Viscosities and Interfacial Properties of 1-Methyl-3-butylimidazolium Hexafluorophosphate and 1-Isobutenyl-3-methylimidazolium Tetrafluoroborate Ionic Liquids

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Room temperature ionic liquids (RTILs) are potential alternative solvents in chemical reaction or separation process. The viscosity of RTIL, interfacial properties of air−RTIL, organic compounds−RTIL, and solid−RTIL are of general importance. The viscosities of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and 1-isobutenyl-3-methylimidazolium tetrafluoroborate ([iBeMIM][BF_4]) ionic liquids (ILs) have been determined from (288.15 to 313.15) K. The surface tension/contact angle on solids of [BMIM][PF_6] and [iBeMIM][BF_4] ILs have been measured at 298.15 K. The liquid−liquid interfacial tension for [BMIM][PF_6] with 21 organic compounds have also been determined at 298.15 K. The relationship between the interfacial tensions and activity coefficients at infinite dilution of solutes in IL is discussed.

Introduction

Room temperature ionic liquids (RTILs) are considered as possible green solvents, which have many useful properties, such as non-volatility, non-flammability, thermal and chemical stability, wide liquidus range, and favorable solvency for many kinds of organic, inorganic, and polymeric compounds. Much of the interest in ionic liquids (ILs) has focused on their application to catalytic reaction, separation process, and electrochemistry, especially the use of imidazolium-based ILs.[1−3] Recent research indicates that RTILs are a potential alternative for conventional organic solvents to separate aliphatic/aromatic hydrocarbons, alkanes/alkenes, and olefin isomers.[4−7] In previous works, we have researched the separation of aromatic hydrocarbons from paraffins and the separation of hexene isomers using [BMIM][PF_6] or [iBeMIM][BF_4] ILs.[8−10] Although ILs have bigger separation ability than conventional organic solvents, such as dimethyl sulfoxide, sulfolane, or *N*-methyl pyrrolidone, the transport properties of ILs must be considered before their practical application to extraction or extractive distillation processes.

It is well-known that RTILs are generally viscous, which is unfavorable for their application in industrial process. There are some viscosity data of ILs in the literature. While for the same IL at the same temperature, such as for [BMIM][PF_6] at 293.15 K, different researchers give remarkably different results within the range of (201 to 382) mPa·s.[11−14] Accurate viscosity data of ILs are needed for understanding the physical property of ILs and designing task-specific ILs.

The interfacial properties of air−RTIL, organic compounds−RTIL, and solid−RTIL are also extremely important for the application of RTILs in the chemical industry because they determine the wetting ability, mixing degree, and phase separation speed. Also the liquid−liquid interfacial tension between organic compounds and RTIL give insight into the surface activity of solutes and RTIL itself.[15,16] The interfacial tensions between some hydrocarbons and [BMIM][PF_6] have been measured, and a quantitative structure−property relationship (QSPR) model for interfacial tensions and the structure descriptor of hydrocarbons has been developed. Until now, there has been little data on the interfacial properties of RTILs, which limits the utility of RTILs in chemical reaction, separation process, and electrochemistry.

In this paper, the viscosity of [BMIM][PF_6] and [iBeMIM][BF_4] ILs have been measured from (288.15 to 313.15) K. The surface tensions/contact angles on stainless sheet of [BMIM][PF_6] and [iBeMIM][BF_4] ILs have been measured at 298.15 K. The liquid−liquid interfacial tensions for [BMIM][PF_6] with 21 organic compounds have also been determined at 298.5 K.

Experimental Section

Chemicals. 1-Butyl-3-methylimidazolium ([BMIM][PF_6]) and 1-isobutenyl-3- methylimidazolium tetrafluoroborate ([iBeMIM][BF_4]) ILs were obtained from the Institute of Chemistry, Chinese Academy of Sciences. The crude IL including chloride impurity was diluted by a small amount of dichloromethane to lower the viscosity and filtered a couple of times by being passed through a silica column to remove chloride impurity. The organic liquid phase obtained from the filtration method was tested for the residual chloride salt through the concentrated $AgNO_3$ solution. No clear precipitation of AgCl was found by the naked eye, which means that chloride impurity was almost all adsorbed by silica. The water contents in the ionic liquids were determined by the Karl Fischer method. The water content in [BMIM][PF_6] and [iBeMIM][BF_4] was (430 and 480) ppm, respectively. The structures of IL products were characterized by FT−IR and NMR spectroscopy. The ILs were purified by vacuum evaporation for 12 h at 353 K before use. Pentane and other organic reagents were purchased from Shanghai Reagent

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Factory and Beijing Chemical Plant with purities > 99.0 mass %.

