



# Isobaric molar heat capacities of 1-ethyl-3-methylimidazolium acetate and 1-hexyl-3-methylimidazolium acetate up to 16 MPa



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## ABSTRACT

Isobaric molar heat capacities of 1-ethyl-3-methylimidazolium acetate ( $[C_2C_2Im][OAc]$ ) and 1-hexyl-3-methylimidazolium acetate ( $[C_6C_6Im][OAc]$ ) were measured in the temperature range  $T = (303–393)$  K and at pressures up to 16 MPa. The relative expanded uncertainty of the isobaric molar heat capacity is estimated to be less than 1%. Based on the experimental data in our work and from literature, the isobaric molar heat capacities of  $[C_2C_2Im][OAc]$  and  $[C_6C_6Im][OAc]$  were found to rise with the increasing temperature and the carbon atoms number on the cations, and fall with the increasing pressure. Correlations based on the experimental data were promoted to evaluate the heat capacity of  $[C_2C_2Im][OAc]$  and  $[C_6C_6Im][OAc]$ , the absolute relative deviation between calculation and experimental data is less than 1%.

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## 1. Introduction

Ionic liquids (ILs) are considered to be a new kind of green solvents, which contribute to solve the environmental and energy issues, have potential to replace traditional solvents in many chemical engineering applications [1]. The study of ILs and their applications, in both industry and academia, has grown rapidly over the past decade. Because of their unique chemical and physical properties, they can be applied in many fields such as synthetic chemistry, sensors, solar cells, solid-state photocells and batteries and used as thermal fluids, lubricants, and hydraulic fluids [2–7].

Isobaric heat capacity is related to several other thermodynamic properties, such as entropy, enthalpy and Gibbs free energy, which are also used routinely for heat-transfer calculations for chemical engineering unit operations such as heat exchangers and reactors. Isobaric heat capacity data are required for the design of many industry processes, especially for chemical industry process conducted at high pressure, such as supercritical fluid extraction, petroleum fraction [8–11]. Accurate measurements of the heat capacities of ILs are needed in many areas of physics, chemistry and chemical engineering. Many works focus on measuring and predicting  $C_p$  of ILs have been done recent years. Ficke et al. [12] determined three different binary water + liquid systems from (283.15–348.15) K. Ghanem et al. [13] measured the  $C_p$  of a series of

synthesized ionic liquids based on 1-octyl-3-methylimidazolium with glycinate, alaninate, serinate, proline and asparaginate anions. Paulechka et al. [14] determined the  $C_p$  of 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ( $[C_2C_2Im][NTf_2]$ ) and 1-octyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ( $[C_8C_8Im][NTf_2]$ ). Albert et al. [15], Gardas et al. [16] and Nancarrow et al. [17] have promoted many models based on group contribution method to predict  $C_p$  of pure ILs. However, only a few researches were conducted to study heat capacity of ILs in high pressure regions. Sanmamed et al. studied the isobaric heat capacity of 1-ethyl-3-methylimidazolium tetrafluoroborate ( $[C_2C_2Im][BF_4]$ ), 1-butyl-3-methylimidazolium tetrafluoroborate ( $[C_4C_4Im][BF_4]$ ), 1-hexyl-3-methylimidazolium tetrafluoroborate ( $[C_6C_6Im][BF_4]$ ) and 1-octyl-3-methylimidazolium tetrafluoroborate ( $[C_8C_8Im][BF_4]$ ) in the temperature and pressure intervals of (283.15–323.15) K and (0.1–60) MPa using a micro DSCII calorimeter [18]. Safarov et al. measured the isobaric heat capacity of 1-butyl-3-methylimidazolium acetate ( $[C_4C_4Im][OAc]$ ) in the temperature range  $T = (203.15–413.15)$  K and pressure up to 140 MPa [19]. Hamidova et al. measured the specific heat capacity of 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ( $[C_4C_4Im][NTf_2]$ ) with the pressure up to 140 MPa using a Pyris 1 DSC Differential Scanning Calorimeter from Perkin Elmer Inc [7]. Safarov et al. calculated the  $C_p$  of 1-hexyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ( $[C_6C_6Im][NTf_2]$ ) at  $T = (273.15–413.15)$  K and pressures up to  $p = 140$  MPa [20] with an empiric equation of state.

