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Short Articles

Enthalpy of Solution of Amino Acid Ionic Liquid 1-Butyl-3-methylimidazolium Glycine

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A new novel amino acid ionic liquid [C_4mim][Gly] (1-butyl-3-methylimidazolium glicine) was prepared by the neutralization method. The molar enthalpies of solution, $\Delta_{sol}H_m$(wc), of [C_4mim][Gly] 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 enthalpies of solution of [C_4mim][Gly] with known amounts of water, $\Delta_{sol}H^0_m$(wc), were obtained. To eliminate the effect of the small amount of water in [C_4mim][Gly], 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 of [C_4mim][Gly] without water, $\Delta_{sol}H^0_m = (-46.02 \pm 0.19)\ \mathrm{kJ \cdot mol^{-1}}$. Using Glasser's lattice energy theory, the hydration enthalpy of the glycine anion $[\mathrm{Gly}]^-$ was estimated.

Introduction

Since Wilkes et al.[1] synthesized the air- and water-stable ionic liquid (IL) [C_2mim][BF_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 for pure ionic liquids have still not been studied systematically yet. One of the reasons is the presence of water in ILs. In general, water is the most likely impurity for ionic liquids, and the small amounts of water in IL may cause large changes of the thermodynamic properties. Trace amounts of water are difficult to remove from ILs using common methods, especially for amino acid ionic liquids.

As a continuation of our previous investigation,[7,8] this paper reports on the molar enthalpies of solution of an IL [C_4mim][Gly] (1-butyl-3-methylimidazolium glycine) with various water contents, $\Delta_{sol}H_m$(wc), that were measured by the solution−reaction isoperibol calorimeter at (298.15 ± 0.01) K. Then, according to Archer's method,[9] the standard molar solution enthalpies of [C_4mim][Gly] with given water content, $\Delta_{sol}H^0_m$(wc), can be obtained. To eliminate the effect of the small amount of water in [C_4mim][Gly], in terms of standard addition method, the linear fitting of $\Delta_{sol}H^0_m$(wc) against water content in [C_4mim][Gly] was carried out to give a straight line with the intercept being the standard molar solution enthalpies of [C_4mim][Gly] without water, $\Delta_{sol}H^0_m$. In terms of Glasser's lattice energy theory,[10] the hydration enthalpy of the glycine anion $[\mathrm{Gly}]^-$ was estimated.

Experimental Section

Chemicals. Deionized water was distilled in a quartz still, and its conductance was $(0.8\ \text{to}\ 1.2)\cdot 10^{-4}\ \mathrm{S \cdot m^{-1}}$. 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. Chlorobutane, 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.

[C_4mim][Cl] was synthesized according to Wilkes' method, and analysis of [C_4mim][Cl] by ^{1}H NMR resulting in a spectrum was in agreement with the literature.[11]

Preparation of [C_4mim][Gly]. According to Fukumoto's method,[6] [C_4mim][Gly] was synthesized by preparing 1-butyl-3-methylimidazolium hydroxide ([C_4mim][OH]) aqueous solution from [C_4mim][Cl] using anion exchange resin (IRA201) over a 100 cm column, and aqueous solution was added dropwise to a slightly excess equimolar aqueous glycine solution. The mixture was stirred under cooling for 12 h. Then, water was evaporated at $T = (313.15\ \text{to}\ 323.15)$ K under reduced pressure. Under vigorous stirring, the mixed solvent of acetonitrile/methanol (volume ratio 9/1) was added. The mixture was then filtered to remove excess glycine. The filtrate was evaporated to remove solvents. The product was dried in vacuo for 2 days at $T = 353.15$ K. The structure of [C_4mim][Gly] was confirmed by ^{1}H NMR (Varian XL-300,

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Table 1. Values of Molar Solution Enthalpy of Ionic Liquid [C_4mim][Gly], $\Delta_{sol}H_m$(wc), with Known Additional Mass Fractions of Water, w_2, and with Different Molalities at 298.15 K

