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# Study on the enthalpy of solution and enthalpy of dilution for the ionic liquid [C$_3$mim][Val] (1-propyl-3-methylimidazolium valine)

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ABSTRACT

A new amino acid ionic liquid (AAIL) [C$_3$mim][Val] (1-propyl-3-methylimidazolium valine) was prepared by the neutralization method. Using the solution-reaction isoperibol calorimeter, molar solution enthalpies of the ionic liquid [C$_3$mim][Val] with known amounts of water and with different concentrations in molality were measured at $T = 298.15$ K. In terms of standard addition method (SAM) and Archer's method, the standard molar enthalpy of solution for [C$_3$mim][Val] without water, $\Delta_s H^\circ_m = (-55.7 \pm 0.4)$ kJ $\cdot$ mol$^{-1}$, was obtained. The hydration enthalpy of the cation [C$_3$mim]$^+$, $\Delta H_+$ ([C$_3$mim]$^+$) = $-226$ kJ $\cdot$ mol$^{-1}$, was estimated in terms of Glasser's theory. Using the RD496-III heat conduction microcalorimeter, the molar enthalpies of dilution, $\Delta_D H_m(m_i \rightarrow m_f)$, of aqueous [C$_3$mim][Val] with various values of molality were measured. The values of $\Delta_D H_m(m_i \rightarrow m_f)$ were fitted to Pitzer's ion-interaction model and the values of apparent relative molar enthalpy, $^{\varphi}L$, calculated using Pitzer's ion-interaction model.

## 1. Introduction

Since amino acid ionic liquids (AAILs) were successfully synthesized from natural amino acids by Fukumoto *et al.* [1] and Tao *et al.* [2] AAILs have attracted considerable attention from industry and the academic community as a new-generation "greener" ionic liquid (IL) [3–6]. The AAILs have strong hydrogen-bonding ability, which is useful for dissolving biomaterials such as DNA, cellulose, and other carbohydrates. Therefore, AAILs have been expected to be applied in various fields, such as industrial chemistry and pharmaceutical chemistry.

The enthalpy of solution and enthalpy of dilution provide the basic thermodynamic data for application of AAILs. As a continuation of our previous investigation [7–9], this paper reports that (1) a new amino acid ionic liquids [C$_3$mim][Val] (1-propyl-3-methylimidazolium valine) was prepared by the neutralization method according to Fukumoto *et al.* [1]; (2) the molar enthalpies of solution for IL liquid [C$_3$mim][Val] were measured at $T = 298.15$ K. Since AAILs can strongly form hydrogen bonds with water, which is problematic impurity, in order to eliminate the effect of the impurity water the standard addition method (SAM) [9] was used in these measurements. (3) The value of the standard molar enthalpy of solution, $\Delta_s H^\circ_m$, for [C$_3$mim][Val] was determined in terms of Archer's method [10] and using Glasser's theory of lattice energy [11], hydration enthalpy of cation [C$_3$mim]$^+$ was estimated (4). The molar enthalpy of dilution, $\Delta_D H_m(m_i \rightarrow m_f)$, of aqueous [C$_3$mim][Val] with various molality concentrations was measured. The values of the apparent relative molar enthalpy, $^{\varphi}L$, were calculated using Pitzer's ion-interaction model, respectively [12–15].

## 2. Experimental

### 2.1. Chemicals

Deionised water was distilled in a quartz still, and its conductance was (0.8 to 1.2) $\cdot$ 10$^{-4}$ S $\cdot$ m$^{-1}$. The AR grade valine was recrystallized twice and was dried under reduced pressure. The 1-methylimidazole was distilled under reduced pressure prior to be used. Chloropropane, ethyl acetate, and acetonitrile were distilled and then stored over molecular sieves in tightly sealed glass bottles, respectively. The KCl was dried in a vacuum oven at $T = 408$ K for 6 h, THAM (Tris-(hydroxymethyl)aminomethane), GR grade reagent, was dried in a vacuum oven before use. The source and purity of the materials are listed in table 1.

