Short Articles

Enthalpy of Solution of Amino Acid Ionic Liquid 1-Ethyl-3-methylimidazolium Ammonioacetate

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The molar enthalpies of solution, $\Delta_{sol}H_m$(wc), of 1-ethyl-3-methylimidazolium ammonioacetate (EMIGly) with various amounts of water and with various molalities were measured by the solution−reaction isoperibol calorimeter at (298.15 ± 0.01) K. According to Archer's method, the standard molar enthalpis of solution of EMIGly with a known amount of water, $\Delta_{sol}H^0{}_m$(wc), were obtained. In order to eliminate the effect of the small amount of water in EMIGly, a linear fitting of $\Delta_{sol}H^0{}_m$(wc) against water content was carried out so that a good straight line was obtained, and the intercept was the standard molar enthalpy of solution, $\Delta_{sol}H^0{}_m$ (pure IL EMIGly) = (−34.6 ± 0.5) kJ·mol^{-1}. Using Glasser's theory of lattice energy, the hydration enthalpy of the anion of glycine was estimated.

Introduction

Since Wilkes et al.[1] synthesized the air- and water-stable ionic liquid (IL) $EMIBF_4$ (1-ethyl-3-methylimidazolium tetrafluoroborate), ILs have attracted considerable attention from industry and the academic community as "green solvents". The study on air- and moisture-stable ionic liquids has become the subject of an increasing number of scientific investigations documented in the literature.[2–5] Especially, Fukumoto et al.[6] succeeded in synthesizing amino acid ionic liquids from 20 natural amino acids. These have a strong hydrogen bonding ability that is useful for dissolved biomaterials, such as DNA, cellulose, and other carbohydrates. Thus, these amino acid ionic liquids should be used in a variety of applications, such as intermediates for peptide syntheses, chiral solvents, functional materials, and biodegradable ionic liquids.

While investigation of the synthesis and the application of ILs in catalytic and separation processes, as well as in electrochemistry, has made remarkable progress during the recent years, physicochemical properties have still not been studied systematically in the literature for pure ILs yet. One of the main reasons is impure water in ILs. In general, water is the most problematic impurity for ionic liquids, and the small amounts of water in ILs may cause large changes of the thermodynamic properties. The trace water is difficult to be removed from ILs using a common method, especially for amino acid ionic liquids.

As a continuation of our previous investigation,[7–9] this paper reports that the molar enthalpy of solution, $\Delta_{sol}H_m$(wc), of an IL EMIGly (1-ethyl-3-methylimidazolium ammonioacetate, where ammonioacetate ≡ glycine) with various water contents was measured by the solution−reaction isoperibol calorimeter at (298.15 ± 0.01) K. Then, according to Archer's method,[10] the standard molar solution enthalpies of EMIGly with a given water content, $\Delta_{sol}H^0{}_m$(wc), were obtained. In order to eliminate the effect of the small amount of water in EMIGly, in terms of standard addition method (SAM), the linear fitting of $\Delta_{sol}H^0{}_m$(wc) against water content in EMIGly was carried out so that a good straight line was obtained, and the intercept was the standard molar solution enthalpies of EMIGly without water, $\Delta_{sol}H^0{}_m$ (pure IL EMIGly). In terms of Glasser's theory of lattice energy,[11] the hydration enthalpy of the glycine anion (Gly^-) was estimated.

Experimental

Chemicals. Deionized water was distilled in a quartz still, and its conductance was (0.8 to 1.2·10^{-4}) S·m^{-1}. The AR grade Glycine was recrystallized twice from water and was dried under reduced pressure. 1-Methylimidazole was obtained from ACROS and was distilled under reduced pressure prior to being used. Bromoethane, ethyl acetate, and acetonitrile were distilled and then stored over molecular sieves in tightly sealed glass bottles, respectively. KCl with a purity more than 99.99 % was dried in a vacuum oven at 408 K for 6 h, and THAM (tris(hydroxymethyl)aminomethane), GR grade reagent, was dried in a vacuum oven before use.

Preparation of 1-Ethyl-3-methylimidazolium Bromide (EMIB). EMIB was synthesized by refluxing the 1-methylimidazole with excess bromoethane at 50 °C for 48 h. The excess bromoethane was removed by evaporation, and crude product was recrystallized twice from acetonitrile/ethyl acetate. The resulting precipitate was brownish and dried in vacuo for 24 h under reduced pressure.