$10^3\ w_2$	m $mol \cdot kg^{-1}$	$-\Delta_{sol}H_m$(wc) $kJ \cdot mol^{-1}$	$-Y$ $kJ \cdot mol^{-1}$
8.00	0.01275	45.33 ± 0.44	45.12 ± 0.44
	0.01989	45.26 ± 0.26	45.00 ± 0.26
	0.02906	45.13 ± 0.18	44.82 ± 0.18
	0.03626	45.01 ± 0.15	44.67 ± 0.14
	0.04094	44.95 ± 0.14	44.59 ± 0.14
	0.04529	44.92 ± 0.12	44.54 ± 0.12
	0.05079	44.87 ± 0.12	44.47 ± 0.11
12.08	0.01504	45.13 ± 0.43	44.90 ± 0.42
	0.02031	45.08 ± 0.28	44.82 ± 0.27
	0.02991	44.97 ± 0.17	44.66 ± 0.17
	0.03628	44.93 ± 0.15	44.59 ± 0.14
	0.04996	44.81 ± 0.12	44.42 ± 0.12
25.29	0.01671	44.12 ± 0.30	43.88 ± 0.30
	0.02125	44.04 ± 0.25	43.77 ± 0.25
	0.03044	43.95 ± 0.18	43.64 ± 0.18
	0.03724	43.90 ± 0.15	43.56 ± 0.15
	0.05110	43.74 ± 0.11	43.34 ± 0.11
38.42	0.01695	43.29 ± 0.32	43.05 ± 0.32
	0.02116	43.20 ± 0.28	42.93 ± 0.28
	0.02946	43.09 ± 0.20	42.78 ± 0.19
	0.03682	43.02 ± 0.15	42.68 ± 0.15
	0.05054	42.79 ± 0.12	42.40 ± 0.11
50.34	0.01773	41.90 ± 0.37	41.65 ± 0.37
	0.02196	41.77 ± 0.29	41.50 ± 0.29
	0.03234	41.64 ± 0.19	41.32 ± 0.18
	0.03855	41.50 ± 0.16	41.15 ± 0.16
	0.05220	41.30 ± 0.11	40.90 ± 0.11

DMSO, δ/ppm relative to TMS): 0.866−0.915 (t, 3H, J = 7.35 Hz), 1.205−1.279 (m, 2H, J = 7.4 Hz), 1.738−1.787 (m, 2H, J = 7.35 Hz), 2.721 (s, 2H), 2.998 (d, 2H), 3.886 (s, 2H), 4.179−4.227 (q, 2H, J = 7.2 Hz), 7.753 (s, 1H), 7.704 (s, 1H), 9.868 (s, 1H). Elemental analysis: (Calcd for $C_{10}H_{19}N_3O_2 \cdot 1.3H_2O$) C, 50.74; H, 9.20; N, 17.75; O, 22.31; (Exptl for $C_{10}H_{19}N_3O_2 \cdot 1.3H_2O$): C, 51.10; H, 9.64; N, 17.35; O, 21.91. The thermal decomposition temperature, T_d (483.5 K), of [C_4mim][Gly] was determined by thermogravimetric analysis using a TA Instruments (SDT) model Q600 thermogravimetric analyzer.

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 $mol \cdot dm^{-3}$ HCl(aq) at (298.15 ± 0.01) K. The mean molar solution enthalpies are $\Delta_{sol}H_m$ = (17542 ± 31) $J \cdot mol^{-1}$ for KCl and (−29794 ± 28) $J \cdot mol^{-1}$ for THAM, which are in good agreement with the corresponding published data: (17536 ± 9) $J \cdot mol^{-1}$ for KCl[14,15] and (−29739 ± 10) $J \cdot mol^{-1}$ for THAM.[15] These results verified that the isoperibol calorimeter was looking correctly. Series of samples of water-contained [C_4mim][Gly] were prepared, and their molar enthalpies of solution were measured.

