Enthalpy of Dilution of Aqueous [C_4mim][Gly] at 298.15 K

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A novel amino acid ionic liquid [C_4mim][Gly] (1-butyl-3-methylimidazolium glycine) was prepared by a neutralization method. The molar enthalpies of dilution, $\Delta_D H_m(m_i \rightarrow m_f)$, of aqueous [$C_4$mim][Gly] at various molalities were measured at (298.15 ± 0.01) K. The values of the apparent relative molar enthalpy, $^{\varphi}L$, were calculated by using both the extended Debye−Hückel equation and the Pitzer equation, which were in good agreement within experimental error. In terms of $^{\varphi}L$, the molar enthalpies of solution of [C_4mim][Gly], $\Delta_s H_m$, at various molalities were estimated. The estimated values of $\Delta_s H_m$ were consistent with the experimental values previously obtained.

1. Introduction

Since Kou et al.[1,2] and Fukumoto et al.[3] successfully synthesized amino acid ionic liquids (AAILs) from natural ions and biomolecules, new "natural ILs" or "bio-ILs" were heralded that are expected to find application in the fields of biological, medical, and pharmaceutical sciences. AAILs have become one of the most rapidly growing new research areas of ionic liquids (ILs) and have attracted considerable attention from industry and the academic community.[4−9]

In spite of the recent rise in the research on ILs, comparatively little is still known as far as their properties, and those of their mixtures and solutions, are concerned.[10] As for the latter, a detailed knowledge of the behavior of mixtures of IL + water is certainly important from both industrial and fundamental perspectives. For instance, accurate data of the enthalpy of dilution are required for optimization of the design of some industrial processes.[11] Although many workers have measured the enthalpies of dilution of some electrolytes, to our knowledge, no measurements of the enthalpy of dilution for IL are presently available.[12−14] In the present work, we synthesized [C_4mim][Gly] (1-butyl-3-methylimidazolium glycine) and measured the molar enthalpies of dilution, $\Delta_D H_m(m_i \rightarrow m_f)$, of aqueous [$C_4$mim][Gly] at various molalities at (298.15 ± 0.01) K. The apparent relative molar enthalpies, $^{\varphi}L$, were determined from the extended Debye−Hückel model and the Pitzer model.[15] The molar enthalpies of solution of [C_4mim][Gly], $\Delta_s H_m$, at various molalities that were estimated in terms of $^{\varphi}L$ were consistent with the experimental data obtained before.[7]

2. Experimental Section

2.1. Chemicals. AR grade glycine (mass fraction higher than 99.7 %) was recrystallized from water and was dried under reduced pressure. 1-Methylimidazole was obtained from ACROS and was distilled under reduced pressure prior to use. Chlorobutane, ethyl acetate, and acetonitrile obtained from ACROS were distilled and then stored over molecular sieves in tightly sealed glass bottles. KCl with a purity more than 99.99 % (spectral purity) was dried in a vacuum oven at 408 K for 6 h. THAM (tris(hydroxymethyl)aminomethane), GR grade reagent (mass fraction higher than 99.8 %), was dried in a vacuum oven before use. An anion-exchange resin (type 717) was purchased from Shanghai Chemical Reagent Co. Ltd. and activated as follows. The resin was first immersed in water and dipped in 2 mol·L^{-1} hydrochloric acid solution for two days to eliminate the impurities, then washed away by deionized water until neutral conditions, then dipped in 2 mol·L^{-1} NaOH solution for two days and washed away by deionized water until neutral. The above procedures were repeated three times.

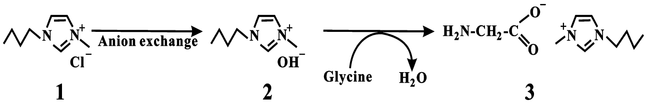

Figure 1. Preparation scheme of the ionic liquids [C_4mim][Gly] by the neutralization method. 1, [C_4mim][Cl]; 2, [C_4mim][OH]; 3, [C_4mim][Gly].

