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The physical properties of aqueous solution of room-temperature ionic liquids based on imidazolium: Database and evaluation

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Abstract

We report the systematic studies of the physical properties of systems involving imidazolium based ionic liquids and water. The measurements of density ρ, refractive index Δ_n, viscosity η, specific conductance κ and surface tension γ were made over the whole concentration range. The equivalent conductivity Λ_m was calculated. The physical properti`es of the solutions changed with the change of association between ionic liquid and water. The physical properties of the solutions also vary with the alkyl length on the cation and polarity of anion.

Keywords: Ionic liquids; Aqueous solution; Physical property; Density; Refractive index; Viscosity; Specific conductance; Surface tension

1. Introduction

Ionic liquids (ILs) are substances with melting points below 100 °C composed solely by ions (so "classical" high temperature molten salts are not included in this definition). At present, there are currently available interesting air-stable and water-stable ILs that are increasingly employed to progressively replace organic solvents in a variety of chemical process. This is mainly because they are nonvolatile, non-flammable, and in some cases, stable up to temperatures of 400 °C.

Nowadays, the applications of ionic liquids in polymer material processing have received a lot of attention [1,2,3]. Because water is a good solvents of RTILs, scientists usually use ionic liquids as solvent and water as coagulation. In order to obtain the basic data of this new polymer processing system, polymer/ionic liquid/water, we studied the rheological behavior of some polymer/ionic liquids solution such as polyacrylonitrile/BMIMCl solution, [4] poly(*m*-phenyleneisophthalamide)/BMIMCl solution, [5] and so on. Beyond doubt, the data of physical properties of ionic liquid/water solution is also very useful, for example, determining the concentration of the coagulation bath. Liu et al. [6] studied the physical properties of aqueous solution of ionic liquid $BMIMBF_4$ and proposed the schematic model of the structure change. Calvar et al. [7] studied the physical properties of the ternary mixture ethanol/water/BMIMCl. Nishida et al. [8] studied the physical and electrochemical properties of ionic liquid C_nMIMBF_4 and told us the advantages of ionic liquid electrolyte. Gutowski et al. [9] studied the mutual coexistence curve for the $BMIMCl/K_3PO_4$/water system by cloud point method and indicated the potential use in separations applications. Freire et al. [10] investigated the influence of the water content on the surface tensions of aqueous solution of ionic liquids $BMIMPF_6$ and $OMIMPF_6$. Cadena et al. [11] studied the volumetric properties of ionic liquid/CO_2 systems and indicated the network of cations and anions. Wang et al. [12] studied the aggregation behavior of $[BMIM]BF_4$ and C_nMIMBr (n=4,6,8,10,12) in aqueous solutions by conductivity measurement. Xu et al. [13] reported conductivity and viscosity of AMIMCl/water/ethanol system from 293.15 K to 333.15 K. Up to now, though many papers reported the physical properties of aqueous solution of ionic liquids and analyzed the physical origin of the micro-structures, there are not enough for us to support the application. Therefore, this work is focused on the physical properties of density, refractive index, viscosity, conductivity and surface tension over the whole concentration range. The basic research of how

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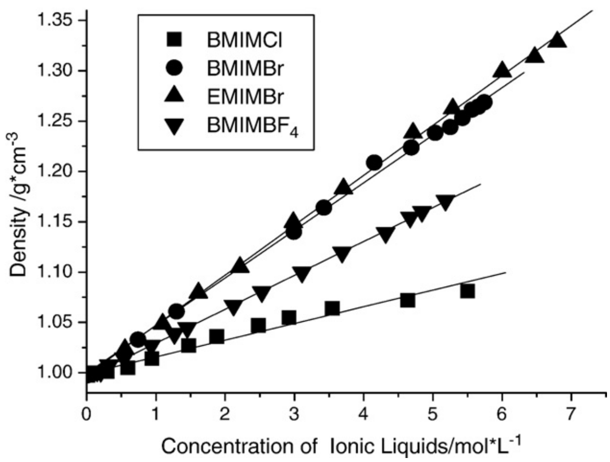

Fig. 1. Concentration dependence of density for aqueous solution of ionic liquids.

the components and different structure of ionic liquids affects the physical properties gives us more necessary information.

2. Experimental

2.1. Materials

The chlorobutane, chloropropene, bromoethane, bromobutane, 1-methylimidazole, ethyl acetate, acetone and sodium tetrafluoroborate were supplied by Sinopharm Chemical Reagent Co., Ltd (AR). Ionic liquids were prepared based on the reported procedures [14].