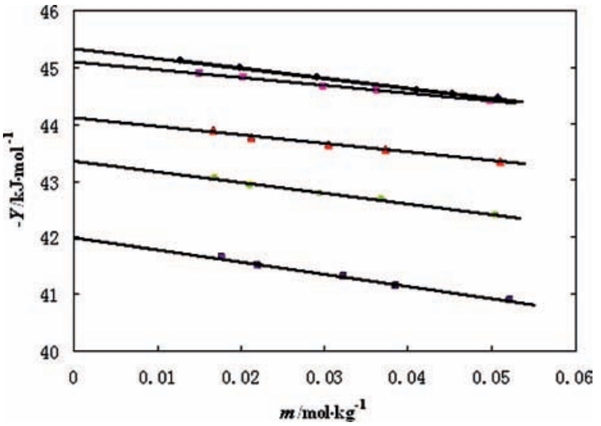

Figure 1. Plot of Y (extrapolation function calculated from eq 1 against m (molality) at various mass fractions of water in [C_4mim][Gly], w_2: ◆, $10^3\ w_2$ = 8.00; pink ■, $10^3\ w_2$ = 12.08; red ▲, $10^3\ w_2$ = 25.29; green ●, $10^3\ w_2$ = 38.42; maroon ■, $10^3\ w_2$ = 50.34.

Table 2. Values of Standard Molar Solution Enthalpy of [C_4mim][Gly] Containing Various Mass Fractions of Water at 298.15 K and the Standard Deviation of Linear Regressions[a]

$10^3\ w_2$	$-\Delta_{sol}H^0_m$(wc) $kJ \cdot mol^{-1}$	β	s $kJ \cdot mol^{-1}$
8.00	45.34 ± 0.17	−17.70	0.02
12.08	45.10 ± 0.19	−13.77	0.02
25.29	44.11 ± 0.18	−15.13	0.02
38.42	43.35 ± 0.19	−18.64	0.02
50.34	42.00 ± 0.19	−21.31	0.03

[a] w_2 is water mass fraction, β is empirical constant, s is standard deviation.

Results and Discussion

Molar Solution Enthalpy of [C₄mim][Gly] Containing Various Amounts of Water. The values of molar solution enthalpy, $\Delta_{sol}H_m$(wc), of water-contained [C_4mim][Gly] with various molalities at (298.15 ± 0.01) K are listed in Table 1. The uncertainty of molalities, m, is less than $2.0 \cdot 10^{-5}$ $mol \cdot kg^{-1}$.

Standard Molar Solution Enthalpy $\boldsymbol{\Delta_{sol}H^0_m}$. 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 [C_4mim][Gly] with known amounts of water, $\Delta_{sol}H^0_m$(wc), can be obtained using the following equation

$$Y = \Delta_{sol}H_m(wc) - (A_H/b)\ln(1 + bI^{1/2}) = \Delta_{sol}H^0_m(wc) + \beta m \qquad (1)$$

where m is molality; I is ionic strength ($I = m$ for the 1:1 type electrolyte [C_4mim][Gly]); b is a constant to be 1.2;[16] A_H is the Debye−Hückel parameter for enthalpy and whose value was from the literature;[16] β is an empirical constant; and Y is an 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.

From Figure 1 and Table 2, the values of $\Delta_{sol}H^0_m$(wc) decrease with an increase of water content in [C_4mim][Gly]. According to the Standard Addition Method, the values of $\Delta_{sol}H^0_m$(wc) were plotted against the water content in [C_4mim][Gly]; a straight line was obtained (see Figure 2); and the standard deviation was s = 0.19 $kJ \cdot mol^{-1}$. The intercept of the line gives the standard molar solution enthalpy of pure ionic liquid [C_4mim][Gly] without water, $\Delta_{sol}H^0_m$ = (−46.02 ± 0.19) $kJ \cdot mol^{-1}$. This shows that the standard addition method is suitable. The relationship between $\Delta_{sol}H^0_m$(wc) and mass fraction, w_2, of water in [C_4mim][Gly] is expressed as the following empiric equation

