Electrical Conductivity of Caprolactam Tetrabutylammonium Bromide Ionic Liquids in Aqueous and Alcohol Binary Systems[†]

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The electrical conductivities of binary systems of caprolactam tetrabutylammonium bromide ionic liquid + solvent (solvent = water, ethanol, 2-propanol, 1-butanol) systems were measured at ionic liquid mole fractions from ($3.60 \cdot 10^{-4}$ to $6.82 \cdot 10^{-2}$) and temperatures from (290.55 to 342.25) K. The conductivities of the mixtures increase with increasing temperature, increasing concentration of ionic liquid, and decreasing caprolactam/tetrabutylammonium bromide mole ratio in the ionic liquid. The conductivity values of the binary systems (ionic liquid + solvent) decrease with the solvent in the following order: water > ethanol > 2-propanol > 1-butanol.

Introduction

Because of their unique chemical and physical properties, such as low volatility, nonflammability, high thermal stability, and high solvation capacity,[1−3] ionic liquids (ILs) have attracted a number of research groups to investigate their synthesis[4] and applications..[5−8] To know ILs well and develop applications with the most adequate ILs, it is necessary to know their physical properties. Experimental data for various physical properties are useful for the development of theoretical models to explain and predict them. The determination and understanding of basic physical and transport properties of ILs, such as density,[9,10] viscosity,[11] surface tension,[12] refractive index,[13] and thermal decomposition, are vital for process design and equipment options. In spite of the importance and utility of ILs, accurate values for many of their fundamental physical, chemical, and thermodynamic properties are still scarce.

Electrical conductivity (κ) is a measure of the movement of an electric charge. The knowledge of conductivity, one of the basic pure component properties for any substance, is necessary for many engineering applications. Vila[14] studied the influence of the anion and cation sizes on the temperature dependence of the electrical conductivity of nine different imidazolium-based ILs covering their liquid phase and observed that the electrical conductivity increased with the increasing anion size from Cl^- to BF_4^- and then decreased for larger anion sizes. Yu[15] found that κ for several ILs could be expressed and correlated as a function of temperature. The temperature dependence of κ was successfully correlated using an empirical modified Vogel−Tamman−Fulcher (VTF)-type equation. The electrical conductivity dramatically increased with water content up to a maximum and then decreased.[16] The conductivities of the mixtures increased with increasing concentration of the solvent and temperature.[17] Inoue[18] performed measurements on aqueous solutions of long-chain imidazolium ILs and determined the break points in the specific conductivity versus concentration plot, indicating that the molecular aggregates (i.e., micelles) were formed in aqueous solutions of these IL species.

To determine whether caprolactam (CPL) tetrabutylammonium bromide (TBAB) ILs are easy to ionize and the influence of solvents on the ionization and electrical conductivity of CPL TBAB ILs, the electrical conductivities of binary systems containing these ILs and various solvents (water, ethanol, 2-propanol, and 1-butanol) were determined at mole fractions from ($3.60 \cdot 10^{-4}$ to $6.82 \cdot 10^{-2}$) and temperatures from (290.55 to 342.25) K.

Experimental Methods

Materials. TBAB ($C_{16}H_{36}NBr$, CAS no. 1643-19-2, purity > 99.5 %) was obtained from Jintan Huadong Chemical Research Institute, China. White crystalline CPL powder ($C_6H_{11}NO$, CAS no. 105-60-2, purity > 99.5 %) was obtained from Shijiazhuang Refinery, China. Ethanol, 2-propanol, and 1-butanol (purity > 99.7 %) were obtained from Tianjin Kewei Chemical Institute. Water was deionized before use. The aqueous solutions were prepared by mass with a weighing accuracy of 10^{-4} g. The standard KCl solution used for the calibration of the conductivity meter was supplied by Merck and had $c = 0.1\ mol \cdot m^{-1}$ and an electrolytic conductivity of $1.415 \cdot 10^{-1}\ S \cdot m^{-1}$ at 298.15 K. ILs with different mole ratios of CPL and TBAB were synthesized and characterized in our laboratory following procedures reported elsewhere.[19] CPL TBAB ILs ($n_{CPL}/n_{TBAB} = 2, 4, 6$) were prepared by mixing 2, 4, and 6 mol of CPL, respectively, with 1 mol of TBAB. The water contamination of the ILs was determined using the Karl Fischer technique. The mole fraction of water in the ILs (x_{H_2O}) was less than 0.005.