2.2. Density

The densities of the samples were determined by gravimetric analysis measuring the weight of the sample in a 25 ml calibrated density bottle. Each measurement was repeated three times at 25±0.1 °C and the average values were calculated.

2.3. Refractive index

All measurements were made with a 2WAJ Abbe's refractive index instrument. Deionized water was used as a reference for calibration. All measurements were taken at 25±0.1 °C and repeated three times. Average values were calculated.

2.4. Viscosity

The viscosities of the samples were measured with an Ostwald viscometer. For each analysis, a 10 ml sample was used and the measurements were performed three times. The temperature of the sample was maintained to 25±0.1 °C via an external temperature controller. The average values were calculated.

2.5. Surface tension

The surface tension of each sample was measured with OCA30 of Dataphysics Company. For each analysis, the Pendant Drop Method was used and the surface tension was calculated by Young–Laplace equation. All measurements were taken at 25±0.1 °C and repeated three times, average values were calculated.

2.6. Conductivity

The conductivity measurements were carried out with a DDSJ-308A conductivity instrument. Before and after measurements, the instrument was calibrated with KCl solution. The temperature of the sample was kept constant at 30±0.1 °C. Each measurement was repeated three times and the average values were calculated.

3. Results and discussion

3.1. Density and refractive index

The ideal molar volume equation:

$$V_m = x_1 V_1 + x_2 V_2$$
$$V_m = (x_1 \mathrm{MW}_1 + x_2 \mathrm{MW}_2)/d_m = x_1(\mathrm{MW}_1/d_1) + x_2(\mathrm{MW}_2/d_2)$$

can be transformed into

$$d_m = \varphi_1 d_1 + \varphi_2 d_2$$

where:

V	Molar volume
d	Density
MW	Molar mass
φ	Volume fraction

subscripts m, 1, 2: binary mixture, liquid 1, liquid 2.

Fig. 1 shows the curves of the density of solution versus molar concentration of ionic liquids. According to the ideal molar volume equation, the curve of the density of ideal solution is linear. As Fig. 1 shows, the density of solution versus molar concentration of ionic liquids obeys the ideal molar volume equation as an ideal solution. Similarly, the linear refractive index versus molar concentration is pretty much what would be expected for an ideal solution (see Fig. 2), given the vastly different sizes of water versus the ionic liquids. From the linear

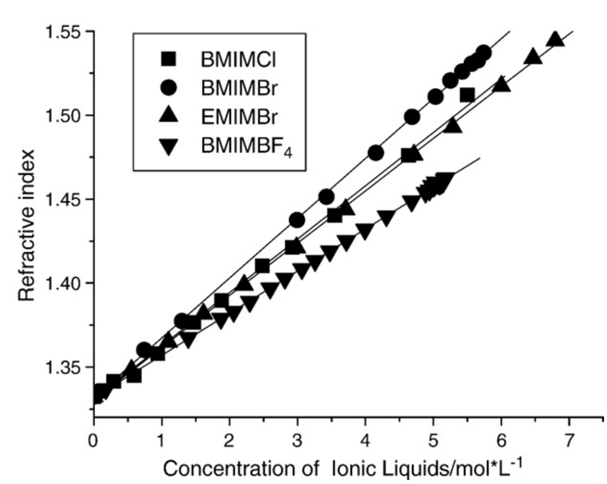

Fig. 2. Concentration dependence of refractive index for aqueous solution of ionic liquids.

Table 1
The linear relationship of the density and refractive index with the concentration of ionic liquids

Ionic liquid	Density–concentration relationship	Refractive index–concentration relationship
BMIMCl	$d=0.99922+0.01658C$	$n=1.33088+0.03177C$
BmimBr	$d=0.9996+0.0473C$	$n=1.33176+0.03564C$
EmimBr	$d=0.99762+0.04963C$	$n=1.33048+0.03113C$
$BMIMBF_4$	$d=0.9957+0.03369C$	$n=1.33192+0.02508C$

relationship of the density and refractive index with the concentration of ionic liquids (see Table 1), the concentration of water in ionic liquids can be estimated in the process of chemical separation. Rebelo et al. [15], Malham et al. [16], Gaillon et al. [17] and Gardas et al. [18] studied the volumetric properties of aqueous solutions of $BMIMBF_4$ or other similar ionic liquids by thermodynamic analysis and experimental method. All of them find that there is a nanostructure in the solution because of micelle or aggregation. There are differences between the behavior of the aqueous solutions of short chain imidazolium ionic liquid and long chain imidazolium ionic liquid. Many researchers studied the density of other ionic liquids aqueous solution and volumetric properties at different temperature [19,20,21,22].