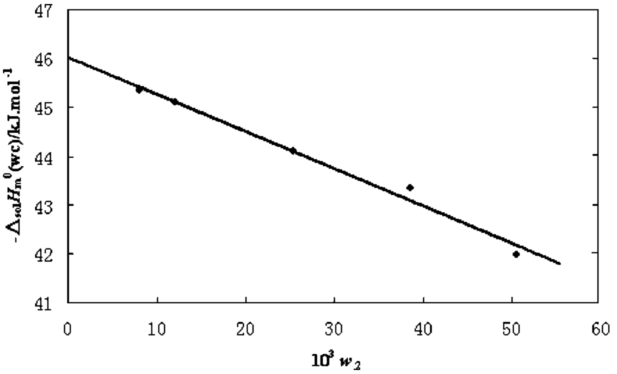

Figure 2. Plot of $\Delta_{sol}H^0_m$(wc) vs w_2 (the fitting equation, $\Delta_{sol}H^0_m(\mathrm{wc}) = (-46.025 - 7.62)\cdot 10^{-5}\,w_2$, with the correlation coefficients, $r > 0.98$, and standard deviation, $s = 0.19$ kJ·mol^{-1}).

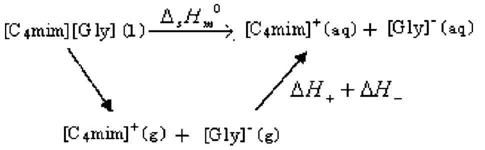

Figure 3. Thermodynamic cycle for estimation of the hydration enthalpy of ionic liquid [C$_4$mim][Gly].

$$\Delta_{sol}H^0_m(\mathrm{wc}) = \Delta_{sol}H^0_m + aw_2 \qquad (2)$$

where $\Delta_s H^0_m$([C$_4$mim][Gly]) is the standard molar enthalpy of solution of water-free IL and a is an empiric constant.

Estimation of Ionic Hydration Enthalpy. The hydration enthalpy of ionic liquid [C$_4$mim][Gly] was estimated using the value of $\Delta_{sol}H^0_m$ (pure ionic liquid) in terms of the following thermodynamic cycle (see Figure 3).

According to the thermodynamic cycle

$$\Delta_{sol}H_m(\text{pure IL [C}_4\text{mim][Gly]}) = \mathrm{U} + (\Delta H_+ + \Delta H_-) \qquad (3)$$

where $(\Delta H_+ + \Delta H_-)$ is the hydration enthalpy of [C$_4$mim][Gly] and U is crystal lattice energy which can be estimated by Glasser's equation[10]

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

where $M_m = 213.19$ g·mol^{-1} and ρ is density of [C$_4$mim][Gly] which was measured by a Westphal balance, that is $\rho = 1.1375$ g·cm^{-3}. The calculated value of U is 449 kJ·mol^{-1}, so that the hydration enthalpy of [C$_4$mim][Gly], $(\Delta H_+ + \Delta H_-) = (-495 \pm 2.5)$ kJ·mol^{-1}. There are only ion−water interactions and no ion−ion interactions at infinite dilution, hence the contributions of the cation and the anion to molar hydration enthalpy have additivity. Since the hydration enthalpy of cation [C$_4$mim]$^+$, ΔH_+([C$_4$mim]$^+$), is −214 kJ·mol^{-1},[17] the hydration enthalpy of the glycine anion [Gly]$^-$, $\Delta H_-(\mathrm{Gly}^-) = -281$ kJ·mol^{-1}, is obtained. In comparison with −227 kJ·mol^{-1} of hydration enthalpy of BF$_4^-$,[18] the hydration of Gly$^-$ is stronger.

Supporting Information Available:

Additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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