Conductivity. The conductivities were determined using a conductivity meter produced by Shanghai Precision & Scientific Instrument Co., Ltd. (DDS-307). The uncertainty of the measurements was $1 \cdot 10^{-7}\ S \cdot m^{-1}$. All of the liquid solutions were prepared gravimetrically using an EL204 balance with an uncertainty of 0.0001 g [Mettler Toledo Instruments (Shanghai) Co., Ltd.]. The fixed volume of sample (50 mL) was placed in a glass tube that was immersed in a water bath whose temperature was controlled, and a precision thermometer was used to determine the temperature with an uncertainty of ± 0.01 K. The conductivity cell was zeroed in air and then calibrated using the standard KCl solution before it was put in the sample to be measured. It was estimated that the uncertainty of the conductivity data was less than 3 %.

Results and Discussion

Effect of Temperature and Concentration. In Tables 1 to 3 and Figures 1 to 7), we present the electrical conductivities of binary

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Table 1. Electrical Conductivities of Water, Ethanol, 2-Propanol, and 1-Butanol

	κ/S·m^{-1}			
T/K	water	ethanol	2-propanol	1-butanol
298.15	$2.667\cdot10^{-3}$	$4.130\cdot10^{-4}$	$5.201\cdot10^{-5}$	$4.401\cdot10^{-5}$
303.15	$2.873\cdot10^{-3}$	$5.045\cdot10^{-4}$	$7.000\cdot10^{-5}$	$5.552\cdot10^{-5}$
308.15	$3.225\cdot10^{-3}$	$5.842\cdot10^{-4}$	$7.503\cdot10^{-5}$	$6.580\cdot10^{-5}$
313.15	$3.492\cdot10^{-3}$	$6.438\cdot10^{-4}$	$8.081\cdot10^{-5}$	$6.903\cdot10^{-5}$
318.15	$3.751\cdot10^{-3}$	$7.114\cdot10^{-4}$	$8.425\cdot10^{-5}$	$8.000\cdot10^{-5}$

Table 2. Electrical Conductivities of the Binary Systems IL (1, $n_{CPL}/n_{TBAB} = 2$) + Solvent (2) from T = (298.15 to 318.15) K at the Mole Fraction x_1

	κ/S·m^{-1}			
T/K	water, $x_1 = 3.60\cdot10^{-4}$	ethanol, $x_1 = 1.16\cdot10^{-3}$	2-propanol, $x_1 = 1.52\cdot10^{-3}$	1-butanol, $x_1 = 1.83\cdot10^{-3}$
298.15	$6.427\cdot10^{-2}$	$1.746\cdot10^{-2}$	$4.990\cdot10^{-3}$	$3.661\cdot10^{-3}$
303.15	$7.073\cdot10^{-2}$	$1.859\cdot10^{-2}$	$5.072\cdot10^{-3}$	$3.678\cdot10^{-3}$
308.15	$7.115\cdot10^{-2}$	$1.929\cdot10^{-2}$	$5.190\cdot10^{-3}$	$3.706\cdot10^{-3}$
313.15	$7.153\cdot10^{-2}$	$1.936\cdot10^{-2}$	$5.497\cdot10^{-3}$	$3.750\cdot10^{-3}$
318.15	$7.348\cdot10^{-2}$	$1.942\cdot10^{-2}$	$5.605\cdot10^{-3}$	$3.781\cdot10^{-3}$

Table 3. Electrical Conductivities of the Binary Systems IL (1, $n_{CPL}/n_{TBAB} = r$) + 2-Propanol (2) from T = (298.15 to 318.15) K at the Mole Fraction $x_1 = 6.05\cdot10^{-3}$

