Conductivities and Viscosities of the Ionic Liquid [bmim][PF_6] + Water + Ethanol and [bmim][PF_6] + Water + Acetone Ternary Mixtures

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The conductivities and viscosities of the room-temperature ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) + water + ethanol and [bmim][PF_6] + water + acetone ternary mixtures were determined in the temperature range from 288.15 K to 308.15 K, and the mole fraction of the solvents in the mixtures was up to 0.48. The conductivities of the mixtures increased with increasing concentration of the solvents and temperature in the solvent concentration range studied. An increase in temperature or solvent concentration results in reduction in the viscosities of the mixtures.

Introduction

Room-temperature ionic liquids (ILs) are novel organic salts composed of anions and cations. Owing to their unique chemical and physical properties, such as high thermal stability, low melting temperature, and excellent solubility in many polar and nonpolar organic substances, they have been recognized as alternative solvents for organic synthesis[1−4] and separations.[5−7] Because of their negligible volatility, ILs are also considered as environmentally benign solvents which can replace traditional organic solvents. Furthermore, the lengths of the substituted alkane chains of the cationic core and the anionic precursors can be tailored, which makes them versatile "tunable solvents" for diverse technologies. In light of their wide electrochemical voltage windows, ionic liquids are attracting increased attention for use in solar batteries,[8−9] electrochemical capacitors,[10] superoxide electrochemistry,[11,12] and electrochemical synthesis.[13]

Physical properties of different ILs have been reported in the literature, including conductivity and viscosity.[14,15] In practice, besides ILs, the systems usually contain other components. Therefore, the physical properties of the mixtures are crucial for various applications, and many mixtures containing ILs have been investigated. For example, the phase behaviors of supercritical (SC) CO_2 + IL,[5,16] water + IL,[17] and ethanol + water + [bmim][PF_6],[18−19] the conductivity[20] and the viscosity[21] of the supercritical CO_2 + [bmim][PF_6] mixture, and the effect of impurities on the viscosity of [bmim][PF_6][22] have been reported recently.

Up to now, most studies related with ILs are limited to binary mixtures. In this work we determined the conductivities and viscosities of [bmim][PF_6] + water + ethanol and [bmim][PF_6] + water + acetone ternary mixtures at different conditions. Study of ternary mixtures is of importance because many applications require complex mixtures (e.g. reaction systems).

Experimental Section

Materials. Ethanol (>99.8%) and acetone (99.9%) were produced by Beijing Chemical Reagent Factory. Deionized water with a conductivity of 2×10^{-7} S·cm^{-1} was used. [bmim][PF_6] was prepared using the procedures reported by other authors.[23] The IL was dried at 50 °C in a Teflon beaker under vacuum (about 10^{-4} bar) for 3 days before use. The concentration of water was 0.1 wt %, and the residual chloride in the IL was 0.002 mol/L, which were determined by the apparatus and procedures used in our previous work.[20]

Conductivity. The conductivity was determined with a conductivity meter produced by Shanghai Precision & Scientific Instrument Co., LTD (DDS-307), which could be accurate to ±1.0%. All the liquid solutions were prepared gravimetrically using a DT-100 balance with an accuracy of 0.0001 g (Shanghai Scientific Instrument Company). In the experiment, the solution and the electrode were sealed in a glass tube, which was placed in a constant temperature water bath. The temperature of the water bath was controlled with a Haake-D8 controller, and the temperature fluctuation was less than ±0.05 K. It was estimated that the accuracy of the conductivity data was better than ±3%.

Viscosity. The viscosity was determined by a traditional technique (Ubbelohde viscometer, according to Poiseuiele Law). The viscometer was calibrated using standard oils of different viscosities provided by the National Standard Bureau of China. The reproducibility of the measurements was better than ±1%, and it was estimated that the data were accurate to ±3%.

Results and Discussion

Conductivity. To verify the reliability of the apparatus, we first determined the conductivity of the [bmim][PF_6] at 298.15 K, and the result agreed very well with the literature value.[14]

Tables 1 and 2 list the conductivities of [bmim][PF_6] (1) + water (2) + ethanol (3) and [bmim][PF_6] (1) + water (2) + acetone (3) mixtures of different compositions in the temperature range from 288.15 to 308.15 K. The dependence of the conductivity on temperature and composition is illustrated in Figures 1 and 2. In the tables and figures, x_2 is the mole fraction of water, and x_3 stands for the mole fraction of ethanol or acetone.