It was previously shown that the IL anion plays a crucial role

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toward the pretreatment and processing of biomass [21]. As a new-generation “greener ionic liquid”, acetate-based ionic liquids (AcAILs) are useful for an enzyme-‘friendly’ co-solvent for resolution of amino acids [22], ultrasonic irradiation towards synthesis of trisubstituted imidazoles [23], some catalytic reactions [24], dissolve cellulose [25] and assist transdermal delivery of sparingly soluble drugs [26]. The ILs studied are named 1-ethyl-3-methylimidazolium acetate ( $[C_1C_2Im][OAc]$ ) and 1-hexyl-3-methylimidazolium acetate ( $[C_1C_6Im][OAc]$ ).  $[C_1C_2Im][OAc]$  was successfully used as alternative solvent for native chemical ligation of peptide fragments to produce model peptide LYRAXCRANK ( $X = G, A, L, N, Q, K$ , and  $F$ ) [27]. Mara et al. [21] reported the isobaric heat capacity data of  $[EMIM][OAc]$  at the temperature  $T = 293.15$  K and atmosphere pressure, but in other temperature and pressure region, the  $C_p$  of  $[C_1C_2Im][OAc]$  is vacant. Additionally, there is no accurate  $C_p$  experimental data of  $[C_1C_6Im][OAc]$ , which is considered to have potential to act as solvent in  $CO_2$  separation processes [28]. Only the isobaric heat capacity of  $[C_1C_6Im][OAc]$  was calculated at the temperature  $T = 298.15$  K at atmosphere pressure by Wei et al. [29] using a linear relation between the standard molar enthalpies and  $T$ .

In this work, experimental isobaric heat capacities of  $[C_1C_2Im][OAc]$  and  $[C_1C_6Im][OAc]$  were measured in the temperature range from  $T = (303–393)$  K along five isobars (0.1, 4, 8, 12 and 16 MPa), and about 100 experimental data points were obtained. Based on the experimental results, correlations are presented for the calculation of isobaric molar heat capacities of  $[C_1C_2Im][OAc]$  and  $[C_1C_6Im][OAc]$ .

## 2. Experiment

### 2.1. Chemical

In this work, the  $[C_1C_2Im][OAc]$  and  $[C_1C_6Im][OAc]$  were purchased from Shanghai Chengjie Chemical Company Limited with a purity  $\geq 99.0$  wt% in mass fraction, their formulas are  $C_8H_{14}N_2O_2$  and  $C_{12}H_{22}N_2O_2$ , respectively. The purification processes were synthesized by dissolving 1-ethyl-3-methylimidazolium chloride (or 1-hexyl-3-methylimidazolium chloride) in absolute ethyl alcohol solution with potassium acetate ethanol. Then the solution was stirred for 24 h at 298.15 K and freeze for 24 h at 255.15 K. The filtrate was separated and added in silver acetate, stirring for 24 h at 298.15 K. Dichloromethane was added in the filtrate. After 3 times filtration and drying at 343.15 K in vacuum for 24 h,  $[C_1C_2Im][OAc]$  was made. The same process is with  $[C_1C_6Im][OAc]$ . The ILs was dried at the temperature of 393 K and the pressure of 100 Pa for 24 h for purification. Water amount  $1 \times 10^{-4}$  mass fraction measured with Metrohm 831 Karl Fischer Titrator. Br content is less than 1500 ppm and 2500 ppm for  $[C_1C_2Im][OAc]$  and  $[C_1C_6Im][OAc]$ , respectively. The calculation purity of each IL is 99.84 wt% and 99.76 wt%. Their details are listed in Table 1.

