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# Study on the thermodynamic properties for ionic liquid [C<sub>6</sub>mim][OAc](1-hexyl-3-methylimidazolium acetate)

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### ABSTRACT

Using the solution-reaction isoperibol calorimeter, molar enthalpies of solution in water,  $\Delta_{sol}H_m$ , for ionic liquid [C<sub>6</sub>mim][OAc] with different molalities were measured in the temperature range from (288.15 to 308.15 ± 0.01) K with an interval of 5 K. According to Archer's method, the values of the standard molar enthalpies of solution,  $\Delta_{sol}H_m^\theta$ , were obtained for [C<sub>6</sub>mim][OAc], respectively. According to Glasser's theory of lattice energy, the hydration enthalpy of cation and anion in infinite dilution aqueous [C<sub>6</sub>mim][OAc] was calculated, ( $\Delta H_+ + \Delta H_-$ ) = -598 kJ mol<sup>-1</sup>, at 298.15 K. The hydration enthalpy of [C<sub>6</sub>mim]<sup>+</sup>, the hydration enthalpy of [C<sub>6</sub>mim]<sup>+</sup> is a little bit weaker. A linear relationship was found by plotting the experimental values of  $\Delta_{sol}H_m^\theta$  against (*T*-298.15) K. The standard molar heat capacity of solution,  $\Delta C_{p,m}^\theta$  = 313 J K<sup>-1</sup> mol<sup>-1</sup>, was obtained from the slope of the regression line, the specific heat capacity of solution,  $\Delta C_{p,m}^\theta$  = 1.38 J g<sup>-1</sup> K<sup>-1</sup>, and the apparent relative molar heat capacity,  ${}^{\Phi}C_p$ , were also calculated for [C<sub>6</sub>mim][OAc].

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#### 1. Introduction

Due to minuscule vapor pressure, non-flammability and dual natural polarity, ionic liquids (ILs) have been applied in many physical-chemical fields [1]. As a new-generation "greener ionic liquid", acetic acid ionic liquids (AcAILs) have attracted considerable attention from industry and the academic community because they have several unique properties including strong solubility and good catalytic properties, which are useful for an enzyme-'friendly' co-solvent for resolution of amino acids [2], ultrasonic irradiation towards synthesis of trisubstituted imidazoles [3], assisted transdermal delivery of sparingly soluble drugs [4], some catalytic reactions [5], and dissolve cellulose [6].

It is well known that enthalpy, molar heat capacity, specific heat capacity of solution, and the apparent relative molar heat capacity,  ${}^{\Phi}C_p$ , for [C<sub>6</sub>mim][OAc] are the basic thermodynamic data, and these basic data, as well as other thermodynamic properties, are of great importance to any industrial processes for application of AcAILs. The density, surface tension, and other physicochemical properties for the homologue of AcAILs were previously reported [7–9]. As a continuation of our previous investigation [7–13], this paper

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http://dx.doi.org/10.1016/j.fluid.2014.03.011 0378-3812/© 2014 Elsevier B.V. All rights reserved. reports that (1) Using the water as solvent, the molar enthalpies of solution for IL [C<sub>6</sub>mim][OAc] were measured in the temperature range of (288.15 to 308.15±0.01) K with an interval of 5 K. (2) The values of the standard molar enthalpy of solution,  $\Delta_{sol}H_m^{\theta}$ , for [C<sub>6</sub>mim][OAc] in the temperature range of (288.15 to 308.15±0.01) K were obtained according to of Archer's method [14], and the hydration enthalpy of cation and anion in infinite dilution aqueous [C<sub>6</sub>mim][OAc] was obtained at 298.15 K according to Glasser's theory of lattice energy. The hydration enthalpy of the cation,  $\Delta H^+$  ([C<sub>6</sub>mim]<sup>+</sup>), was obtained at 298.15 K. (3) The standard molar heat capacity of solution,  $\Delta C_{p,m}^{\theta}$ , for [C<sub>6</sub>mim][OAc] was obtained from the slope of the straight line of  $\Delta_{sol}H_m^{\theta}$  vs. (*T*–298.15) K, the specific heat capacity,  ${}^{\phi}C_p$ , were also calculated for [C<sub>6</sub>mim][OAc].

