4044 J. Chem. Eng. Data **2010,** *55,* 4044–4047

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

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The molar enthalpies of solution, $\Delta_{\mathrm{sol}}H_{\mathrm{m}}(\mathrm{wc})$, of a new amino acid ionic liquid 1-butyl-3-methylimidazolium glutamine [Bmim][Glu], containing various amounts of water and with various aqueous molalities, were measured with a solution-reaction isoperibol calorimeter at (298.15 ± 0.01) K, where wc denotes water content. The standard molar enthalpies of solution of [Bmim][Glu] with given amounts of water, $\Delta_{\mathrm{sol}}H^0_{\mathrm{m}}(\mathrm{wc})$, were obtained according to Archer's method. To eliminate the effect of the small amount of water in [Bmim][Glu], a linear fitting of $\Delta_{\mathrm{sol}}H^0_{\mathrm{m}}(\mathrm{wc})$ versus the water content was carried out, and the intercept, $\Delta_{\mathrm{sol}}H^0_{\mathrm{m}}$ (pure ionic liquid) $= -(40.55 \pm 0.06)\ \mathrm{kJ \cdot mol^{-1}}$, is the standard molar enthalpy of solution of anhydrous [Bmim][Glu]. Furthermore, the Glasser's theory of lattice energy was used to estimate the hydration enthalpy of glutamine anion $[\mathrm{Glu}]^-$.

Introduction

Ionic liquids (ILs) are a family of liquid compounds formed solely of ions at room temperature and are experiencing great attention from both academic and industrial community in the past decade[1−11] because of their unique properties as a "green" solvent and reaction medium.[2−5] Recently, amino acid ILs based on natural amino acids were synthesized successfully by Fukumoto et al.[11−13] and Kou et al.[14,15] The characteristics of these "greener solvents" includes an excellent ability to dissolve biomaterials (DNA, cellulose, and carbohydrates) resulting from strong hydrogen bonding interaction. Thus, these amino acid ILs can be applied in a variety of areas including biological, medical, and pharmaceutical sciences.

While investigation of the synthesis and the application of ILs in catalytic[16] and separation processes,[17] as well as in electrochemistry,[9] have made remarkable progress during recent years, physicochemical properties have not been studied systematically.[18] One of the leading reasons is the ubiquitous water impurity in ILs and trace water are difficult to remove from the IL using common methods, especially for amino acid ILs. The small amounts of water in the IL may cause large changes of the thermodynamic properties. 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.

As a continuation of previous investigation,[19−22] this paper reports using the standard addition method (SAM), the enthalpy of solution of [Bmim][Glu] (1-butyl-3-methylimidazolium glutamine) was determined by the solution-reaction isoperibol calorimeter at (298.15 ± 0.01) K. First, molar enthalpies of solution of the samples, $\Delta_{\mathrm{sol}}H_{\mathrm{m}}(\mathrm{wc})$, contained given various amounts of water and with different molalities of the [Bmim][Glu] were measured. Then, according to Archer's method,[23] the standard molar solution enthalpies of [Bmim][Glu] with a constant amount of water, $\Delta_{\mathrm{sol}}H^0_{\mathrm{m}}(\mathrm{wc})$, were determined. To eliminate the effect of the small amount of water in [Bmim][Glu], the $\Delta_{\mathrm{sol}}H^0_{\mathrm{m}}(\mathrm{wc})$ against water content in [Bmim][Glu] was linearly fitted. A good straight line was obtained, and the intercept was the standard molar solution enthalpies of [Bmim][Glu] without water, $\Delta_{\mathrm{sol}}H^0_{\mathrm{m}}$ (pure [Bmim][Glu]). Subsequently, the hydration enthalpy of the glutamine anion (Glu^-) was estimated through Glasser's theory of lattice energy.[24]

Experimental Section

Chemicals. The synthetic intermediate, 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]), was synthesized according to Wilkes' method,[25] and the ^{1}H NMR spectrum was in agreement with the literature.[25] 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 glutamic acid was recrystallized twice from water and was dried under reduced pressure. KCl with a purity greater than 99.99 % was dried in a vacuum oven at 408 K for 6 h. THAM [tris-(hydroxymethyl)aminomethane], a GR grade reagent, was dried in a vacuum oven before use.