2.2. Preparation of IL [C_4mim][Gly]. The IL [C_4mim][Gly] was prepared by a neutralization method (see Figure 1) according to Fukumoto et al.[4] First, [C_4mim]Cl was synthesized according to the literature.[16] Then, aqueous 1-alkyl-3-methylimidazolium hydroxide ([C_4mim][OH]) was prepared from [C_4mim]Cl using an anion-exchange resin over a 100 cm column. With that, aqueous solutions of the fresh [C_4mim][OH] were added dropwise to a slightly excess aqueous glycine solution. The mixture was stirred for 12 h under cooling, and the solvent water was removed by distillation under reduced pressure. To this reaction mixture, the mixed solvent (volumetric ratio as acetonitrile/methanol = 9/1) was added under strong stirring. The mixture was then filtered to remove excess glycine. The filtrate was evaporated to remove solvents. The product of [C_4mim][Gly] was dried in vacuo for 2 days at 353.15 K. The structure of the resulting IL based on glycine was confirmed by ^{1}H NMR spectroscopy (Varian XL-300), and the spectrum of ^{1}H NMR is shown in Figure S1 (Supporting Information). Analysis of [C_4mim][Gly] by ^{1}H NMR resulting in a spectrum is in good agreement with the literature (see Table S1, Supporting Information).[7] Differential scanning calorimetric measurements (Perkin-Elmer Pyris 6 DSC, see Figure S2, Supporting Information) showed no peak due to melting for the IL [C_4min][Gly]. As shown in Figure S3 (Supporting Information), thermal gravimetric analysis (NETZSCH STA 449C thermal analyzer) revealed that the IL [C_4mim][Gly] was stable to (483.5

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10.1021/je8009539 CCC: $40.75

Table 1. Enthalpy of Dilution (from m_i to m_f) and the Apparent Relative Molar Enthalpy for Aqueous [C$_4$mim][Gly] at 298.15 K

m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$\Delta_D H_m$ / kJ·mol^{-1}	$^{\varphi}L_f$(D) / kJ·mol^{-1}	$^{\varphi}L_i$(D) / kJ·mol^{-1}	$^{\varphi}L_f$(P) / kJ·mol^{-1}	$^{\varphi}L_i$(P) / kJ·mol^{-1}
3.6583	0.1427	−8.232 ± 0.018	0.561	8.793	0.619	8.851
3.3535	0.1357	−7.369 ± 0.021	0.549	7.918	0.606	7.975
3.0403	0.1282	−6.391 ± 0.022	0.534	6.925	0.592	6.983
2.7380	0.1200	−5.521 ± 0.017	0.518	6.039	0.575	6.096
2.4575	0.1112	−4.914 ± 0.020	0.502	5.416	0.558	5.472
2.3031	0.1065	−4.313 ± 0.021	0.493	4.806	0.548	4.861
2.1528	0.1017	−4.072 ± 0.022	0.483	4.555	0.537	4.609
1.9008	0.0936	−3.321 ± 0.018	0.465	3.786	0.518	3.839
1.7189	0.0861	−3.020 ± 0.027	0.449	3.469	0.499	3.519
1.4568	0.0764	−2.356 ± 0.041	0.426	2.782	0.474	2.830
1.2612	0.0675	−2.083 ± 0.021	0.404	2.487	0.449	2.532
1.0410	0.0564	−1.591 ± 0.037	0.374	1.965	0.415	2.006
0.7932	0.0461	−1.204 ± 0.011	0.343	1.547	0.379	1.583
0.5322	0.0393	−0.796 ± 0.022	0.320	1.116	0.353	1.149

± 0.1) K. The water content (w_2) of the AAIL was determined by a Karl Fischer moisture titrator (ZSD-2 type) to be less than 0.7 % (by weight). In comparison with the literature ([C$_2$mim][Gly], $T_g = -65$ °C), the glass-transition temperature of [C$_4$mim][Gly] in this work [$T_g = -(42.3 \pm 0.1)$ K] was higher (less negative) which may be due to the different lateral chain, as Fukumoto et al.[4] reported that an increase of the alkyl side-chain length coincided with a gradual increase of T_g.

2.3. Measurement of Enthalpy of Dilution for the IL. An RD496-CK2000 heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China) was used for the measurement of the enthalpy of dilution. The balance used for weighting was a METTLER AE-240 (Mettler Toledo). The temperature of the calorimetric experiment was (298.15 ± 0.01) K. Additional double-layer glass tubes were put in the 15 mL stainless steel sample cell and reference cell of the calorimeter.

To check the performance of the microcalorimeter, calorimetric measurements on the enthalpy of a solution of KCl (spectral purity) in deionized water were made.[17] The experimental mean value, (17.246 ± 0.004) kJ·mol^{-1}, of the standard enthalpy of solution, $\Delta_{sol}H_m^0$, is in excellent agreement with that of (17.241 ± 0.018) kJ·mol^{-1} reported in the literature.[17,18] This result shows that the device for measuring the enthalpy of solution used in this work is reliable. A series of samples of aqueous [C$_4$mim][Gly] at various molalities were prepared, and their molar enthalpies of dilution were measured using the RD496-CK2000 microcalorimeter.