Experimental Procedure. The viscosities of [BMIM][PF_6] and [iBeMIM][BF_4] were measured from (288.15 to 313.15) K using the Brookfield DV-II+ Pro digital rotational viscometer with a rotational speed of 100 rpm. The uncertainty of the rotational speed was ± 0.1 rpm. About 2 mL of IL was put in a sample cup whose temperature was determined by a resistance temperature detector (RTD), and the temperature was controlled by a Brookfield TC-02 thermostat water bath. The uncertainty of temperature was ± 0.02 K. The accuracy of the viscometer was ± 1 % in the full range, and the repeatability was ± 0.2 % declared by the manufacturer. The expanded uncertainty in the viscosity measurements was estimated to be ± 1.24 % on the basis of the 95 % confidence level.

The surface tensions/contact angles on stainless sheet of [BMIM][PF_6] and [iBeMIM][BF_4] were measured using a JC2000A contact angle/surface tension meter with a data processing program. The accuracy of the contact angle/surface tension meter was ± 0.25°. The temperature of measuring chamber was kept at 298.15 K by an OMRON temperature controller with an accuracy of ± 0.1 K. The expanded uncertainties in the contact angle measurements were ± 2.46° for [BMIM][PF_6] and ± 1.02° for [iBeMIM][BF_4] on the basis of the 95 % confidence level. The surface tensions were measured using the pendant drop method. Ionic liquid, in a 10 mL flat-headed microsyringe, was extruded to slowly form a drop. The camera was focused so that the edge of the drop was clear. Then the drop was photographed with the camera, and the graphs were transferred to a computer and processed using the data processing program. The contact angle on a stainless sheet was measured using the same equipment. The stainless sheet was 15 mm long, 10 mm wide, and 1 mm thick. The stainless sheet was put in the square groove of the contact angle/surface tension meter after being cleaned. The ionic liquid drop was dripped down slowly from a 10 μL microsyringe to the sheet. The graphs of the drop on the sheet were taken and transferred to the computer. From the amplificatory photos, the contact angles were determined.

The surface tensions were calculated as follows:

$$\gamma = \frac{\Delta\rho g V}{2\pi r \phi\left(\frac{r}{V^{1/3}}\right)} \tag{1}$$

where $\Delta\rho$ is the difference between the densities of the measured ionic liquids and air, g is the gravitational constant, V is the volume of the detached drop, r is the outer tip radius, and $\varphi(r/V^{1/3})$ is a correction term determined by Earnshaw et al.[17] This term is used to correct for the liquid that remains on the tip of the capillary, tension forces that are not vertical, and the pressure difference across the curved drop surface. The major error resource for the pendant drop method is the determining of the drop volume. The drop diameter and the bottom coordinate must be determined from the drop graphs with great care. The expanded uncertainties in the surface tension measurements were estimated to be ± 2.1 $mN\cdot m^{-1}$ for [BMIM][PF_6] and ± 1.7 $mN\cdot m^{-1}$ for [iBeMIM][BF_4] on the basis of the 95 % confidence level.

The liquid−liquid interfacial tensions were determined using a rotated drop method by a XZD-3 interfacial tension/contact angle meter at 298.15 K. The temperature was controlled automatically by an electric heating system with an accuracy of ± 0.1 K. A rotational speed was 1200 rpm, and the uncertainty of rotational speed was ± 0.1 %. A drop of liquid is enclosed in a container filled with a denser liquid and subjected to sufficiently high rotation rates with respect to a horizontal axis. The light liquid will migrate to the axis of rotation and assume a cylindrical shape with hemispherical ends. This method holds true only if the liquids are in gyrostatic equilibrium (or rigid body rotation) (i.e., if every element of the liquid inside the rotating tube is stationary relative to the wall of the tube). Gyrostatic equilibrium is only attained at high enough rotation rates that gravitational forces perpendicular to the axis of rotation are negligible as compared with centrifugal forces. A schematic diagram of the drop under rotation at angular velocity ω is shown in Figure 1.