Preparation of the IL [Bmim][Glu]. According to the method of Fukumoto et al.,[11] [Bmim][Glu] was synthesized by neutralization[4,26] of the 1-butyl-3-methylimidazolium hydroxide aqueous solution which is derived from the BMIC by the method of ion exchange and a slightly excess equimolar glutamic acid aqueous solution. The mixture was stirred under cooling for 12 h, and water was evaporated at 323.15 K. The mixture was then filtered to remove excess glutamic acid. Filtrate was evaporated to remove solvents. The product of [Bmim][Glu] was dried in vacuo for 2 days at 353 K. The resulting IL [Bmim][Glu] was characterized by ^{1}H NMR spectroscopy (Varian XL-300). Differential scanning calorimetric (DSC, Mettler-Toledo DSC823e) measurements showed that [Bmim][Glu] had no melting point, but a glass transition temperature (T_{g}) ranging from (237 to 242) K. The table of ^{1}H NMR chemical shifts and the trace of DSC and T_{g} of the [Bmim][Glu] had been reported in our previous work.[26] The mole fraction of water content, determined by a Karl Fischer moisture titrator (ZSD-2 type), was less than $3.0 \cdot 10^{-4}$.

Determination of the Molar Enthalpies of Solution. On the basis of other calorimetric apparatus[27,28] an online solution-

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10.1021/je100137g

Table 1. Values of Molar Solution Enthalpy of IL [Bmim][Glu], $\Delta_{sol}H_m$(wc), and the Extrapolation Function, Y, with Known Additional Mass Fractions of Water, w_2, and with Different Molalities at 298.15 K[a]

	m	$\Delta_{sol}H_m$(wc)	Y
$10^3\ w_2$	$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
7.60	0.01251	−37.09 ± 0.40	−37.30 ± 0.40
	0.01472	−36.46 ± 0.24	−36.68 ± 0.24
	0.01602	−36.13 ± 0.20	−36.36 ± 0.21
	0.01851	−35.69 ± 0.18	−35.94 ± 0.18
	0.02051	−35.29 ± 0.15	−35.55 ± 0.14
	0.02214	−34.95 ± 0.15	−35.22 ± 0.15
	0.02402	−34.34 ± 0.13	−34.62 ± 0.13
	0.01923	−35.51 ± 0.11	−35.76 ± 0.12
	0.02629	−34.02 ± 0.11	−34.31 ± 0.12
18.10	0.01519	−36.00 ± 0.42	−36.23 ± 0.42
	0.01614	−35.73 ± 0.18	−35.97 ± 0.18
	0.01847	−35.32 ± 0.34	−35.57 ± 0.32
	0.01954	−35.05 ± 0.13	−35.30 ± 0.12
	0.02056	−34.79 ± 0.13	−35.06 ± 0.13
	0.02619	−33.72 ± 0.12	−34.01 ± 0.12
22.44	0.01401	−35.11 ± 0.34	−35.33 ± 0.34
	0.01709	−34.53 ± 0.32	−34.77 ± 0.32
	0.01797	−34.35 ± 0.26	−34.60 ± 0.26
	0.01949	−34.07 ± 0.16	−34.33 ± 0.16
	0.02135	−33.62 ± 0.12	−33.89 ± 0.12
	0.02468	−32.68 ± 0.12	−32.97 ± 0.12
	0.02625	−32.21 ± 0.11	−32.51 ± 0.12
37.51	0.01165	−34.81 ± 0.44	−35.01 ± 0.40
	0.01493	−34.07 ± 0.26	−34.29 ± 0.26
	0.01780	−33.38 ± 0.18	−33.62 ± 0.18
	0.01985	−32.93 ± 0.16	−33.19 ± 0.16
	0.02140	−32.36 ± 0.11	−32.63 ± 0.11
	0.02231	−32.39 ± 0.11	−32.67 ± 0.12

[a] w_2 is water mass fraction. The plus-minus deviation equals $(0.001/\Delta T)\cdot\Delta_{sol}H_m$(wc).

reaction isoperibol calorimeter was constructed, and the detailed experimental procedure was described previously.[19,20]

The performance and accuracy of the calorimetric system was tested by measuring the molar enthalpy of solution of KCl in water and THAM in 0.1 $\mathrm{mol \cdot dm^{-3}}$ HCl(aq) at 298.15 K with an uncertainty of ± 0.01 K. The mean molar solution enthalpies, $\Delta_{sol}H_m = (17542 \pm 31)\ \mathrm{J \cdot mol^{-1}}$ for KCl and $(-29794 \pm 28)\ \mathrm{J \cdot mol^{-1}}$ for THAM, are in good agreement with the corresponding published data: $(17536 \pm 9)\ \mathrm{J \cdot mol^{-1}}$ for KCl[29,30] and $(-29739 \pm 10)\ \mathrm{J \cdot mol^{-1}}$ for THAM, where the uncertainties ± 31 and ± 28 are the range of deviation of each determination from the average value of six determinations, respectively.[30] These results verified that the isoperibol calorimeter can be applied in the work. According to the SAM method, a series of samples of water-contained [Bmim][Glu] were prepared, and their molar enthalpies of solution were measured using the isoperibol calorimeter.