#### 2. Experimental

#### 2.1. Chemicals

KCl was placed into a vacuum oven and baked at 408.15 K for 6 h before use, as well as THAM (Tris-(hydroxymethyl) aminomethane) for 6 h. The ultrapure water was used. Pure IL [C<sub>6</sub>mim][OAc] was purchased, the water content ( $w_2$  is the water mass fraction,  $w_2 < 0.005$ ) in the ILs was determined by use of a Karl Fischer







Table 1

The source	and	purity	of the	materials
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Chemical name	Source	Purification method	Mass fraction purity (%)	electrical resistivity, $(M\Omega cm)$
KCl THAM (Tris-(hydroxymethyl) aminomethane) [C6mim][OAc] Acetic acid Halogen	Shenyang Reagent Co. LTD Shenyang Reagent Co. LTD Lanzhou Institute of Chemical Physics	No further purification No further purification No further purification	>0.9999 >0.9997 ≥0.99 <0.002 <0.0012	
H <sub>2</sub> O	Ultrapure water			18.2

moisture titrator (ZSD-2 type). The source and purity of the materials and the mass fraction contribution of the impurities for  $[C_6 \text{mim}][OAc]$  are listed in Table 1.

#### 2.2. Determination of enthalpy of solution

An on-line solution-reaction isoperibol calorimeter system was developed based on calorimetric apparatus previously reported in literature [15–17]. The calorimeter consists of a set of water thermostat, a 200 ml pyrex-glass plated silver Dewar, a 4 ml glass sample cell, a calibration heater, a glass-sheathed thermistor probe, an amplifier, a circuit used as an A/D converter and a personal computer for data acquisition and processing. The detailed experimental procedure has been described elsewhere [11].

The performance and accuracy of the calorimetric system were examined by measuring the molar enthalpy of solution of KCl in water and THAM [Tris-(hydroxymethyl) aminomethane] in 0.1 mol dm<sup>-3</sup> HCl (aq) at (298.15 ± 0.01) K. The mean molar solution enthalpies are  $\Delta_{sol}H_m = (17,542 \pm 31) \text{ Jmol}^{-1}$  for KCl and  $(-29,794 \pm 28) \text{ Jmol}^{-1}$  for THAM, which were in good agreement with the corresponding published data:  $(17,536 \pm 9) \text{ Jmol}^{-1}$  for KCl [18,19] and  $(-29,739 \pm 10) \text{ Jmol}^{-1}$  for THAM [19]. The accuracy of the temperature measurement device is ±0.0001. These results suggest that the calorimeter can be used for determining molar enthalpies of solution in the study. The molar enthalpies of solution in ultrapure water of [C<sub>6</sub>mim][OAc] with different molalities,  $\Delta_{sol}H_m$ , were measured at the temperature range of (288.15 to 308.15 ± 0.01) K with an interval of 5 K.

#### 3. Results and discussion

3.1. The standard molar enthalpy of solution,  $\Delta_{sol}H_m^{\theta}$ , for AcAIL [ $C_6$ mim][OAc]

The measured values of molar solution enthalpy,  $\Delta_{sol}H_m$ , of [C<sub>6</sub>mim][OAc] and various molarities at (288.15 to 308.15 ± 0.01)

#### Table 2

Values of molar solution enthalpy for ionic liquid  $[C_6 mim][OAc]$ ,  $\Delta_{sol}H_m$  (kJ mol<sup>-1</sup>), and extrapolation function, Y (kJ mol<sup>-1</sup>), at 288.15 K, pressure p = 0.1 MPa.