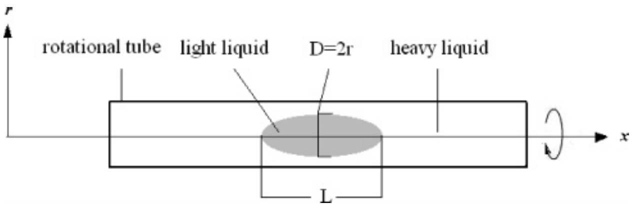

Figure 1. Schematic diagram of the drop under rotation.

The liquid−liquid interfacial tension σ can be obtained using the Vonnegut formula:

$$\sigma = \frac{1}{4}\omega^2 r^3 \Delta\rho f(L/D) \tag{2}$$

where ω is the rotational speed of centrifugal tube; $\Delta\rho$ is the difference between the densities of ILs and organic compounds; r and D are the radial radius and diameter of rotated drop, respectively; L is the axial length; and $f(L/D)$is a correcting factor being related to L/D, which can be looked up from an accompanied table supplied by the manufacturer of the equipment. This equation is only valid if L/D is greater than 4.

The liquid−liquid interfacial tension measurements were repeated for four times. The arithmetic mean for each case was accepted as the final experimental results. The expanded uncertainty in the liquid−liquid interfacial tensions measurements was estimated to be ± 1.31 % on the basis of the 95 % confidence level.

Because ILs tend to pick up moisture from the environment and the water contents of ILs have crucial influence on their properties, care should be taken during the preservation and measurements. The ILs were put into ground glass stoppered flasks, respectively. The bottlenecks of the flasks were sealed with Teflon tape to protect the ILs from moisture. Taking the IL from the flasks must be as quick as possible to reduce the exposure time. During the measurements of viscosity and liquid−liquid interfacial tensions, the ILs were enclosed in a circular groove or tube. The contact time of ILs with air was so short that the small quantity of absorbed moisture does not affect their properties markedly. For the measurements of surface tension/contact angles, the ILs were put into a microsyringe, the second or third drop was used as measuring object, and the photo of the drop was made quickly. Therefore, the moisture absorbed during the measurements was negligible.

Results and Discussion

Viscosity. The viscosities of [BMIM][PF_6] and [iBeMIM][BF_4] were listed in Table 1. The literature results[11−14] are also given in Table 1.

It can be seen from Table 1 that there are notable differences in the viscosity data of [BMIM][PF_6]. The trace impurity in the IL maybe is the major influencing factor. For example, the dissolved water will decrease the viscosities of hydrophobic ILs

Table 1. Viscosities of [BMIM][PF$_6$] and [iBeMIM][BF$_4$] from T = (288.15 to 313.15) K

	η/mPa·s		
T/K	[BMIM][PF$_6$]		[iBeMIM][BF4]
288.15	400.2	(231,[b] 521[c])	214.2
293.15	294.0	(308,[a] 201,[b] 369,[c],382[d])	158.7
296.15	245.8		133.4
298.15	217.9	(173,[b] 272[c])	118.5
301.15	182.7		100.4
303.15	162.9	(173,[a] 149,[b] 202[c])	88.9
305.15	145.1		79.8
308.15	123.2	(127,[b] 158.4[c])	68.0
311.15	104.0		58.6
313.15	95.0	(109,[b] 120,[c] 119[d])	53.4

[a] Ref 11. [b] Ref 12. [c] Ref 13. [d] Ref 14.

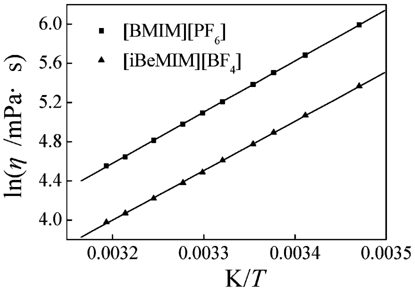

Figure 2. Plot of experimental values of ln η against 1/T and fitted curve for [BMIM][PF$_6$] and [iBeMIM][BF$_4$].

