Physicochemical Property Estimation of an Ionic Liquid Based on Glutamic Acid−BMIGlu

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A new amino acid ionic liquid (AAIL) based on glutamic acid, 1-butyl-3-methylimidazolium glutamine (BMIGlu), was prepared by Fukumoto's method and characterized by ^{1}H NMR, differential scanning calorimetry (DSC), and Karl Fischer moisture titration techniques. The density and surface tension of BMIGlu were measured in the temperature range of (308.15 to 343.15) K by the standard addition method (SAM), and then the values of pure BMIGlu were obtained through the linear extrapolation. Furthermore, the volume and surface properties were also discussed.

Introduction

Ionic liquids (ILs) have received much attention and are experiencing explosive growth in many areas of research and practical applications.[1–6] They present a wide range of complex physical and chemical behaviors,[7] including ambient vapor pressures ranging from ultra high vacuum to weakly volatile, a substantial variety of distinct condensed phases, including multiple crystal isomorphs, glasses, amorphous plastic and liquid crystal phases, and deep supercooling, and interesting dynamical and transport phenomena. Recently, amino acid ionic liquids (AAILs, "natural ILs" or "bio-ILs")[7–10] of the origin of natural amino acids have become a hot topic because of their excellent ability to dissolve biomaterials (DNA, cellulose, and carbohydrates) and great potential for applications in biological, medical, and pharmaceutical sciences. Therefore, the fabrication of new bio-ILs and exploration of their properties (especially the fundamental physicochemical properties) are essential and nonevasive issues for further applications. In this field, the estimation of thermodynamic quantities provides valuable insight into the origins of their special behaviors,[11–16] which is well-developed and is recommended in much recent work.

Herein, we report the preparation, characterization, and fundamental physicochemical property estimation (according to Fukumoto's method[9]) of a new AAIL based on glutamic acid: 1-butyl-3-methylimidazolium glutamine salt (BMIGlu). The density and surface tension of BMIGlu were measured in the temperature range of (308.15 to 343.15) K, and the values of pure BMIGlu were obtained through a good linear fit and extrapolation.[11,17] The volume and surface properties were also discussed by Glasser's theory.[12]

Experimental Section

Chemicals. The *N*-methylimidazole (Acros, analytical reagent) and chlorobutane (Beijing Co. Chemicals, analytical reagent) were distilled under nitrogen atmosphere. Glutamine was recrystallized twice from water and dried under reduced pressure. Deionized water was distilled in a quartz still, and its conductance was (0.8 to 1.2)·10^{-4} S·m^{-1}. Ethyl acetate and acetonitrile were distilled and stored over molecular sieves in tightly sealed glass bottles. Anion-exchange resin (type 717) was purchased from Shanghai Chemical Reagent Co. Ltd. and activated by regular method before use.

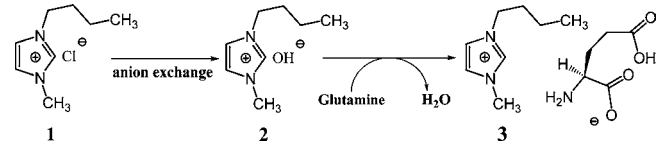

Figure 1. Scheme of the preparation of ionic liquids [Bmim][Glu] by the neutralization method: 1, [Bmim]Cl; 2, [Bmim][OH]; 3, [Bmim][Glu].