$W^{a}\left( g ight)$	$m ( m molkg^{-1})$	$-\Delta_{\rm s}H_m$ (kJ mol <sup>-1</sup> )	$\Delta T^{\rm b}$ (K)	$-Y(kJ mol^{-1})$
0.3843	0.01700	$53.46 \pm 0.025$	$0.1960\pm0.0001$	$53.66 \pm 0.025$
0.4452	0.01970	$53.31 \pm 0.026$	$0.2112 \pm 0.0001$	$53.53\pm0.026$
0.4839	0.02141	$53.20 \pm 0.029$	$0.2312 \pm 0.0001$	$53.42 \pm 0.029$
0.5529	0.02446	$53.07 \pm 0.032$	$0.2536 \pm 0.0001$	$53.31 \pm 0.032$
0.5945	0.02630	$52.91 \pm 0.034$	$0.2704 \pm 0.0001$	$53.15 \pm 0.034$
0.6539	0.02890	$52.79 \pm 0.039$	$0.3128 \pm 0.0001$	$53.05\pm0.039$
0.6872	0.03040	$52.64 \pm 0.040$	$0.3216 \pm 0.0001$	$52.90\pm0.040$
0.7453	0.03297	$52.50 \pm 0.044$	$0.3480 \pm 0.0001$	$52.78\pm0.044$
0.7898	0.03494	$52.36 \pm 0.047$	$0.3744 \pm 0.0001$	$52.64 \pm 0.047$
0.8548	0.03782	$52.18 \pm 0.048$	$0.3848 \pm 0.0001$	$52.47\pm0.048$
0.9054	0.04006	$52.04 \pm 0.051$	$0.4064 \pm 0.0001$	$52.34 \pm 0.051$
0.9818	0.04344	$51.90 \pm 0.054$	$0.4344 \pm 0.0001$	$52.21\pm0.054$

<sup>a</sup> Sample mass,  $W = \pm 0.0001$ ,  $m = \pm 5.04 \times 10^{-6}$ .

<sup>b</sup> Experimental temperature difference,  $\Delta T = \pm 0.0001$ .

#### Table 3

Values of molar solution enthalpy for ionic liquid  $[C_6 \text{mim}][OAc]$ ,  $\Delta_{\text{sol}} H_m$  (kJ mol<sup>-1</sup>), and extrapolation function, Y (kJ mol<sup>-1</sup>), at 293.15 K, pressure *p* = 0.1 MPa.

W <sup>a</sup> (g)	$m (\mathrm{mol}\mathrm{kg}^{-1})$	$-\Delta H_m$ (kJ mol <sup>-1</sup> )	$\Delta T^{b}$ (K)	$-Y(kJ mol^{-1})$
0.3809	0.01685	$52.11 \pm 0.023$	$0.1824 \pm 0.0001$	$52.33 \pm 0.023$
0.4638	0.02050	$51.98\pm0.027$	$0.2144 \pm 0.0001$	$52.22\pm0.027$
0.5021	0.02221	$51.85\pm0.027$	$0.2176 \pm 0.0001$	$52.10\pm0.027$
0.5497	0.02430	$51.69 \pm 0.030$	$0.2368 \pm 0.0001$	$51.95\pm0.030$
0.6079	0.02690	$51.54 \pm 0.034$	$0.2696 \pm 0.0001$	$51.81\pm0.034$
0.6597	0.02919	$51.40 \pm 0.038$	$0.3000 \pm 0.0001$	$51.68 \pm 0.038$
0.7139	0.03159	$51.22\pm0.040$	$0.3208 \pm 0.0001$	$51.51\pm0.040$
0.7734	0.03421	$51.08\pm0.043$	$0.3456 \pm 0.0001$	$51.39 \pm 0.043$
0.8317	0.03680	$50.93 \pm 0.046$	$0.3704 \pm 0.0001$	$51.25\pm0.046$
0.8971	0.03970	$50.80\pm0.051$	$0.4064 \pm 0.0001$	$51.12\pm0.051$
0.9354	0.04139	$50.64 \pm 0.051$	$0.4096 \pm 0.0001$	$50.98 \pm 0.051$
0.9787	0.04330	$50.49\pm0.053$	$0.4248 \pm 0.0001$	$\textbf{50.83} \pm \textbf{0.053}$

<sup>a</sup> Sample mass,  $W = \pm 0.0001$ ,  $m = \pm 5.04 \times 10^{-6}$ .