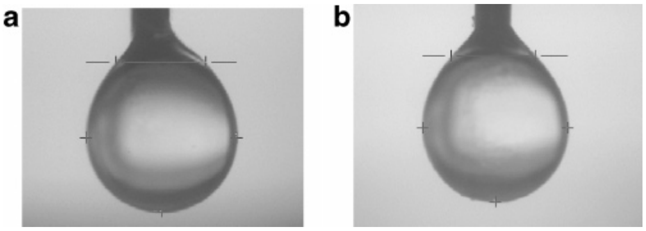

Figure 3. Photos of ionic liquids drops. (a) [BMIM][PF$_6$]. (b) [iBeMIM]-[BF$_4$].

drastically.[18] Furthermore, the temperature control and the rotational speed are also important error sources. Because the temperature of the rotary barrel was controlled by a thermostat water bath for the rotational viscometer, there are some difference between the water bath temperature and the rotary barrel temperature. The temperature must be kept constant for at least 30 min to eliminate this difference. In general, the viscosities of ILs are higher by 1 or 2 orders of magnitude than that of the normal organic solvents. From the experimental data and the measurement results of the literature,[19,20] it can be seen that for the imidazolium-based IL the anion of IL has a major influence on the viscosity. And the viscosity of IL with the [PF$_6$]-anion is about one time greater than an IL with the [BF$_4$] anion. The temperature dependence of viscosity was studied for the two ILs over the temperature range of (288.15 to 313.15) K, and the plots were fitted with the logarithmic form of the Arrhenius equation:

$$\ln \eta = \ln \eta^{\infty} + E_{\eta}/RT \tag{3}$$

The activation energy for viscous flow E_η and the viscosity at infinite temperature η^∞ were calculated from the slope and intercept respectively of the Arrhenius plot. E_η is the energy barrier that must be overcome in order for the ions to move past each other in the RTIL. The larger is E_η, the harder it is for the ions to move past each other. The viscosity at infinite temperature η^∞ is governed purely by the geometric structure of the ions in the RTIL. The viscosity data of two ILs were well fitted by the Arrhenius equation. In this paper, the standard deviations (SD) were calculated by applying the following expression:

$$\mathrm{SD} = \sqrt{\frac{\sum_{i=1}^{N} (Y_{i,\mathrm{exp}} - Y_{i,\mathrm{cal}})^2}{N}} \tag{4}$$

The standard deviations were 0.00417 and 0.00631, respectively, for the Arrhenius regression of [BMIM][PF$_6$] and [iBeMIM][BF$_4$]. The Arrhenius plots for [BMIM][PF$_6$] and [iBeMIM][BF$_4$] are shown in Figure 2. The E_η of [BMIM][PF$_6$] and [iBeMIM][BF$_4$] are (43.47 and 41.97) kJ·mol^{-1}, respectively. The η^∞ are (5.271 × 10^{-6} and 5.260 × 10^{-6}) mPa·s, respectively.

Surface Tensions. The pictures for [BMIM][PF$_6$] and [iBeMIM][BF$_4$] drops are shown in Figure 3. The surface tensions for two ILs at 298.15 K are (53.1 and 51.8) mN·m^{-1}, respectively. Compared with the surface tensions of dimethylsulfoxide (43.0 mN·m^{-1}) and *N*-methyl pyrrolidone (41.0 mN·m^{-1}) at the same temperature,[21] the surface tensions of these ILs are greater than the normal organic solvents, which is an advantage in the phase separations when ILs are used as extraction solvents.

Contact Angles. The photos of the ionic liquid drops on the stainless steel sheet are shown in Figure 4. The contact angles for [BMIM][PF$_6$] and [iBeMIM][BF$_4$] on the stainless steel sheet are 69.5° and 62.7°, respectively. Therefore the two ILs can wet the surface of stainless steel but cannot spread significantly. Because of the high viscosity and large contact angles of the ILs, they are prone to form thick liquid film on the surface of stainless steel equipment, which can result in flooding problems when ILs are used as extraction solvents. New ILs with low viscosity and small contact angle on the surface of steel or ceramics are urgently needed. High-performance equipment such as a centrifugal extractor is the other method for the viscous system.

Liquid−Liquid Interfacial Tensions. The experimental interfacial tensions between [BMIM][PF$_6$] and organic solutes (such as alkanes, 1-hexene, aromatic hydrocarbons, water, alcohols, esters, and propanoic acid) are listed in Table 2. Because the mutual solubility of ketones, formic acid, or acetic acid with IL is so high that a stable interface cannot be formed, the rotated drop method is not appropriate for these organic liquids.