Preparation of the IL BMIGlu. The IL intermediate BMIC (1-butyl-3-methylimidazolium chloride) was synthesized by the method of Wilkes et al.[18] The melting point of the product is (339 to 341) K. Its NMR spectrum is in good agreement with that in the literature. The IL BMIGlu was prepared by a neutralization method (see Figure 1) according to Fukumoto et al.[9] Initially, aqueous 1-butyl-3-methylimidazolium hydroxide {[Bmim][OH]} was prepared from BMIC using anion-exchange resin in a 100 cm column. The onium hydroxide aqueous solution was added dropwise to a slightly excess glutamine aqueous solution. The mixture was stirred under cooling for 12 h. The water was evaporated under reduced pressure. Then the mixed solvent (volumetric ratio: acetonitrile/methanol = 9/1) was added to the mixture with vigorous stirring. The mixture was then filtered to remove excess glutamine. The filtrate was evaporated to remove solvents. Finally, the product of BMIGlu was dried in vacuo for 2 days at 353 K. The resulting IL BMIGlu was characterized by ^{1}H NMR spectroscopy (Varian XL-300) (Table S1 of the Supporting Information). Differential scanning calorimetric (DSC, Mettler-Toledo DSC823e) measurements showed that BMIGlu had no melting point, but a glass transition temperature (T_g) ranging from (237 to 242) K. The trace of DSC and T_g are listed in Figure S1 of the Supporting Information. The mass fraction of water content,

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Table 1. Values of Density, ρ, of the Ionic Liquid BMIGlu Containing Various Mass Fractions of Water w at the Temperature Range of (308.15 to 343.15) K[a]

	T/K							
$10^3\ w$	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
				ρ/g·cm^{-3}				
0.25			1.1862	1.1841	1.1819	1.1794	1.1770	1.1752
1			1.1853	1.1832	1.1810	1.1784	1.1761	1.1744
2.4			1.1838	1.1816	1.1795	1.1773	1.1750	1.1733
3.6			1.1823	1.1802	1.1784	1.1760	1.1739	1.1726
7.8	1.1838	1.1812	1.1782	1.1763	1.1748	1.1723	1.1708	1.1695
10.5	1.1811	1.1786	1.1755	1.1740	1.1721	1.1702	1.1684	1.1676
10.63	1.1808	1.1782	1.1751	1.1735	1.1719	1.1700	1.1680	1.1669
11.96	1.1792	1.1767	1.1741	1.1723	1.1712	1.1691	1.1671	1.1658
13.26	1.1779	1.1756	1.1726	1.1712	1.1698	1.1674	1.1660	1.1650
0	1.1924	1.1894	1.1863	1.1841	1.1819	1.1794	1.1770	1.1752
s·10^4	1.3	1.7	1.6	2.2	2.1	2.1	1.6	2.2

[a] w is the mass fraction of water. s is the uncertainty of fitting.

Table 2. Values of Surface Tension, γ, of the Ionic Liquid BMIGlu Containing Various Mass Fractions of Water w at the Temperature Range of (308.15 to 343.15) K[a]

	T/K							
$10^3\ w$	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
				γ/mJ·m^{-2}				
2.8	51.1	49.7	47.9	46.1	44.1	41.8	40.2	38.7
6.9	53.5	51.9	50	48.2	46.2	44.1	42.6	41.2
7.8	54.4	52.4	50.7	49.1	46.9	44.9	43.2	41.9
11.05	56.2	54.2	52.4	50.7	48.7	46.7	44.8	43.7
14.26	58.3	56.3	54.4	52.5	50.4	48.4	46.9	45.5
0	49.3	48	46.2	44.5	42.5	40.2	38.6	37.1
s·10	1.2	1.1	1.0	1.4	0.8	1.2	1.1	0.9

[a] w is the mass fraction of water. s is the uncertainty of fitting.

determined by a Karl Fischer moisture titrator (ZSD-2 type), was less than $3.0 \cdot 10^{-4}$.

Measurement of Density and Surface Tension. Because of the strong hydrogen bonding ability of the AAIL BMIGlu, it is hard to remove the small amounts of water in the IL by common methods. To eliminate the effect of the water impurity, the standard addition method (SAM) was applied to the measurement of densities and surface tensions.[11,17] According to the SAM, a series of samples of BMIGlu containing water were prepared.

The densities of pure water were first measured by a Westphal balance. The results were in good agreement with those in literature[19] at (308.15 to 343.15) K. The uncertainty[20] of the measurement was $\pm$ 0.0002 g·cm^{-3}. The temperature in the cell was regulated to $\pm$ 0.01 K with a solid thermostat. Then the densities of the samples were measured at the temperature range of (308.15 to 343.15) K. The values are listed in Table 1.