### 2.2. Preparation of [C$_3$mim][Val]

According to the method of Fukumoto *et al.* [1], [C$_3$mim][Val] was synthesized. First, [C$_3$mim]Cl was synthesized according to literature[16,17]. The aqueous solution of 1-propyl-3-methylimidazolium hydroxide ([C$_3$mim][OH]) was then prepared from [C$_3$mim]Cl using anion exchange resin (IRA201) over a 100 cm column. However, [C$_3$mim][OH] is not particularly stable, and the solution should be used immediately after preparation. This hydroxide aqueous solution was added drop wise to a slightly

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**TABLE 1**
The source and purity of the materials.

| Mass fraction purity | Source |
|---|---|
| Ethyl acetate ⩾ 0.997 | Shenyang Reagent Co. Ltd. |
| Acetone ⩾ 0.997 | Shenyang Reagent Co. Ltd. |
| Acetonitrile ⩾ 0.997 | Shenyang Reagent Co. Ltd. |
| Valine ⩾ 0.998 | Shenyang Reagent Co. Ltd. |
| 1-Methylimidazole ⩾ 0.998 | ACROS |
| Chloropropane ⩾ 0.998 | Shenyang Reagent Co. Ltd. |
| THAM (Tris-(hydroxymethyl) aminomethane) ⩾ 0.9999 | Shenyang Reagent Co. Ltd. |
| KCl ⩾ 0.9999 | Shenyang Reagent Co. Ltd. |

excess equimolar valine aqueous solution. After the mixture was stirred under cooling for 12 h, the water was evaporated at (40 to 50) °C under reduced pressure. Finally, under vigorous stirring, the mixed solvent of acetonitrile/methanol (volumetric ratio 9/1) was added and filtered to remove excess valine. The filtrate was evaporated to remove solvents. The product was dried *in vacuo* for 2 days at 80 °C. Analysis of the product by $^1$H NMR gave a spectrum identical to that for [C$_3$mim][Val]. The mass fraction of water of the product determined with a Karl Fischer moisture titrator (ZSD-2 type) was 0.00800.

### *2.3. Measurement of enthalpy of solution for the IL*

On the basis of other calorimetric apparatus [18–20], the online solution-reaction isoperibol calorimeter was constructed and the detailed experimental procedure is described elsewhere [9].

The performance and accuracy of the calorimetric system were 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 $T = (298.15 \pm 0.01)$ K. The mean molar solution enthalpies are $\Delta_{sol}H_m = (17542 \pm 31)$ J · mol$^{-1}$ for KCl and $(-29794 \pm 28)$ J · mol$^{-1}$ for THAM, which are in good agreement with the corresponding published data: $(17536 \pm 9)$ J · mol$^{-1}$ for KCl [21,22] and $(-29739 \pm 10)$ J · mol$^{-1}$ for THAM [22].These results show that calorimeters can be applied in our research work.

Since the AAILs can form strong hydrogen bonds with water, the small amount of water in the AAILs is difficult to remove by common methods, so that trace water becomes the most problematic impurity. In order to eliminate the effect of the impurity water, the standard addition method (SAM) was applied to these measurements. According to SAM, a series of samples of water-contained [C$_3$mim][Val] was prepared and the values of their molar enthalpies of solution with different molality concentration and with known amounts of water, $\Delta_{sol}H_m$(wc), were measured at $T = 298.15$ K.

### *2.4. Measurement of enthalpy of dilution for the aqueous [C$_3$mim][Val]*

The RD496-CK2000 heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China) was used in the measurement. To check the performance of the microcalorimeter, calorimetric measurements on the enthalpy of a solution of KCl (spectral purity) in deionised water were made according to the literature [20]. The experimental standard enthalpy of solution of KCl is in excellent agreement with that reported in the literature [20]. This result shows that the device for measuring the enthalpy of solution used in this work is reliable. Therefore, a series of samples of aqueous [C$_3$mim][Val] with various initial molality, $m_i$, were prepared and their molar enthalpies of dilution were measured.