	κ/S·m^{-1}		
T/K	$r = 2$	$r = 4$	$r = 6$
298.15	$1.297\cdot10^{-2}$	$1.026\cdot10^{-2}$	$7.932\cdot10^{-3}$
303.15	$1.337\cdot10^{-2}$	$1.065\cdot10^{-2}$	$8.243\cdot10^{-3}$
308.15	$1.371\cdot10^{-2}$	$1.098\cdot10^{-2}$	$8.545\cdot10^{-3}$
313.15	$1.403\cdot10^{-2}$	$1.125\cdot10^{-2}$	$8.689\cdot10^{-3}$
318.15	$1.432\cdot10^{-2}$	$1.146\cdot10^{-2}$	$8.865\cdot10^{-3}$

systems containing a CPL TBAB IL and solvent (water, ethanol, 2-propanol, or 1-butanol) at mole fractions from ($3.60\cdot10^{-4}$ to $6.82\cdot10^{-2}$) and temperatures from (290.55 to 343.65) K. The electrical conductivities of the binary systems containing IL ($n_{CPL}/n_{TBAB} = 2$) and water increased monotonically with increasing temperature. When the temperature reached 315 K, the κ value did not change much and maintained a relatively balanced state. As shown in Figures 5, 6, and 7, the electrical conductivities ultimately increased as the concentration of IL in the mixture increased. The variation of the conductivities for the four binary systems was similar to that for the binary systems [Bmim][BF_4] + H_2O and [Bmim][PF_6] + H_2O for temperatures ranging from (293.2 to 353.2) K, as reported elsewhere.[20]

Effect of Solvent. In Figure 6, over the range of κ values for the IL ($n_{CPL}/n_{TBAB} = 2$) in water and alcohols (ethanol, 2-propanol, and 1-butanol), the κ values of the binary systems decrease with the solvent in the following order: water > ethanol > 2-propanol > 1-butanol. From Table 1, we know the κ values of pure solvents decrease in the following order: water > ethanol > 2-propanol > 1-butanol. From the obtained experimental results, we see that the κ values for the binary system in water are larger than those in the alcohols. The permittivity of alcohol is much lower than that of water. The permittivities of the alcohols decrease in the following order: ethanol > 2-propanol > 1-butanol. The κ values decrease with decreasing permittivity. Thus, the κ values of the binary system decrease in the following order: water > ethanol > 2-propanol > 1-butanol.

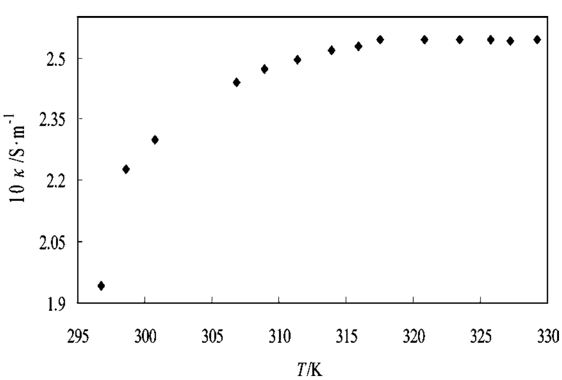

Figure 1. Electrical conductivity of the binary system IL (1, $n_{CPL}/n_{TBAB} = 2$) + water (2) as a function of temperature T at the mole fraction $x_1 = 6.05\cdot10^{-3}$.