Where d is the density (g ml^{-1}), n is the refractive index and C is the mole concentration of ionic liquids (mol L^{-1}).

Comparing with curves of BmimBr and EmimBr, the density of ionic liquids decreases and the refractive index increases with the length of alkyl chain increases, which is due to the bulginess of the volume of cation. There are no clear rules of the change of density with the anion.

3.2. Viscosity and surface tension

Other researchers found that the decrease of the viscosity of ionic liquids by the addition of cosolvents followed a different pattern depending on the nature of the cosolvents, possibly due to differences in polarities which led to different interactions with the ions in the RTILs [23,24]. In this study, the magnitude of the increase of viscosity of the mixture is great for the concentration of ionic liquid (see Fig. 3). When the ionic liquid concentration increases, the viscosity does not increase a great deal in the dilute solution but increase rapidly in the concentrated solution. The solution of ionic liquid BMIMCl or EmimBr is solidified when its concentration is higher than the critical value.

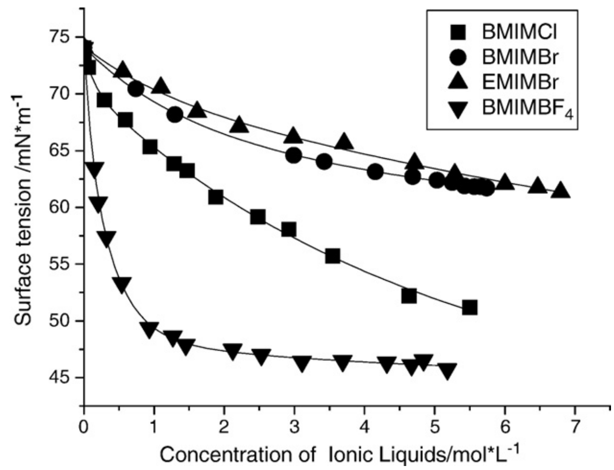

Fig. 4. Concentration dependence of surface tension for aqueous solution of ionic liquids.

As Fig. 4 shows, the surface tension of ionic liquids aqueous solution decreases while the concentration increases. Comparing with the other three ionic liquids, the effect of water on the surface tension of $BMIMBF_4$ shows a distinct trend. The surface tension of mixture decreased rapidly in dilute solution but almost did not change in the concentrated solution. The results show that $BMIMBF_4$ mainly acts as a surfactant in the aqueous solution. For cationic surfactant systems, the growth of micelle increases very strongly with increasing counter ion size, so the $BMIMBF_4$ has more obvious critical micelle concentration (c.m.c). Modaressi et al. [25] studied the surface tension of aqueous solutions of $BMIMPF_6$ and $BMIMCH_3SO_4$ which substituted with a short alkyl chain. Results of that study show that ionic liquids based on 1-alkyl-3-methylimidazolium salts are very active at the surfaces. In aqueous solution they

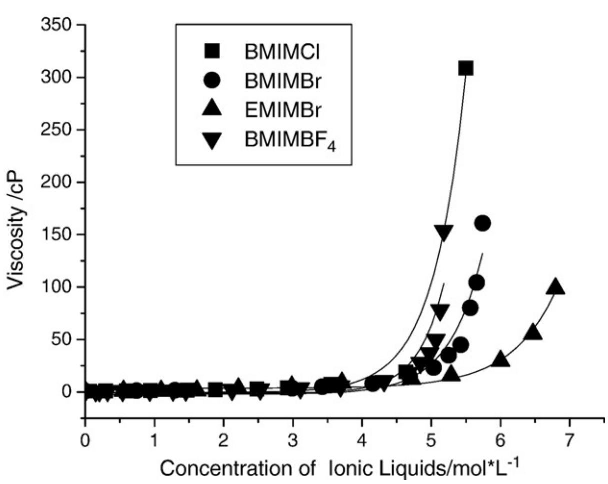

Fig. 3. Concentration dependence of viscosity for aqueous solution of ionic liquids.