### 2.2. Apparatus

The measurements were carried out using a flow calorimeter which designed for measuring the isobaric heat capacity of high-

temperature and high-pressure fluids. The details were described in previous works [30–32]. Fig. 1 and Fig. 2 show the schematic view of our apparatus and the experimental cell. Pre-dried ionic liquids were placed in a hermetic container, via the precision plunger type pump (Scientific Systems, Series 1500 HPLC Pump) controlling the flow rate of sample and providing constant pressure to the experimental system. The pressure was controlled by the back-pressure valve and measured with two pressure transmitters (Rosemount, 3051S; 0–10 MPa) with accuracies of 0.025% FS. The flow of fluid was checked by weighting method with an analytical balance (ME204, Mettler Toledo, uncertainty 0.2 mg). In order to reduce heat loss, a double vacuum cylinder which consists on an inside and outside cylinder was used. The heater which was used to give a temperature rise to the water, is put inside the tube that the fluid went through in order to reduce the heat loss. Temperature in the experimental cell was controlled by two electrical heaters and two platinum resistant thermometers (PRT). Two PRTs were inserted into the copper blocks to obtain the temperatures of fluid before and after heating. All the PRTs were purchased from Fluke Corporation with an uncertainty 0.01 K. The temperatures, the pressure and the heating power of micro-heater were recorded by Keithley 2002 multimeter.

### 2.3. Work equation

The isobaric heat capacity  $C_p$  is defined by the following relation [10,33,34].

$$C_p(p, T) = \frac{P}{q_m \cdot \Delta T} - \frac{P_0}{q_m \cdot \Delta T} = C_{p(\text{ob})} - \frac{P_0}{q_m \cdot \Delta T} \quad (1)$$

where  $q_m$  is the mass flow of fluid through the calorimeter;  $P$  is the heat flow obtained from the heater;  $\Delta T$  is the temperature increment, defined as the difference between the temperature of the sample before and after heated;  $T = (T_1 + T_2)/2$ ,  $T_1$  and  $T_2$  are the inlet and outlet temperatures.  $C_{p(\text{ob})}$  is the observed isobaric heat capacity.  $P_0$  denotes the heat loss from the sample in per unit time, caused by the heat transfer from the sample and the calorimeter to surroundings, and heat loss from the heater lead-in wires [35,36].  $P_0$  is dependent of temperature increment  $\Delta T$ , but independent of mass flow rate. From Eq. (1), it can be found that the influence of the heat loss on the experimental result for  $C_p$  will become small when mass flow rate  $q_m$  increases with the fixed  $\Delta T$ . Therefore,  $C_p$  was measured using different  $q_m$  ( $6–10 \text{ g min}^{-1}$ , interval is  $1 \text{ g min}^{-1}$ ) to determine the influence of the heat loss keeping  $\Delta T$  and the experimental temperature and pressure unchanged. When the relative deviation between the measured isobaric molar heat capacities using  $q_m$  and the next  $q_m$  is smaller than 0.1%, we take the value at this  $q_m$  is the real  $C_p$ . During this work, at the temperature of 303 K and pressure of 0.1 MPa, the relative deviation between the isobaric heat capacities at  $9 \text{ g min}^{-1}$  and  $10 \text{ g min}^{-1}$  is smaller than 0.1% as shown in Table 2, so  $C_{p, \text{ob}}$  is considered as the real  $C_p$  at  $q_m = 10 \text{ g min}^{-1}$ .

### 2.4. Assessment of uncertainties

The expanded uncertainties of temperature, pressure and power

**Table 1**  
The chemicals used in this work.

Chemical name	Supplier	Chemical formula	Purity in mass fraction <sup>a</sup>	Purification method
$[C_1C_2Im][OAc]$	Shanghai Chengjie	$C_8H_{14}N_2O_2$	$\geq 99$ wt%	Vacuum drying
$[C_1C_6Im][OAc]$	Shanghai Chengjie	$C_{12}H_{22}N_2O_2$	$\geq 99$ wt%	Vacuum drying

<sup>a</sup> As stated by the supplier.

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