Using the tensiometer of the forced bubble method (DPAW type produced by Sang Li Electronic Co.), the surface tension of pure water was measured and was in good agreement with the literature.[19] The uncertainty of the measurement was $\pm$ 0.1 mJ·m^{-2}. The surface tension of water-containing BMIGlu samples was measured by the same method at the temperature range of (308.15 to 343.15) K and is listed in Table 2.

The values of density and surface tension at the temperature range of (308.15 to 343.15) K were plotted against the mass fraction of water content w. Good straight lines were obtained (see Figures 2 and 3). The intercepts of the fitted lines were the values of pure IL BMIGlu with no water (w = 0). The correlation coefficients, r, of all linear regressions are all larger than 0.99, and the uncertainty of fitting, s, is in the 10^{-4} order of magnitude. These facts show that the SAM is suitable for BMIGlu.

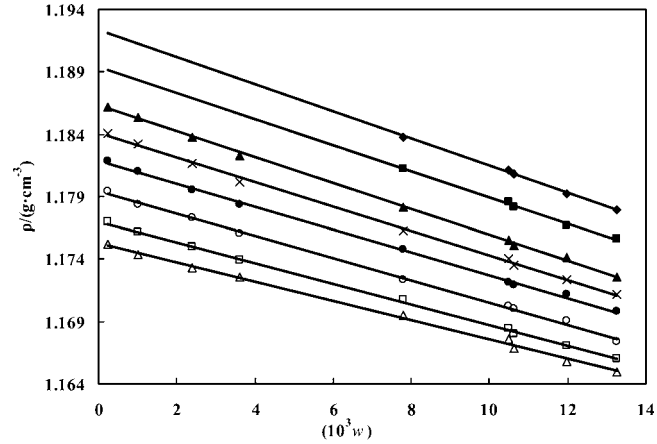

Figure 2. Plot of experimental data ρ vs the mass fraction of water ($10^3\ w$) in BMIGlu at a temperature range of (308.15 to 343.15) K: ◆, 308.15 K; ■, 313.15 K; ▲, 318.15 K; ×, 323.15 K; ●, 328.15 K; ○, 333.15 K; □, 338.15 K; △, 343.15 K; and —, linear fit of data.

Results and Discussion

The density and surface tension of pure BMIGlu (w = 0) at the temperature range of (308.15 to 343.15) K were obtained by experimental data measured by SAM and linear fitting extrapolation. They are listed in Tables 1 and 2, respectively.

Volumetric Properties of the BMIGlu. The natural log of the density values of pure BMIGlu (w = 0) at different

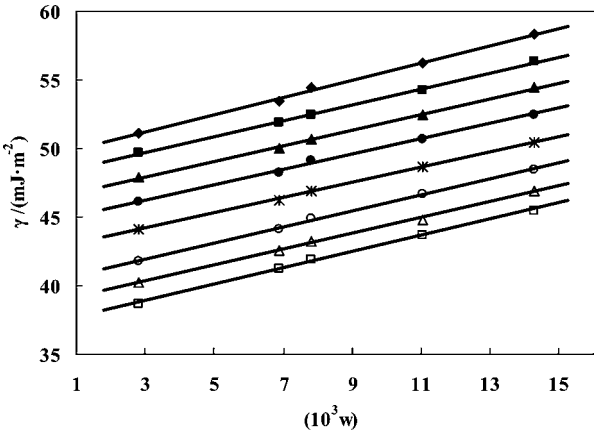

Figure 3. Plot of γ vs mass fraction of water (10^3 w) in BMIGlu at a temperature range of (308.15 to 343.15) K: ◆, 308.15 K; ■, 313.15 K; ▲, 318.15 K; ●, 323.15 K; ∗, 328.15 K; ○, 333.15 K; △, 338.15 K; □, 343.15 K; and —, linear fit of data.

temperatures versus T are plotted, and an empirical equation ln $\rho = 0.3972 - (3.84 \cdot 10^{-4})T$ is obtained (see Figure S2 of the Supporting Information). The fitting correlation coefficient, $r = 0.999$, with an uncertainty equal to $1.6 \cdot 10^{-4}$, is obtained, too. The slope of the equation is the thermal expansion coefficient of BMIGlu, α, as it is defined by following equation:

$$\alpha = -(\partial \ln \rho/\partial T)_p \quad (1)$$

Then the α derived from experimental data is $3.8 \cdot 10^{-4}$ K^{-1}.