Results and Discussion

Molar Solution Enthalpy of [Bmim][Glu] Containing Various Amounts of Water. The values of molar enthalpy of solution, $\Delta_{sol}H_m$(wc), of water-containing [Bmim][Glu] with various molalities at (298.15 ± 0.01) K measured with the solution-reaction isoperibol calorimeter are listed in Table 1. The uncertainty of molalities of samples, m, is less than $2.0 \cdot 10^{-5}\ \mathrm{mol \cdot kg^{-1}}$.

Standard Molar Solution Enthalpy $\Delta_{sol}H_m^0$ (Pure IL [Bmim][Glu]). If the infinite dilution of ILs in water is selected as the reference state, according to Archer's method,[23] in terms of a Debye−Hückel limiting term, the values of the molar standard enthalpy of solution of [Bmim][Glu] with a known amounts of water, $\Delta_{sol}H^0{}_m$(wc), can be obtained using the following equation:

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

where m is molality, I is ionic strength, b is a constant 1.2,[31] A_H is the Debye−Hückel parameter for enthalpy at 298.15 K and whose value was from the literature, 1986,[31] 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 the fitting straight lines 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, it is clear that the values of $\Delta_{sol}H_m{}^0$(wc) decrease with increasing water content in [Bmim][Glu]. According to the SAM, the values of $\Delta_{sol}H^0{}_m$(wc) were plotted against the water content in [Bmim][Glu]; a straight line was obtained (see Figure 2), and the correlation coefficient of linear regressions, r, is larger than 0.99. The intercept of the line is the standard molar solution enthalpy of pure IL [Bmim][Glu] without water, that is, $\Delta_{sol}H_m{}^0(\text{pure IL}) = -(40.55 \pm 0.06)\ \mathrm{kJ \cdot mol^{-1}}$. This shows that the SAM is suitable in the experiments. The relationship between $\Delta_{sol}H_m{}^0$(wc) and water mass fraction, w_2, is expressed as the following empirical equation:

$$\Delta_{sol}H_m{}^0(\mathrm{wc}) = \Delta_{sol}H_m{}^0(\mathrm{pure[Bmim][Glu]}) + aw_2 \tag{2}$$

where $\Delta_{sol}H_m{}^0$(pure [Bmim][Glu]) is the standard molar enthalpy of solution of water-free [Bmim][Glu] and $a = 0.08$ is an empirical constant.

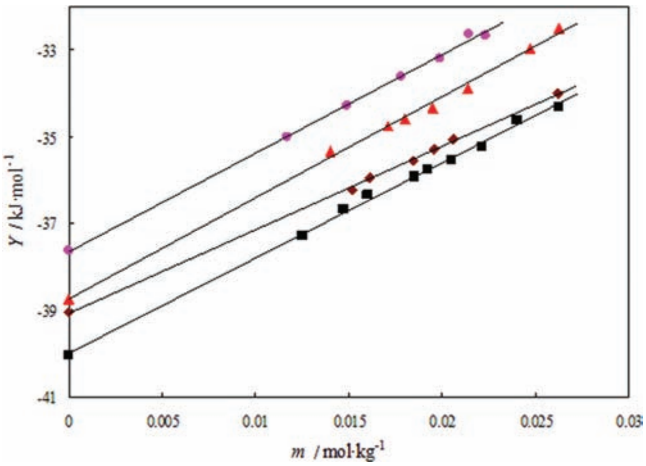

Figure 1. Plot of values of the extrapolation function, $\Delta_{sol}H_m(Y)$, vs molalities of [Bmim][Glu] with known additional mass fractions of water (■, $10^3\ w_2 = 7.60$; ◆, $10^3\ w_2 = 18.10$; ▲, $10^3\ w_2 = 22.40$; ●, $10^3\ w_2 = 37.51$).