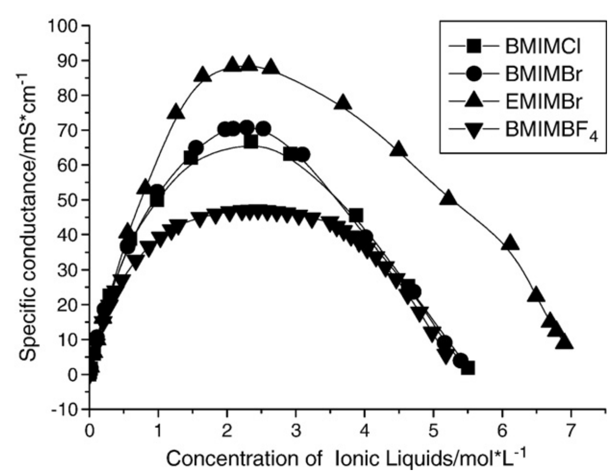

Fig. 5. Concentration dependence of specific conductance for aqueous solution of ionic liquids.

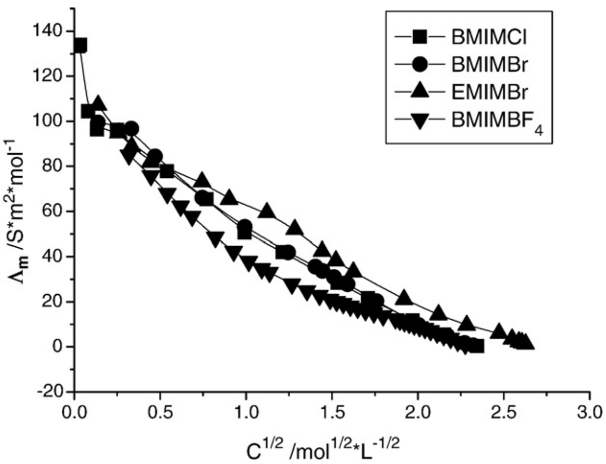

Fig. 6. Equivalent conductivity Λ_m versus square root of concentration of aqueous solution of ionic liquids.

form aggregates that self-assembly in 3D network. Other researchers also got similar results by surface tension and SFG measurement [26].

3.3. Conductivity

The plots of Fig. 5 suggest that the ionic liquid aqueous solution goes through two different regions: the water-rich region and the salt-rich region. Similar distinct regions in (Ag/TI)NO_3 and water systems were also identified by other researchers [27]. Mixtures of ionic liquids and water display the classical properties of concentrated saline solutions with a maximum conductivity. The conductivity increases sharply in the water-rich region and decreases linearly in the salt-rich region. The conductivity of ionic liquids aqueous solution increases when the hydrophilic of anion and the length of alkyl chain increases. The equivalent conductivity of ionic liquids is calculated (see Fig. 6). As we know, the equivalent conductivity of strong electrolytes such as sulfuric acid changes a little when the concentration increases. In opposition, the equivalent conductivity of weak electrolytes such as acetic acid decreases sharply at dilute region and charges a little when the concentration increases. The curve of equivalent conductivity of ionic liquids is different from either sulfuric acid or acetic acid. Equivalent conductivity decreases in the whole concentration range. Li et al. [28] studied the viscosity and conductivity of the mixtures formed from $BMIMBF_4$ with several common solvents. They found that the solvents of higher dielectric constant seem to have a larger effect on the viscosity and the conductivity of the solutions. They concluded that organic solvents enhance the ionic association of the ionic liquids, while water promotes significantly dissociation. Other researchers [29,30] also reported the similar result in the systems of ionic liquids based on imidazolium and water.

4. Conclusion

In conclusion, the effect of the components on the physical properties of aqueous solution of room-temperature ionic liquids was studied as can be used for engineering design. The physical properties changed sharply in different concentration. The mixture behaves as an ideal solution in the density and refractive index measurement. The concentration of water in ionic liquids can be estimated by the density and refractive index in the process of chemical separation. The trend of surface tension change of $BMIMBF_4$, which mainly acts as a cationic surfactant aqueous solution, is different from other three ionic liquids. The curve of equivalent conductivity of ionic liquids is different from either sulfuric acid or acetic acid. Interestingly water–ionic liquid interactions have been identified and discussed. The physical properties of the solutions also vary with the alkyl length on the cation and polarity of anion but the rule of the change is not very clear.

It is very important to understand the interactions between the traditional organic solvents just like water and the RTILs, which can be accomplished by the measurements of the physical properties. It is helpful to support the application of the RTILs in polymer processing system. More and more ionic liquids which can dissolve polymers will be synthesized because ionic liquid is designable. The study on synthesis and physical properties of other polymer-dissoluble ionic liquids is under way.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molliq.2008.01.008.

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