From the experimental density values, the molecular volume, V_m, of pure BMIGlu is calculated through following equation:

$$V_m = M/(N\rho) \quad (2)$$

where M is molar mass of BMIGlu = 285.3/g·mol^{-1}, N is Avogadro's constant, and the value of ρ at 298.15 K, 1.1933 g·cm^{-3}, is obtained by linear extrapolation. The calculated value of V_m for BMIGlu is 0.3972 nm^3.

According to previous work,[17] the volume of the EMIGly is 0.2653 nm^3, less than that of BMIGlu, which should result from the larger volume of the cation [Bmim] and anion [Glu]. That means that the calculated value is reasonable.

In terms of Glasser's theory,[12,13] the standard molar entropy, S^0/J·K^{-1}·mol^{-1}, and the lattice energy, U_{POT}/kJ·mol^{-1}, of the BMIGlu at 298.15 K is calculated by following equations:

$$S^0/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 1246.5(V_m/\text{nm}^3 \text{ per formula}) + 29.5 \quad (3)$$

and

$$U_{POT}/\text{kJ}\cdot\text{mol}^{-1} = 234.6(V_m^{1/3}/\text{nm}^3) + 103.8 \quad (4)$$

So, the standard molar entropy of BMIGlu, S^0(298.2 K)/J·K^{-1}·mol^{-1} = 525, and the lattice energy of BMIGlu, U_{pot}(298.15 K)/kJ·mol^{-1} = 423, are obtained. In comparison with fused salts, the lattice energy of BMIGlu is much lower; for example, U_{POT} = 613 kJ·mol^{-1} for fused CsI at 298.15 K,[19] which has the smallest lattice energy among alkali halides. The low lattice energy is the underlying reason for forming an AAIL at room temperature as pointed out by Krossing.[21]

Properties of Surface for BMIGlu. In general, surface tension, γ, of many liquids almost linearly decreases, while temperature increases. The surface tension of pure BMIGlu ($w = 0$) obtained by the SAM at different temperatures is plotted versus T by the least-squares method, and a good straight line is obtained (see Figure S3 of the Supporting Information). The correlation coefficient is larger than 0.99. From the slope, $(\partial\gamma/\partial T)_p$, of the linear fitting, the surface excess entropy, $S_a = -(\partial\gamma/\partial T)_p = 36.3 \cdot 10^{-6}$ J·m^{-2}, is obtained.

Conclusions

Through the SAM, we determined the density and surface tension of the pure AAIL BMIGlu. Then, some derived physicochemical properties of the pure BMIGlu IL were obtained: the molecular volume $V_m = 0.3972$ nm^3, the standard molar entropy S^0(298.15 K)/J·K^{-1}·mol^{-1} = 525, the lattice energy U_{pot}(298.15 K)/kJ·mol^{-1} = 423, the surface excess entropy, S_a(298.15 K)/J·m^{-2} = $36.3 \cdot 10^{-6}$, and the thermal expansion coefficient of BMIGlu, α(exp) = $3.8 \cdot 10^{-4}$ K^{-1}.

Supporting Information Available:

(1) The ^{1}H NMR spectrum and the shifts of H of BMIGlu (Table S1). (2) The DSC diagram and T_g of BMIGlu (Figure S1). (3) The plot of ln ρ vs T for IL BMIGlu (Figure S2). (4) The plot of γ vs T for the IL BMIGlu (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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