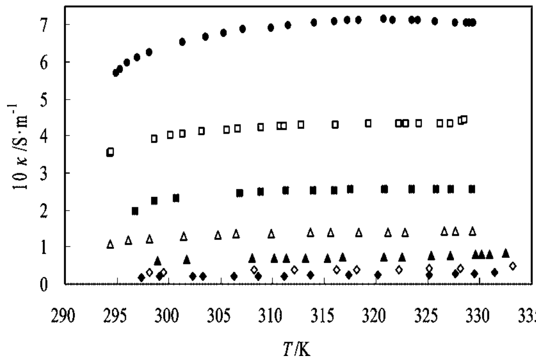

Figure 2. Electrical conductivities of the binary systems IL (1, $n_{CPL}/n_{TBAB} = 2$) + water (2) from x_1 = ($9.01\cdot10^{-5}$ to $5.73\cdot10^{-3}$) as functions of temperature T: ◆, $x_1 = 9.01\cdot10^{-5}$; ◇, $x_1 = 1.80\cdot10^{-4}$; ▲, $x_1 = 3.60\cdot10^{-4}$; △, $x_1 = 7.20\cdot10^{-4}$; ■, $x_1 = 1.44\cdot10^{-3}$; □, $x_1 = 2.88\cdot10^{-3}$; ●, $x_1 = 5.73\cdot10^{-3}$.

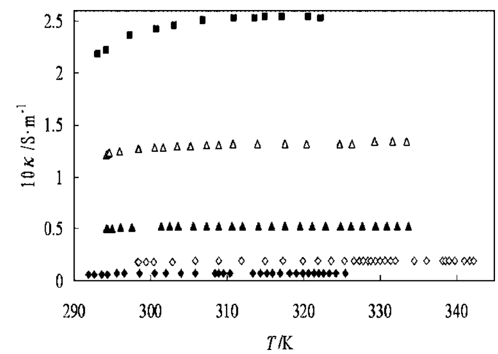

Figure 3. Electrical conductivities of the binary systems IL (1, $n_{CPL}/n_{TBAB} = 2$) + ethanol (2) from x_1 = ($2.90\cdot10^{-4}$ to $4.44\cdot10^{-2}$) as functions of temperature T: ◆, $x_1 = 2.90\cdot10^{-4}$; ◇, $x_1 = 1.16\cdot10^{-3}$; ▲, $x_1 = 4.63\cdot10^{-3}$; △, $x_1 = 1.71\cdot10^{-2}$; ■, $x_1 = 4.44\cdot10^{-2}$.

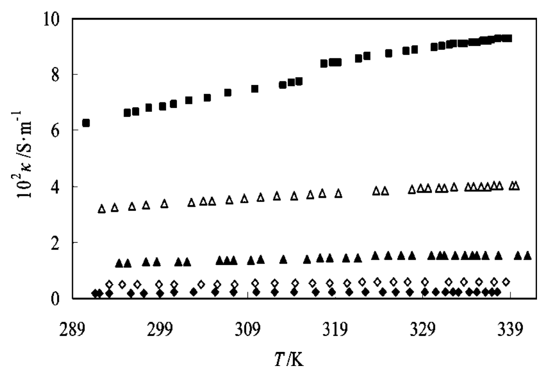

Figure 4. Electrical conductivities of the binary systems IL (1, $n_{CPL}/n_{TBAB} = 2$) + 2-propanol (2) from x_1 = ($3.80\cdot10^{-4}$ to $5.74\cdot10^{-2}$) as functions of temperature T: ◆, $x_1 = 3.80\cdot10^{-4}$; ◇, $x_1 = 1.52\cdot10^{-3}$; ▲, $x_1 = 6.05\cdot10^{-3}$; △, $x_1 = 2.23\cdot10^{-2}$; ■, $x_1 = 5.74\cdot10^{-2}$.

Effect of the Ratio of Caprolactam and Tetrabutylammonium Bromide. The influence of the changing the CPL/TBAB mole ratio in the IL was measured (Figure 7). The κ values of the binary systems IL + 2-propanol were measured and found