From the experimental data in Table 2, it can be seen that the liquid−liquid interfacial tensions are connected with the carbon chain length, degree of unsaturation, and functional group. For different organic liquids with the same carbon number, the interfacial tensions change as following sequence: alkanes > alkene > alcohols > aromatic hydrocarbons. The interfacial tensions were found to decrease with increase of the degree of unsaturation. The interfacial tensions of alkanes are similar. For aromatic compounds, the interfacial tensions increase with an increasing carbon chain length, similar to what is observed with alcohols. The change of interfacial tensions with carbon numbers of alcohols is shown in Figure 5. For primary linear alcohols, there is an approximate linear relationship between the interfacial tension and carbon number (SD =

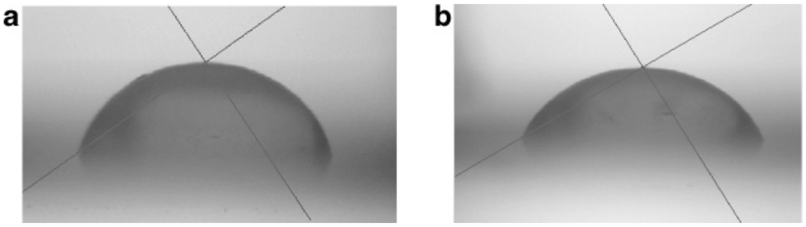

Figure 4. Photos of ionic liquid drops on the stainless sheet. (a) [BMIM][PF_6]. (b) [iBeMIM][BF_4].

Table 2. Interfacial Tension between Organic Compounds and [BMIM][PF_6] at 298.15 K

organic compounds	σ/mN·m^{-1}	organic compounds	σ/mN·m^{-1}
pentane[a]	13.65	ethanol[a]	1.222
hexane[a]	13.39	butanol	4.706
octane[a]	14.29	pentanol	5.325
cyclohexane[a]	13.15	hexanol	5.556
1-hexene[a]	10.42	heptanol	6.410
benzene[a]	2.209	octanol[a]	7.385
toluene[a]	3.000	decanol	7.516
ethyl benzene[a]	3.995	dodecanol	8.788
styrene[a]	1.793	ethyl acetate	11.69
water	10.06	butyl acetate	0.4344
propanoic acid	3.292		

[a] Ref 9.

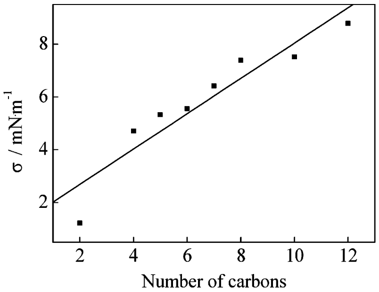

Figure 5. Linear regression of the interfacial tensions with carbon numbers for primary linear alcohols.

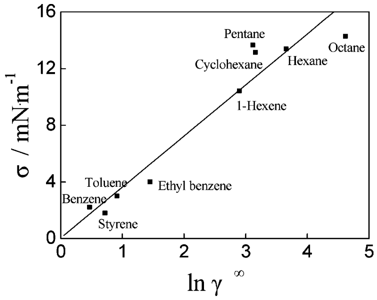

Figure 6. Variation of the interfacial tensions with ln γ^{∞} for hydrocarbons.

0.731 and if ethanol is excluded, SD = 0.274). The interfacial tensions between IL with ethyl acetate and butyl acetate are remarkably different, which is likely to have a connection with the O—C═O group.

The liquid−liquid interfacial tension is probably caused by the asymmetry force field of interfacial molecules and can be regarded as a measurement of molecular interactions. For alkanes, 1-hexene, and aromatic compounds, the interfacial tensions and activity coefficients at infinite dilution γ^{∞} of solutes in IL[8] are compared in Figure 6.

From Figure 6, it can be seen that there is an approximate linear relationship between ln γ^{∞} and interfacial tensions for all the researched hydrocarbons at 298.15 K. While for different groups of homologous compounds, such as benzene, toluene, and ethylbenzene or pentane, hexane, and octane, the slopes of lines are different. In fact, there are complicated relationships between the interfacial tension and ln γ^{∞}. Further detailed research is required.

Conclusions

The viscosities of [BMIM][PF_6] and [iBeMIM][BF_4] ILs have been determined from (288.15 to 313.15) K. The surface tensions/contact angle on solids of these two ILs have been measured at 298.15 K. The liquid−liquid interfacial tension for [BMIM][PF_6] with 21 organic compounds have also been determined at 298.15 K. The relationship between the interfacial tensions and activity coefficients at infinite dilution of solutes in IL is discussed. The high viscosities and large contact angles of ILs are unfavorable characteristics for their application in separation processes. New IL with low viscosity and small contact angle on the surface of equipment or high-performance apparatus such as centrifugal extractor are likely to satisfy the requirements when ILs are used in the extraction process.

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