Preparation of EMIGly. According to Fukumoto's method,[6] EMIGly was synthesized. First, 1-ethyl-3-methylimidazolium hydroxide (EMIOH) aqueous solution was prepared from EMIB using an anion exchange resin (IRA201) over a 100 cm column. EMIOH aqueous solution was added dropwise to a slightly excess equimolar glycine aqueous solution. The mixture was stirred under cooling for 12 h. Then, water was evaporated at 40~50 °C. Under vigorous stirring, the mixed solvent of acetonitrile/methanol (volumetric ratio 9/1) was added. The mixture was then filtered to remove excess glycine. Filtrate was

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Table 1. Values of Molar Solution Enthalpy of Ionic Liquid EMIGly, $\Delta_{sol}H_m$(wc), with Known Additional Mass Fractions of Water, w_2, and with Different Molalities at 298.15 K

$10^3\ w_2$	m mol·kg^{-1}	$-\Delta_{sol}H_m$(wc) kJ·mol^{-1}	$-Y$ kJ·mol^{-1}
6.00	0.01057	33.90 ± 0.15	34.24
	0.02126	33.88 ± 0.13	34.15
	0.03074	33.80 ± 0.11	34.10
	0.03898	33.71 ± 0.10	34.02
	0.05018	33.57 ± 0.08	33.92
	0.06025	33.36 ± 0.07	33.82
28.01	0.01557	31.80 ± 0.14	32.03
	0.02328	31.59 ± 0.13	31.87
	0.03014	31.35 ± 0.11	31.66
	0.03585	31.16 ± 0.09	31.57
	0.04522	31.04 ± 0.08	31.39
41.17	0.01814	31.16 ± 0.13	31.35
	0.02359	30.91 ± 0.12	31.20
	0.03034	30.78 ± 0.11	31.09
	0.03504	30.68 ± 0.11	31.02
	0.04802	30.40 ± 0.10	30.79
52.41	0.01655	29.18 ± 0.14	29.36
	0.01898	29.08 ± 0.14	29.34
	0.02315	29.02 ± 0.12	29.32
	0.03485	28.96 ± 0.11	29.28
	0.050055	28.84 ± 0.09	29.22
87.72	0.01607	27.79 ± 0.13	28.00
	0.02325	27.66 ± 0.12	27.94
	0.03474	27.51 ± 0.11	27.85
	0.04053	27.41 ± 0.08	27.81
	0.05802	27.28 ± 0.07	27.70

evaporated to remove solvents. The product was dried in vacuo for 2 days at 80 °C. Analysis of the product by H NMR gave a spectrum identical to that for EMIGly with a small amount of water. The mass fraction of water content of the product determined with a Karl Fischer moisture titrator (ZSD-2 type) was 0.006. The glass transition temperature of the product was determined by DSC, $T_g = -62$ °C, and was in good agreement with −65 °C of EMIGly in the literature.[6]

Determination of the Molar Enthalpies of Solution. On the basis of other calorimetric apparatuses,[12,13] an online solution−reaction isoperibol calorimeter was constructed, and the detailed experimental procedure was described previously.[8]

The performance and accuracy of the calorimetric system was tested by measuring the molar enthalpy of solution of KCl in water and THAM [tris-(hydroxymethyl)aminomethane] in 0.1 mol·dm^{-3} HCl(aq) at (298.15 ± 0.01) K. The mean molar solution enthalpies are $\Delta_{sol}H_m$ = (17542 ± 31) J·mol^{-1} for KCl and (−29794 ± 28) J·mol^{-1} for THAM, which are in good agreement with the corresponding published data: (17536 ± 9) J·mol^{-1} for KCl[14,15] and (−29739 ± 10) J·mol^{-1} for THAM.[14] These results show that the constructed isoperibol calorimeter can be applied in our research work. Then, according to SAM, a series of samples of water-contained EMIGly were prepared, and their molar enthalpies of solution were measured using the tested isoperibol calorimeter.