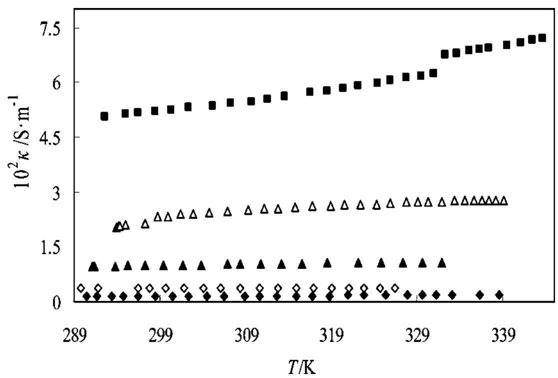

Figure 5. Electrical conductivities of the binary systems IL (1, $n_{CPL}/n_{TBAB} = 2$) + 1-butanol (2) from $x_1 = (3.80 \cdot 10^{-4}$ to $5.74 \cdot 10^{-2})$ as functions of temperature T: ♦, $x_1 = 4.57 \cdot 10^{-4}$; ◇, $x_1 = 1.83 \cdot 10^{-3}$; ▲, $x_1 = 7.27 \cdot 10^{-3}$; △, $x_1 = 2.67 \cdot 10^{-2}$; ■, $x_1 = 6.82 \cdot 10^{-2}$.

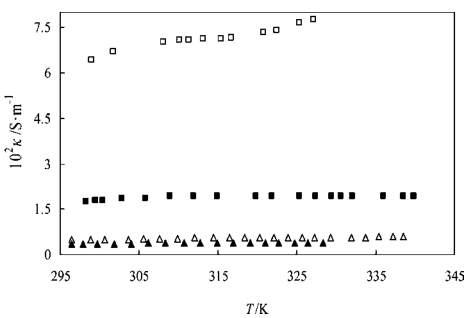

Figure 6. Electrical conductivities of the binary systems IL (1, $n_{CPL}/n_{TBAB} = 2$) + solvent (2) as functions of temperature T: □, water, $x_1 = 3.60 \cdot 10^{-4}$; ■, ethanol, $x_1 = 1.16 \cdot 10^{-3}$; △, 2-propanol, $x_1 = 1.52 \cdot 10^{-3}$; ▲, 1-butanol, $x_1 = 1.83 \cdot 10^{-3}$.

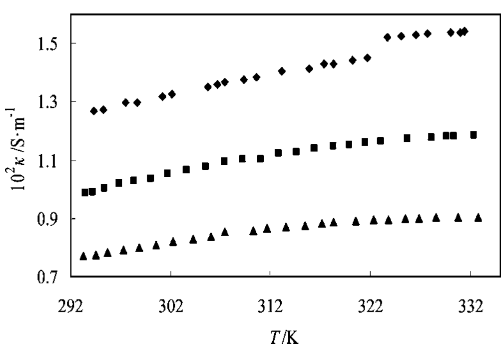

Figure 7. Electrical conductivities of the binary systems IL (1, $n_{CPL}/n_{TBAB} = r$) + 2-propanol (2) as functions of temperature T at the mole fraction $x_1 = 6.05 \cdot 10^{-3}$: ♦, $r = 2$; ■, $r = 4$; ▲, $r = 6$.

to decrease in the following order: ($n_{CPL}/n_{TBAB} = 2$) > ($n_{CPL}/n_{TBAB} = 4$) > ($n_{CPL}/n_{TBAB} = 6$). The κ value decreases with increasing CPL/TBAB mole ratio in the CPL TBAB IL (Table 2) because CPL is neutral and TBAB could ionize out of bromide anions and tetrabutylammonium cations.

Conclusions

In conclusion, the electrical conductivities of binary systems of ILs synthesized with three different values of the CPL/TBAB mole ratio and various solvents (water, ethanol, 2-propanol, and 1-butanol) were measured over a wide range of temperatures and concentrations of the binary systems. The conductivities of the solutions increased with increasing temperature and IL concentration and decreased with the solvent in the following order: water > ethanol > 2-propanol > 1-butanol. The κ values of the mixtures decrease with increasing CPL/TBAB mole ratio: ($n_{CPL}/n_{TBAB} = 2$) > ($n_{CPL}/n_{TBAB} = 4$) > ($n_{CPL}/n_{TBAB} = 6$).

Supporting Information Available:

Tables of electrical conductivities. This material is available free of charge via the Internet at http://pubs.acs.org.

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