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

	$\Delta_{sol}H_m{}^0$		s
$10^3\ w_2$	$\mathrm{kJ \cdot mol^{-1}}$	β	$\mathrm{kJ \cdot mol^{-1}}$
7.60	−40.05	223.717	0.08
18.10	−39.04	189.020	0.07
22.44	−38.75	233.009	0.11
37.51	−37.63	225.99	0.09

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

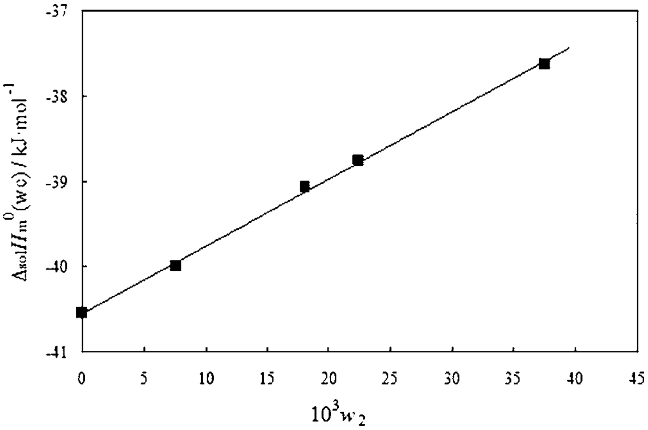

Figure 2. Plot of standard molar solution enthalpy, $\Delta_sH_m^0$(wc), vs the amount of water in [Bmim][Glu] [■, the values of standard molar solution enthalpy of IL [Bmim][Glu] with different water mass fractions (7.60 to 37.51) at 298.15 K; —, linear fit of data].

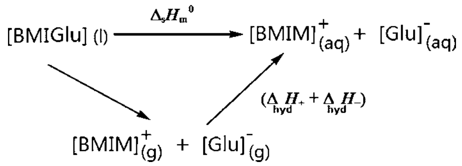

Figure 3. Thermodynamic cycle for estimating the hydration enthalpy of the IL [Bmim][Glu].

Estimation of Ionic Hydration Enthalpy. The hydration enthalpy of the IL [Bmim][Glu] was estimated using the value of $\Delta_{sol}H_m^0$(pure IL) in terms of the thermodynamic cycle in Figure 3.

According to the thermodynamic cycle,

$$\Delta_sH_m^0(\text{pure [Bmim][Glu]}) = U + (\Delta_{hyd}H_+ + \Delta_{hyd}H_-) \tag{3}$$

where $(\Delta_{hyd}H_+ + \Delta_{hyd}H_-)$ is the hydration enthalpy of [Bmim][Glu] and U is crystal lattice energy which can be estimated by Glasser's equation:[24]

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

where M_m (molar mass of [Bmim][Glu]) = 285.3 g·mol^{-1} and ρ is the density of [Bmim][Glu], respectively. Since $\rho = 1.1933$ g·cm^{-3},[26] the calculated value of U is 423 kJ·mol^{-1}, so that the hydration enthalpy of [Bmim][Glu], $(\Delta_{hyd}H_+ + \Delta_{hyd}H_+) = -464$ kJ·mol^{-1}. It is common knowledge that there are only ion−water interactions, no ion−ion interactions in infinite dilution; hence, the contributions of the cation and the anion to molar hydration enthalpy of the [Bmim][Glu] have additivity. Consequently, since the hydration enthalpy of the cation (Bmim$^+$) is −225 kJ·mol^{-1},[32] the hydration enthalpy of the glutamine anion (Glu$^-$) is obtained as −239 kJ·mol^{-1}. The hydration of the glutamine anion is stronger than that of the anion BF_4^-, −227 kJ·mol^{-1}.[33]

Conclusion

In terms of the SAM, the enthalpy of solution, $\Delta_{sol}H_m$(wc), of [Bmim][Glu] containing various mass fractions of water and with different molalities was determined by the solution-reaction isoperibol calorimeter at (298.15 ± 0.01) K. Using Archer's method, the standard molar solution enthalpies of [Bmim][Glu] with constant amounts of water, $\Delta_{sol}H^0_m$(wc), were determined, and the standard molar solution enthalpy of [Bmim][Glu] without water, $\Delta_{sol}H_m^0$(pure IL) = −(40.55 ± 0.06) kJ·mol^{-1}, was obtained by linear fitting. Subsequently, the hydration enthalpy of the glutamine anion (Glu$^-$), $\Delta_{hyd}H_- = -239$ kJ·mol^{-1}, was estimated through Glasser's theory of lattice energy.

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Received for review February 7, 2010. Accepted March 31, 2010. This project was supported by Key Laboratory Project of Liaoning Province Office of Education (2009S003), P. R. China.

JE100137G