Results and Discussion

Molar Solution Enthalpy of EMIGly Containing Various Amounts of Water. The values of molar solution enthalpy, $\Delta_{sol}H_m$(wc), of water-contained EMIGly with various molalities at (298.15 ± 0.01) K are listed in Table 1. The uncertainty of molalities, m, is less than $2.0 \cdot 10^{-5}$ mol·kg^{-1}.

Standard Molar Solution Enthalpy $\Delta_{sol}H_m^0$ (Pure IL EMIGly). If the infinite dilution of ILs in water is selected as the reference state, according to Archer's method,[10] in terms of a Debye–Hückel limiting term, the values of the molar standard enthalpy of solution of IL EMIGly with known amounts of water, $\Delta_{sol}H^0_m$(wc), can be obtained using the following equation

$$Y = \Delta_{sol}H_m(\mathrm{wc}) - (A_H/b)\ln(1 + bI^{1/2}) = \Delta_{sol}H_m(\mathrm{wc}) + \beta m \tag{1}$$

where m is molality; I is ionic strength (= m for the 1:1 electrolyte EMIGly); b is a constant to be 1.2;[16] the Debye–Hückel parameter for enthalpy, A_H = 1984, was from the literature;[16] β is an empirical constant; and Y is the extrapolation function which is calculated from experimental data. The values of Y containing a constant amount of water were fitted to eq 1, and good straight lines were obtained (see Figure 1). The values of $\Delta_{sol}H^0_m$(wc) and β obtained from the intercepts and the slopes of linear fitting are listed in Table 2, respectively. The values of the standard deviation of all linear regressions, s, are also listed in Table 2.

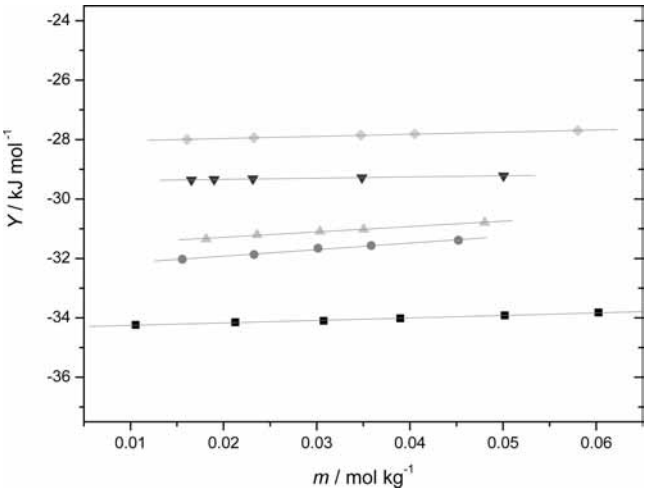

Figure 1. Plot of Y (extrapolation function calculated from eq 1) against m (molality) at various mass fractions of water in EMIGly, w_2: ◆, $10^3\ w_2$ = 87.72; ■, $10^3\ w_2$ = 6.00; ▲, $10^3\ w_2$ = 41.17; ▼, $10^3\ w_2$ = 52.41; ●, $10^3\ w_2$ = 28.01.

Table 2. Values of Standard Molar Solution Enthalpy of EMIGly Containing Various Mass Fractions of Water at 298.15 K and the Standard Deviation of Linear Regressions[a]

$10^3\ w_2$	$\Delta_{sol}H_m{}^0$(wc)/kJ·mol^{-1}	β	s/kJ·mol^{-1}
6.00	−34.34	8.30	0.05
28.01	−32.37	22.1	0.06
41.17	−31.66	18.4	0.05
52.41	−29.41	3.90	0.04
87.72	−28.11	7.20	0.04

[a] w_2 is the water mass fraction.