The sample and water were weighed with a precision of ± 0.00001 g and placed into the inner and outer tubes in the microcalorimeter cell, respectively. In the reference cell, both the outer and inner tubes were empty. After thermal equilibration, the lining in the double-layer glass tube containing aqueous [C$_4$mim][Gly] was broken by a rod. The aqueous [C$_4$mim][Gly] was mixed with water in the outer glass tube, and the thermal effect was recorded automatically on a computer. The total time required for the complete reaction was about 0.5 h. The measured enthalpies of dilution were reproducible to less than 0.002 kJ·mol^{-1} for triplicate runs in this work. The uncertainty of molalities, m, is less than $2.0 \cdot 10^{-5}$ mol·kg^{-1}.

3. Results and Discussion

3.1. Molar Enthalpy of Dilutin of Aqueous [C$_4$mim][Gly] with Various Molalities. The molar enthalpies of dilution, $\Delta_D H_m(m_i \rightarrow m_f)$, of aqueous [C$_4$mim][Gly] at various molalities are given by $\Delta_D H_m(m_i \rightarrow m_f) = Q/n$, where Q is the measured heat at (298.15 ± 0.01) K, n is the number of moles of solute, and m_i and m_f are the molalities of the IL in the initial and final solutions. The experimental results are listed in Table 1. Each value in Table 1 is the average of triplicate measurements. Since the values for $\Delta_D H_m(m_i \rightarrow m_f)$ 0, the dilution of an aqueous solution of [C$_4$min][Gly] is an exothermic process.

3.2. Apparent Molar Enthalpy, $^{\varphi}L$, Obtained from the Extended Debye−Hückel Equation. If the molar enthalpies of dilution, $\Delta_D H_m(m_i \rightarrow m_f)$, of aqueous [C$_4$mim][Gly] are the thermal effect of the dilution of a solution containing 1 mol of solute from m_i to m_f, it can be related to the apparent relative molar enthalpy, $^{\varphi}L$, as follows:

$$\Delta_D H_m(m_i \rightarrow m_f) = {}^{\varphi}L_f - {}^{\varphi}L_i \qquad (1)$$

where $^{\varphi}L_i$ and $^{\varphi}L_f$ are the relative apparent molar enthalpies at the initial and the final concentrations, respectively. According to Leung et al.,[19] $^{\varphi}L$ can be determined with the extended Debye−Hückel equation

$$^{\varphi}L = S_H I^{1/2}[1/(1 + 2I^{1/2}) - (\sigma/3)] + BI + CI^{3/2} \qquad (2)$$

$$\sigma = (3/I^{3/2})[(1 + 2I^{1/2}) - (1 + 2I^{1/2})^{-1} - 2\ln(1 + 2I^{1/2})] \qquad (3)$$

where S_H is the Debye−Hückel limiting-law slope; $S_H = 2.8786$ kJ·kg$^{1/2}$·mol$^{-3/2}$[18] for a 1−1 IL at 298.15 K; I is the molar ionic strength; and B and C are adjustable parameters. The B and C constants of eq 1 can be determined from the experimentally measured enthalpies, $\Delta_D H_m(m_i \rightarrow m_f)$, using the following working equation

$$Y = [\Delta_D H_m(m_i \rightarrow m_f) - S_H\Delta\{I^{1/2}[1/(1 + 2I^{1/2}) - (\sigma/3)]\}]/\Delta I = B + C\Delta I^{3/2}/\Delta I \qquad (4)$$

where Y is an extrapolation function which is calculated from experimental data. Plotting Y vs $\Delta I^{3/2}/\Delta I$, a good straight line is obtained (see Figure 2). $B = -(0.5536 \pm 0.0002)$ kJ·kg·mol^{-2} and $C = (1.3521 \pm 0.005)$ kJ·kg$^{1.5}$·mol$^{-2.5}$ are obtained from the intercept and slope of the straight line. The values of the relative apparent molar enthalpies, $^{\varphi}L_f$(D) and $^{\varphi}L_i$(D), calculated from eq 2 are listed in Table 1.

3.3. Apparent Molar Enthalpy, $^{\varphi}L$, Obtained from the Pitzer Equation. According to Pitzer's theory, the relative apparent molar enthalpy for 1−1 IL [C$_4$mim][Gly] is

$$^{\varphi}L = (A_L/1.2)\ln(1 + 1.2I^{1/2}) - 2RT^2m\beta^{(0)L} - 2RT^2mg(2I^{1/2})\beta^{(1)L} - 2RT^2m^2C^L \qquad (5)$$

$$g(2I^{1/2}) = 2[1 - (1 + 2I^{1/2})\exp(-2I^{1/2})]/(2I^{1/2})^2 \qquad (6)$$

In eq 5, $\beta^{(0)L}$, $\beta^{(1)L}$, and C^L are the Pitzer parameters for enthalpy;

