts, and molten metals. Comparison with literature suggests that the complete removal of water and dissolved atmospheric gases as well as sufficient thermal equilibrium would produce a highly correlated and thus accurate surface tension of ionic liquids.

Keywords: Capillary rise method; Imidazolium-based ionic liquids; Salts of chloride; Iodide; Hexafluorophosphate; Tetrafluoroborate; Surface tension measurement at liquid–vapor equilibrium; Surface entropy; Surface energy

1. Introduction

Recent studies on ordinary physical properties of ionic liquids (ILs) suggest that they are outstanding good and non-coordination solvents of organic and inorganic solutes [1]. The lack of measurable vapor pressure makes the ILs a favorable replacement for volatile liquids, which is an important issue in green chemistry. An IL is an organic salt and its microscopic structure is usually composed of a large cation with low order of molecular symmetry. Hence, the unstable lattice structure lowers the melting point to well-below room temperature. ILs have commonly a high thermal stability at temperatures as high as 200–250 °C and this makes them attractive solvents for a vast variety of chemical and physical applications [1].

The use of such an attractive class of liquid in laboratory and industry is growing and thus precise physical specifications are very important. Imidazolium and pyridinum derivatives are the most common environmentally friendly ILs. Various ILs based on 1-alkyl-3-methylimidazolium have been synthesized and found to be suitable solvents as the substitute for conventional organic solvents in a variety of chemical applications [1]. Methods for the determination of equilibrium thermodynamic and transport properties of ILs have been investigated both experimentally and theoretically [1–3]. Enthalpies of vaporization [4,5], viscosities [6], thermal conductivity [7], aggregation behavior [8], and liquid–liquid interfacial tension [9] of imidazolium-based ILs have been investigated widely. These ILs are also used in multiphase homogeneous catalysis [10]. In this case one phase is chosen to dissolve the catalyst and a second phase contains the reactants and products. Such a process involves a solvation process. It is well-known that a solvation process is not only influenced by the solute–solvent interactions but also by the interfacial tension of solute and solvent [11]. The alkyl chain length of an IL has a marked influence on its density, viscosity, surface tension, melting point, and thermal stability [12–21]. A better understanding of the behavior of

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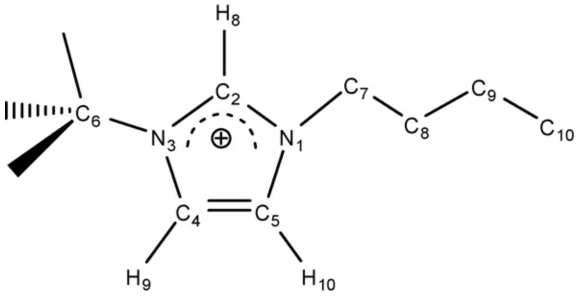

Fig. 1. The structure of 1-alkyl-3-methylimidazolium cation.

an IL as a solvent and as a homogeneous catalysis demands the knowledge of surface tension and its temperature dependence. Obtaining knowledge on the interfacial properties is extremely important to improve their selection and performance.

Essentially most ILs are hygroscopic and therefore they can contain significant amounts of water. Moisture can be extremely harmful in non-aqueous processes involving a variety of ILs. The water content of hydrophobic or hydrophilic 1-alkyl-3-methylimidazolium ILs also depends on the chain length as well as on the nature of the anion [19]. The water content has a strong effect on the physical properties of ILs [19]. Large change of the viscosity of ILs has been observed by a small amount of water. This change is particularly enhanced in the case of chloride salts, which has been attributed to hydrogen bond formation of the chloride anion with the hydrogen atom H_8 [22] (see Fig. 1).

The experimental surface tension of ILs reported in the literature is limited often to certain liquids at a specific temperature [23]. Temperature-dependent surface tension data for ILs is scarce and only three data sets have been reported in literature. The surface tension of 1-butyl-3-methylimidazolium hexafluorophosphate [bmim]PF_6 has been measured in the range 293–400 K. The dried liquid sample has been transferred to a glove box under argon atmosphere for the measurement of surface tension by the maximum bubble pressure method [24]. Another paper reports the surface tension measurement by the ring method of variety of dried ILs including 1-alkyl-3-methyl imidazolium salts of Cl^-, Br^-, $PF_6{}^-$, and $BF_4{}^-$, in the temperature ranges up to 360 K [15]. The surface entropy (negative of the temperature dependence of surface tension) of [bmim]PF_6 by the first paper is different from the second paper. This difference may be attributed to the level of accuracy of the method and the experimental conditions. In the third study, reported as conference abstract [25], the experimental surface tension of pure imidazolium-based ILs has been measured in the temperature range 288–343 K by the ring method. The effect of water content and temperature has been investigated. Very recently the surface tension of two ionic liquids, [hmim]PF_6 and [hmim]BTI (1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)), have been measured by the maximum bubble pressure method for the assessment of the order–disorder transition at the liquid/vapor interface [26]. Another recent paper reports the surface tension measurement of aqueous solutions of imidazoluim-based ionic liquids at 25 °C by the ring method for studying the critical micelle concentration [27].

Further measurements of the surface tension of ILs as a function of temperature provides more data for comparison, motivates improving the experimental methods, provide means to warrant accurate data, and allows characterization of surface properties with high reliability.

In this study we have synthesized 10 ILs and measured the surface tension of these ILs as a function of temperature by the capillary rise method. The ILs are 1-alkyl-3-methylimidazolium salts of chloride, iodide, hexafluorophosphate, and tetrafluoroborate. To achieve high accuracy, care is taken to eliminate water and dissolved gases and to isolate the capillary apparatus from atmospheric water vapor and other gases during the temperature-dependent surface tension measurements.

2. Experimental

2.1. Synthesis of ionic liquids

The ILs are synthesized according to standard methods by the reaction of 1-methylimidazole with an excess of the appropriate amount of haloalkane. The reactants are stirred without additional solvent at 70 °C for 72 h. The [$C_n$mim]X salt, where X = I or Cl and n is the number of carbon atoms in the alkyl chain, is then purified by repeated washing with ethyl acetate (minimum of six washes). The ethyl acetate is then removed from the product first by rotary evaporation (>90 min at 70 °C) before drying overnight at 70 °C under a vacuum [28]. Some details of this synthesis are as given in references [17,24].

2.1.1. [$C_n$mim]X

Equal molar amounts of haloalkane and 1-methylimidazole are added to a round-bottomed flask fitted with a reflux condenser and stirred for 24–72 h at 70 °C until two phases formed. The top phase, containing un-reacted starting material, is decanted and ethyl acetate is added with thorough mixing. The ethyl acetate is decanted followed by the addition of fresh ethyl acetate and this step is repeated twice. Washing with ethyl acetate should be sufficient to remove any un-reacted material from the bottom phase. After the third decanting of ethyl acetate, any remaining ethyl acetate is removed by heating the bottom phase to 70 °C and stirring under vacuum. The product, [C_4mim]Cl, is slightly yellow and may be a transparent solid at room temperature, depending on the amount of water present in that phase [17].

2.1.2. [$C_n$mim]PF_6

[$C_n$mim]Cl is transferred to a 2 l plastic container (lined with a perfluorinated material) followed by the addition of 500 ml deionized water. An aqueous solution of 60% HPF_6 in a 1.1:1 molar ratio is added. As HPF_6 is added, two phases formed, where [$C_n$mim]PF_6 is the bottom phase and HCl is the upper phase. The upper phase is decanted and 500 ml of water is added followed by vigorous shaking and mixing. After the mixture settled, the upper aqueous phase is decanted and more deionized water is again added.