The conductivities of the IL and the mixtures increase as temperature rises, as can be seen from Figures 1 and 2.

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Table 1. Conductivity (σ) and Viscosity (V) of [bmim][PF$_6$] (1) + Water (2) + Ethanol (3) Mixtures

T			$10^4\sigma$	V	T			$10^4\sigma$	V
K	x_2	x_3	S·cm^{-1}	mPa·s	K	x_2	x_3	S·cm^{-1}	mPa·s
288.15	0.20	0.00			298.15	0.31	0.31	122.0	
	0.00	0.20	30.2	200.6		0.35	0.35	142.2	
	0.14	0.06	29.8			0.00	0.48	79.8	30.1
	0.06	0.14	30.3			0.24	0.24	87.1	34.8
	0.10	0.10	29.5			0.34	0.14	85.5	
	0.20	0.20	60.6			0.14	0.34	86.4	
	0.31	0.31	101.8		303.15	0.20	0.00	42.9	99.2
	0.35	0.35				0.00	0.20	43.0	88.4
	0.00	0.48	68.0	48.0		0.14	0.06	42.3	
	0.24	0.24	73.3	54.7		0.06	0.14	43.4	
	0.34	0.14				0.10	0.10	42.1	
	0.14	0.34	72.6			0.20	0.20	80.3	
293.15	0.20	0.00	33.0	166.4		0.31	0.31	132.8	
	0.00	0.20	33.6	148.1		0.35	0.35	153.8	
	0.14	0.06	33.4			0.00	0.48	86.3	24.8
	0.06	0.14	34.6			0.24	0.24	95.5	27.2
	0.10	0.10	33.0			0.34	0.14	96.3	
	0.20	0.20	67.7			0.14	0.34	93.8	
	0.31	0.31	111.7		308.15	0.20	0.00	47.8	78.2
	0.35	0.35	130.9			0.00	0.20	47.5	71.5
	0.00	0.48	73.3	37.7		0.14	0.06	46.8	
	0.24	0.24	80.9	44.2		0.06	0.14	48.5	
	0.34	0.14				0.10	0.10	47.1	
	0.14	0.34	79.5			0.20	0.20	88.0	
298.15	0.20	0.00	37.2	128.7		0.31	0.31	140.5	
	0.00	0.20	38.0	113.7		0.35	0.35	162.5	
	0.14	0.06	36.8			0.00	0.48	93.3.	21.0
	0.06	0.14	38.7			0.24	0.24	103.1	23.3
	0.10	0.10	37.6			0.34	0.14	106.1	
	0.20	0.20	73.5			0.14	0.34	99.8	

Table 2. Conductivity (σ) and Viscosity (V) of [bmim][PF$_6$] (1) + Water (2) + Acetone (3) Mixtures

T			$10^4\sigma$	V	T			$10^4\sigma$	V
K	x_2	x_3	S·cm^{-1}	mPa·s	K	x_2	x_3	S·cm^{-1}	mPa·s
288.15	0.20	0.00			298.15	0.00	0.48	101.7	18.2
	0.00	0.20	29.8	165.0		0.14	0.34	108.0	
	0.10	0.10	31.5			0.24	0.24	169.1	25.8
	0.14	0.06	28.7			0.34	0.14	94.0	
	0.06	0.14	32.2			0.17	0.41	166.6	
	0.00	0.48	92.5	25.1	303.15	0.20	0.00	42.9	99.2
	0.24	0.24	157.7	37.3		0.00	0.20	42.9	79.8
	0.34	0.14	74.8			0.10	0.10	44.2	
	0.14	0.34	96.0			0.14	0.06	41.5	
	0.17	0.41	160.4			0.06	0.14	44.3	
293.15	0.20	0.00	33.0	166.4		0.00	0.48	106.1	16.0
	0.00	0.20	34.2	127.0		0.14	0.34	114.0	
	0.10	0.10	35.5			0.24	0.24	174.1	21.4
	0.14	0.06	33.6			0.34	0.14	106.9	
	0.06	0.14	35.9			0.17	0.41	170.3	
	0.00	0.48	96.5	21.2	308.15	0.20	0.00	47.8	78.2
	0.14	0.37	100.8			0.00	0.20	46.7	64.1
	0.24	0.24	165.0	31.0		0.10	0.10	49.5	
	0.34	0.14	86.0			0.14	0.06	47.0	
	0.17	0.41	162.9			0.06	0.14	48.7	
298.15	0.20	0.00	37.2	128.7		0.00	0.48	110.3	13.8
	0.00	0.20	37.5	100.2		0.24	0.24	178.9	18.6
	0.10	0.10	37.5			0.34	0.14	114.8	
	0.14	0.06	37.3			0.14	0.34	118.2	
	0.06	0.14	39.4			0.17	0.41	173.7	