A_L is the Debye−Hückel parameter for enthalpy, and its value was found in the literature.[15] Combining eq 1 and 5, eq 4 could be rewriten as

$$Y = -[\Delta_D H_m - (A_L/1.2)\Delta\ln(1 + 1.2I^{1/2})]/2RT^2\Delta m = \beta^{(0)L} + \beta^{(1)L}\Delta g(2I^{1/2}) + (m_f + m_i)C^L \quad (7)$$

where Y is an extrapolation function which is calculated from experimental data. In eq 7, all the Δ's are defined according to the following equations

$$\Delta\ln(1 + 1.29I^{1/2}) = \ln(1 + 1.2I_f^{1/2}) - \ln(1 + 1.2I_f^{1/2}) \quad (8)$$

$$\Delta m = m_f - m_i \quad (9)$$

$$\Delta g(2I^{1/2}) = g(2I_f^{1/2}) - g(2I_i^{1/2}) \quad (10)$$

Using the experimental data of apparent molar volume to fit eq 7, the values of $\beta^{(0)L} = (1.3553\cdot10^{-3} \pm 5\cdot10^{-7})$ kg·K^{-1}·mol^{-1}, $\beta^{(1)L} = -(3.6279\cdot10^{-3} \pm 1\cdot10^{-6})$ kg·K^{-1}·mol^{-1}, and $C^L = -(2.4459\cdot10^{-4} \pm 1\cdot10^{-7})$ kg^2·K^{-1}·mol^{-2} with the standard deviation of the fits, $s = 1.5\cdot10^{-5}$, and correlation coefficient, $r = 0.99$, were obtained. The values of the relative apparent molar enthalpy, ${}^{\varphi}L_f(P)$ and ${}^{\varphi}L_i(P)$, calculated from eq 5 are listed in Table 1.

3.4. Estimation of Molar Enthalpy of Solution for IL[C$_4$mim][Gly]. The relationship between the standard molar enthalpy of solution, $\Delta_s H_m{}^0$, and ${}^{\varphi}L$ is[15]

$$\Delta_s H_m = \Delta_s H_m^0 + {}^{\varphi}L \quad (11)$$

where $\Delta_s H_m$ is the molar enthalpy of solution at various concentrations. Since $\Delta_s H_m{}^0 = -(46.02 \pm 0.19)$ kJ·mol^{-1} in the literature,[7] the values of $\Delta_s H_m$ can be estimated in terms of eq 11. The values of the molar enthalpy of solution for several concentrations of solute, $\Delta_s H_m$(D,calcd) and $\Delta_s H_m$(P,calcd), were estimated by using ${}^{\varphi}L$(D) and ${}^{\varphi}L$(P), and their values are presented in Table 2. From Table 2, it can be seen that both estimated values are in good agreement with experimental values $\Delta_s H_m$(exptl).

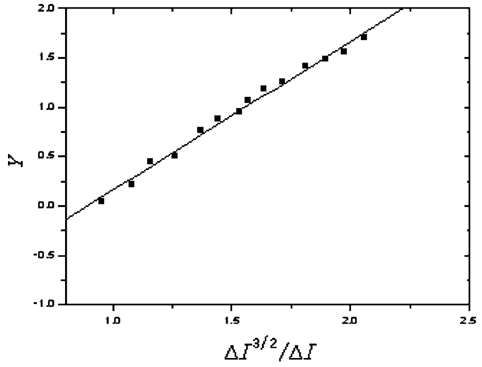

Figure 2. Plot of Y vs $\Delta I^{3/2}/\Delta I$. $Y = -0.5536 + 1.3521\Delta I^{3/2}/\Delta I$. Coefficient of determination $r^2 = 0.99$.

Table 2. Estimated Values of Molar Enthalpy of Solution with Various Concentrations of [C$_4$mim][Gly]

m	$\Delta_s H_m$(exptl)[7]	${}^{\varphi}L$(D)	$\Delta_s H_m$ (D,calcd)	${}^{\varphi}L$(P)	$\Delta_s H_m$ (P,calcd)
mol·kg^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
0.01	−45.70	0.171	−45.849	0.178	−45.842
0.02	−45.49	0.242	−45.778	0.251	−45.769
0.03	−45.29	0.278	−45.742	0.308	−45.712
0.04	−45.11	0.323	−45.697	0.348	−45.672
0.05	−44.93	0.361	−45.659	0.392	−45.628

Supporting Information Available:

Figures S1 to S3 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review December 10, 2008. Accepted June 19, 2009. This project was supported by NSFC (Nos. 20773056, 20771089 and 20873100) and the Science Bureau of Liaoning Province (20072051), P. R. China.

JE8009539