From Figure 1 and Table 2, it is clear that the values of $\Delta_{sol}H_m{}^0$(wc) decrease with an increase of water content in EMIGly. According to SAM, the values of $\Delta_{sol}H^0_m$(wc) were plotted against the water content in EMIGly. A straight line was obtained (see Figure 2), and the correlation coefficient of linear regressions, r, is larger than 0.97. The intercept of the line is the standard molar solution enthalpy of pure ionic liquid EMIGly without water, that is, $\Delta_{sol}H_m{}^0$(pure ionic liquid) = (−34.6 ± 0.5) kJ·mol^{-1}. This shows that the standard addition method is suitable in the experiments The relationship between $\Delta_{sol}H_m{}^0$(wc) and mass fraction, w_2, of water in EMIGly is expressed as the following empiric equation

$$\Delta_{sol}H_m(\mathrm{wc}) = \Delta_{sol}H_m(\text{pure IL EMIGly}) + aw_2 \tag{2}$$

where $\Delta_sH_m{}^0$(pure IL EMIGly) is the standard molar enthalpy

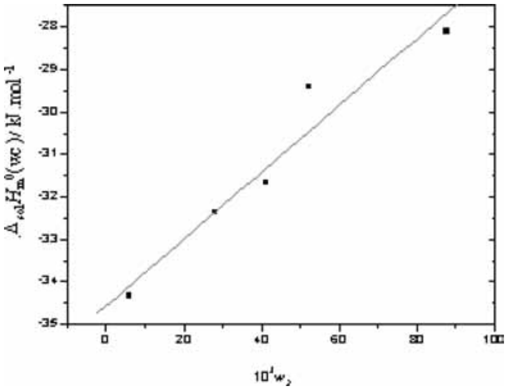

Figure 2. Plot of $\Delta_{sol}H_m{}^0$(wc) vs w_2 (the fitting equation, $\Delta_{sol}H_m{}^0(\text{wc}) = (-34.56 + 7.85 \cdot 10^{-5})w_2$, with the correlation coefficient, $r > 0.97$, and standard deviation, $s = 0.69\ \text{kJ} \cdot \text{mol}^{-1}$).

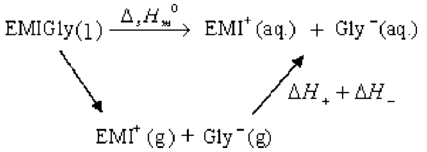

Figure 3. Thermodynamic cycle for estimation of the hydration enthalpy of ionic liquid EMIGly.

of solution of water-free IL EMIGly and *a* is an empiric constant.

Estimation of Ionic Hydration Enthalpy. The hydration enthalpy of ionic liquid EMIGly was estimated using the value of $\Delta_{sol}H_m{}^0$(pure ionic liquid) in terms of the following thermodynamic cycle (see Figure 3).

According to the thermodynamic cycle

$$\Delta_{sol}H_m(\text{pure IL EMIGly}) = U + (\Delta H_+ + \Delta H_-) \qquad (3)$$

where $(\Delta H_+ + \Delta H_-)$ is the hydration enthalpy of EMIGly, U is the crystal lattice energy which can be estimated by Glasser's equation[11]

$$U/\text{kJ} \cdot \text{mol}^{-1} = 1981.2(\rho/M_m)^{1/3} + 103.8 \qquad (4)$$

where $M_m = 185.243\ \text{g} \cdot \text{mol}^{-1}$ and ρ is density of EMIGly. Since $\rho = 1.1589\ \text{g} \cdot \text{cm}^{-3}$,[4] the calculated value of U is 469 $\text{kJ} \cdot \text{mol}^{-1}$, so that the hydration enthalpy of EMIGly $(\Delta H_+ + \Delta H_-) = -504\ \text{kJ} \cdot \text{mol}^{-1}$. It is common knowledge that there are only ion–water interactions and no ion–ion interactions in infinite dilution, hence the contributions of the cation and the anion to molar hydration enthalpy of the EMIGly have additivity. Consequently, the hydration enthalpy of ion $\Delta H_+(\text{EMI}^+) = -233\ \text{kJ} \cdot \text{mol}^{-1}$,[8] and the hydration enthalpy of the glycine anion (Gly^-) is obtained, that is, $-271\ \text{kJ} \cdot \text{mol}^{-1}$. In comparison with $-227\ \text{kJ} \cdot \text{mol}^{-1}$ of hydration enthalpy of $BF_4{}^-$,[17] the hydration of Gly^- is stonger.

Note Added after ASAP Publication: This paper was published ASAP on February 27, 2008. Due to the assignment by the authors of a wrong sign to the molar enthalpies of solution, changes were made to the values of Tables 1 and 2, in eq 4, and in the text regarding the molar enthalpies of solution, and Figures 1 and 2 were replaced. The revised paper was posted on April 23, 2008.

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