The conductivity (σ) is related to the ion mobility and the number of charge carriers, which can be expressed by the following equation.[24]

$$\sigma = \sum n_i \mu_i q_i \tag{1}$$

where n_i is the number of charge carriers of species i, q_i is the charge, and μ_i is the mobility. An increase in temperature results in an increase in the mobility because the viscosity of the liquids is reduced. This is one of the main reasons for the enhancement of the conductivity with increasing temperature.

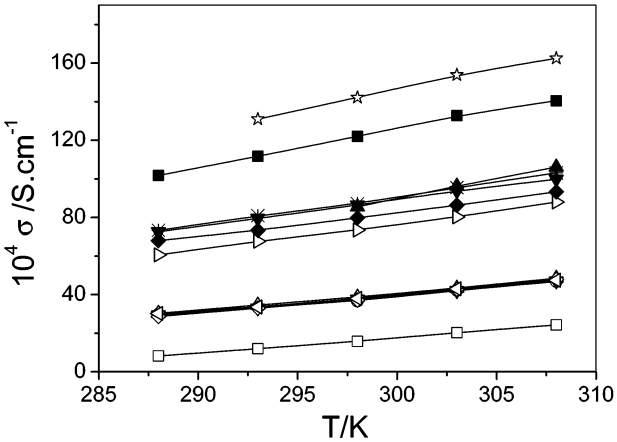

Figure 1. Dependence of the conductivity (σ) of [bmim][PF$_6$] (1) + water (2) + ethanol (3) mixtures on temperature and composition: □, [bmim][PF$_6$]; ○, $x_2 = 0.20$, $x_3 = 0.00$; △, $x_2 = 0.00$, $x_3 = 0.20$; ▽, $x_2 = 0.14$, $x_3 = 0.06$; ◇, $x_2 = 0.06$, $x_3 = 0.14$; open triangle pointing left, $x_2 = 0.10$, $x_3 = 0.10$; open triangle pointing right, $x_2 = 0.20$, $x_3 = 0.20$; ■, $x_2 = 0.31$, $x_3 = 0.31$; ☆, $x_2 = 0.35$, $x_3 = 0.35$; ▲, $x_2 = 0.34$, $x_3 = 0.14$; ▼, $x_2 = 0.14$, $x_3 = 0.34$; ∗, $x_2 = 0.24$, $x_3 = 0.24$; ◆, $x_2 = 0.00$, $x_3 = 0.48$.