<sup>b</sup> Experimental temperature difference,  $\Delta T = \pm 0.0001$ .

K are listed in Tables 2–6 suggesting that the dissolution process of the AcAIL is a typical exothermal.

According to Archer's method [14], in terms of a Debye–Hückel limiting term, the values of the standard molar enthalpy of solution for  $[C_6 \text{mim}][\text{OAc}]$ ,  $\Delta_{\text{sol}} H_m^{\theta}$ , can be obtained using the following equation at the given temperature:

$$Y = \Delta_{\rm sol} H_m - \left(\frac{A_H}{b}\right) \ln\left(1 + bI^{1/2}\right) = \Delta_{\rm sol} H_m^{\theta} + \beta m \tag{1}$$

where *m* is molality, *I* is ionic strength (*I*=*m* for the 1:1 electrolyte [ $C_6$ mim][OAc]), b is a constant to be 1.2 [20],  $A_H$  is the Debye–Hückel parameter for enthalpy and its value at different temperatures was taken from the literature [20],  $\beta$  is empirical constant, *Y* is extrapolation function calculated from experimental data and are listed in Tables 2–6. According to Eq. (1), plotting the values of *Y* against various molarities, the good straight lines were obtained (see Fig. 1). The values of  $\Delta_{sol}H_m^{\theta}$  and  $\beta$  were obtained from the intercepts and the slopes of linear regressions, respectively, and the values of the correlation coefficients, *r*, and the

Values of molar solution enthalpy for ionic liquid  $[C_6 mim][OAc]$ ,  $\Delta_{sol}H_m$  (kJ mol<sup>-1</sup>), and extrapolation function, Y (kJ mol<sup>-1</sup>), at 298.15 K, pressure p = 0.1 MPa.

$W^{a}\left( \mathbf{g} ight)$	$m (\mathrm{mol}\mathrm{kg}^{-1})$	$-\Delta_{\rm s} H_m$ (kJ mol <sup>-1</sup> )	$\Delta T^{\rm b}$ (K)	$-Y(kJ mol^{-1})$
0.4094	0.01811	$50.58 \pm 0.022$	$0.1776 \pm 0.0001$	$50.89 \pm 0.022$
0.4501	0.01991	$50.46\pm0.024$	$0.1928 \pm 0.0001$	$50.73 \pm 0.024$
0.5026	0.02224	$50.34\pm0.027$	$0.2144 \pm 0.0001$	$50.63 \pm 0.027$
0.5604	0.02480	$50.17\pm0.029$	$0.2344 \pm 0.0001$	$50.46 \pm 0.029$
0.6008	0.02658	$50.02\pm0.031$	$0.2472 \pm 0.0001$	$50.32\pm0.031$
0.6557	0.02901	$49.89\pm0.033$	$0.2600 \pm 0.0001$	$50.20\pm0.033$
0.7003	0.03098	$49.79\pm0.036$	$0.2840 \pm 0.0001$	$50.05\pm0.036$
0.7525	0.03329	$49.67\pm0.039$	$0.3088 \pm 0.0001$	$49.94\pm0.039$
0.8078	0.03574	$49.55\pm0.041$	$0.3246 \pm 0.0001$	$49.82\pm0.041$
0.9012	0.03987	$49.32\pm0.045$	$0.3624 \pm 0.0001$	$49.67\pm0.045$
1.0157	0.04494	$49.15\pm0.051$	$0.4072 \pm 0.0001$	$49.53\pm0.045$
1.1374	0.05032	$48.91 \pm 0.056$	$0.4488 \pm 0.0001$	$49.38\pm0.056$

<sup>a</sup> Sample mass,  $W = \pm 0.0001$ ,  $m = \pm 5.04 \times 10^{-6}$ .

<sup>b</sup> Experimental temperature difference,  $\Delta T = \pm 0.0001$ .

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