## 3. Results and discussion

### *3.1. The standard molar enthalpy of solution, $\Delta_{sol}H_m^\circ$, for IL [C$_3$mim][Val]*

The measured values of molar solution enthalpy, $\Delta_s H_m$(wc), of water-contained [C$_3$mim][Val] and with various molalities at $(298.15 \pm 0.01)$ K are listed in table 2. From table 2, the dissolution process of the IL is typically exothermal.

According to the method of Archer method [10], in terms of a Debye–Hückel limiting term, the values of the molar standard enthalpy of solution of [C$_3$mim][Val] with known amounts of water, $\Delta_{sol}H_m^\circ$(wc), can be obtained using the following equation:

$$Y = \Delta_s H_m(\text{wc}) - (A_H/b)\ln(1 + bI^{1/2}) = \Delta_s H_m^\circ(\text{wc}) + \beta m, \qquad (1)$$

where $m$ is molality, $I$ is ionic strength ($I = m$ for the 1:1 electrolyte [C$_3$mim][Val]), $b$ is a constant to be 1.2 [13], the Debye–Hückel parameter for enthalpy, $A_H$ was taken from the literature [13], $\beta$ is an empirical constant, $Y$ is an extrapolation function which is determined from experimental data. The values of $Y$ containing a constant amount of water were fitted to equation (1) and straight lines were obtained (see figure 1). The values of $\Delta_s H_m^\circ$(wc) and $\beta$ obtained from the intercepts and the slopes of linear regressions are listed in table 3, respectively. The values of the correlation coefficients of all linear regressions, $r$, were larger than 0.99 and are also listed in table 3.

From figure 1 and table 3, the absolute values of $\Delta_s H_m^\circ$(wc) decrease with increase of water content in [C$_3$mim][Val]. According to SAM, the values of $\Delta_s H_m^\circ$(wc) were plotted against the water content in [C$_3$mim][Val] and a straight line was obtained (see figure 2). The intercept of the line is the standard molar solution enthalpy of pure ionic liquid [C$_3$mim][Val] without water, $\Delta_{sol}H_m^\circ$ (pure IL [C$_3$mim][Val]) = $(-55.7 \pm 0.4)$ kJ · mol$^{-1}$. This shows that the standard addition method is suitable for application to this work. The relationship between $\Delta_s H_m^\circ$(wc) and $\Delta_s H_m^\circ$ may be expressed as the following empirical equation:

$$\Delta_s H_m^\circ(\text{wc}) = \Delta_s H_m^\circ + a w_2, \qquad (2)$$

where $w_2$ is mass fraction of water in [C$_3$mim][Val], $a = 0.102$ is an empirical constant.

### *3.2. The estimation of ionic hydration enthalpy*

The hydration enthalpy of the ionic liquid [C$_3$mim][Val] was estimated using the value of $\Delta_s H_m^\circ$ of the pure ionic liquid in terms of the following thermodynamic cycle (see figure 3):

$$\Delta_s H_m^\circ(\text{pure IL [C}_3\text{mim][Val]}) = U_{POT} + (\Delta H_+ + \Delta H_-), \qquad (3)$$

where $(\Delta H_+ + \Delta H_-)$ is the hydration enthalpy of the cation and anion in [C$_3$mim][Val], $U_{POT}$ is crystal lattice energy which can be estimated by Glasser's theory of lattice energy [11]:

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

where $M_m = 241.33$ g · cm$^{-3}$ and $\rho$ is density of [C$_3$mim][Val]. Since $\rho = 1.0944$ g · cm$^{-3}$ [6], the calculated value of $U_{POT}$ is 431.7 kJ · mol$^{-1}$, so that the hydration enthalpy of cation and anion in infinite dilution aqueous [C$_3$mim][Val], $(\Delta H_+ + \Delta H_-) = -487.4$ kJ · mol$^{-1}$. It is believed 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 [C$_3$mim][Val] have additivity. Consequently, according to hydration enthalpy of valine anion, $\Delta H_-([\text{Val}]^-) = -261$ kJ · mol$^{-1}$, obtained by Wang [23], the hydration enthalpy of the cation, $\Delta H_+([\text{C}_3\text{mim}]^+) = -226$ kJ·mol$^{-1}$, was determined. In comparison with hydration enthalpy of [C$_2$mim]$^+$,