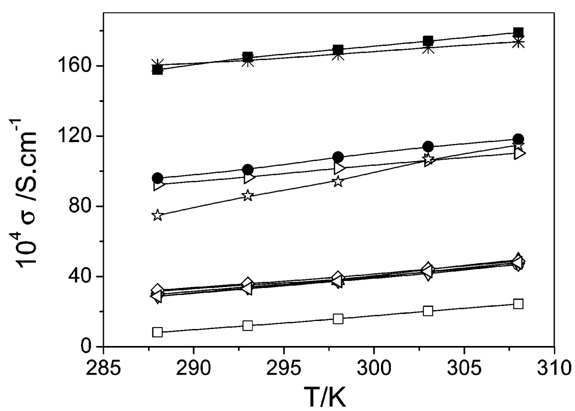

Figure 2. Dependence of the conductivity (σ) of [bmim][PF$_6$] (1) + water (2) + acetone (3) mixtures on temperature and composition: □, [bmim][PF$_6$]; ○, $x_2 = 0.00$, $x_3 = 0.20$; △, $x_2 = 0.10$, $x_3 = 0.10$; ▽, $x_2 = 0.14$, $x_3 = 0.06$; ◇, $x_2 = 0.06$, $x_3 = 0.14$; open triangle pointing left, $x_2 = 0.20$, $x_3 = 0.00$; open triangle pointing right, $x_2 = 0.00$, $x_3 = 0.48$; ■, $x_2 = 0.24$, $x_3 = 0.24$; ☆, $x_2 = 0.34$, $x_3 = 0.14$; ●, $x_2 = 0.14$, $x_3 = 0.34$; ∗, $x_2 = 0.17$, $x_3 = 0.41$.

Figures 1 and 2 also demonstrate that at a fixed temperature the conductivities of the binary and ternary mixtures increase with the concentration of the solvents. For both [bmim][PF$_6$] (1) + water (2) + ethanol (3) and [bmim][PF$_6$] (1) + water (2) + acetone (3) mixtures, the conductivities are nearly independent of the molar ratio of the two added solvents at $x_2 + x_3 = 0.2$. In other words, water, ethanol, acetone, ethanol + water, and acetone + water have similar effects on the conductivity of the IL as their concentrations are lowered. At the higher concentrations of the added solvents, the conductivity depends on both the total concentration of the added solvents and their molar ratios.

Viscosity. The viscosity data determined by different authors at 293.15 K were respectively 318 mPa·s (this work), 285.8 mPa·s,[22] and 371 mPa·s.[23] The results of this work agreed reasonably with the literature values consid-

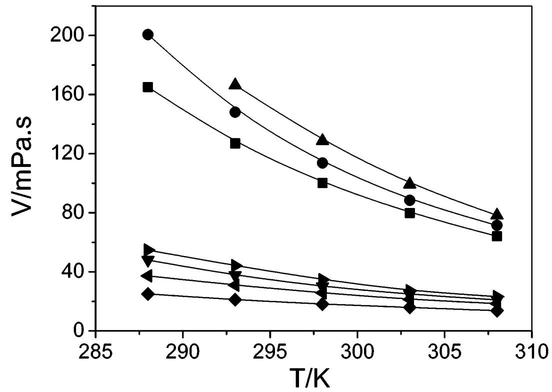

Figure 3. Viscosities (*V*) of the [bmim][PF_6] (1) + water (2) + ethanol (3) and [bmim][PF_6] (1) + water (2) + acetone (3) mixtures. [bmim][PF_6] (1) + water (2) + ethanol (3): ●, $x_2 = 0.00$, $x_3 = 0.20$; ▲, $x_2 = 0.20$, $x_3 = 0.00$; ▼, $x_2 = 0.00$, $x_3 = 0.48$; solid triangle pointing right, $x_2 = 0.24$, $x_3 = 0.24$. [bmim][PF_6] (1) + water (2) + acetone (3): ■, $x_2 = 0.00$, $x_3 = 0.20$; ◆, $x_2 = 0.00$, $x_3 = 0.48$; solid triangle pointing left, $x_2 = 0.24$, $x_3 = 0.24$.

ering the fact that the discrepancy of the data reported in the literature was relatively large.

The viscosities of [bmim][PF_6] (1) + water (2) + ethanol (3) and [bmim][PF_6] (1) + water (2) + acetone (3) mixtures are also presented in Tables 1 and 2 and are illustrated in Figure 3. As expected, an increase in temperature results in the reduction of the viscosity of the IL with and without the solvents. The viscosity of the mixtures decreases with increasing concentration of the solvents. For the binary mixtures with a mole fraction of 0.20, the viscosity follows the order water + IL > ethanol + IL > acetone + IL. For the binary or ternary mixtures with a total solvent mole fraction of 0.48, the viscosity follows the order water + ethanol + IL > ethanol + IL > water + acetone + IL > acetone + IL.

The variation of the viscosity with concentration of the solvents can explain partially the fact that the conductivity increases with increasing concentration of the solvents. Addition of solvents reduces the viscosity of the IL and, therefore, increases the mobility of the ions, resulting in large conductivity.

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