THERMODYNAMIC PROPERTIES OF C_4mim[Tf_2N] IONIC LIQUIDS

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ABSTRACT

Thermogravimetry Analysis (TGA), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) Analysis have been used to determine the thermal stabilities and heat capacities of ionic liquids 1-butyl-3-methylimidazolium bis (trifluoromethane sulfonyl) imide (C_4*mim[*Tf_2*N] at the temperature range of 298-600 K. Heat capacities measured by DTA and DSC methods showed good agreements. Based on the polynomial relationship fitted from the heat capacity data, enthalpy, entropy and Gibbs energy changes were calculated. These results are compared with other ionic liquids. Applications of ionic liquids for heat transfer and thermal energy storage systems are being evaluated.*

INTRODUCTION

Ionic liquid is a liquid that contains essentially only ions. Particularly ionic liquids based on the imidazolium cation have attracted much attention because their low melting point, highly solvating properties, wide electrochemical windows and negligible vapor pressures. Among all the ionic liquids investigated to date, bis (trifluoromethylsulfonyl) imide based ionic liquids have some of the best properties such as relatively low viscosity, good thermal, hydrolytic stability and the widest liquidus ranges [1, 2, 3]. They have near-zero vapor pressure, do not emit the potentially hazardous volatile organic compounds (VOC) associated with many industrial solvents during their transportation, handling, and use. In addition, they are non-explosive and non-oxidizing (non-flammable). These characterizations could contribute to the development of new thermal storage and heat transfer media that provide significant environmental, safety, and health benefits compared to existing solar thermal power plant systems. They have been proposed as both heat transfer and thermal storage fluids [4]. It is only in recent years that significant literature on the properties of ionic liquids has become available [5, 6, 7]. However, few literatures are available on the determination of their thermodynamic properties such as enthalpy, entropy and Gibbs energy change with temperature. Measurement and calculation of thermodynamic properties such as heat capacity are essential to evaluate the potential of ionic liquid application as heat transfer fluid.

In this paper, specific heat capacity measurement was performed for 1-Butyl-3-Methylimidazolium Bis (trifluoromethylsulfonyl) imide ionic liquid (C_4mim[Tf_2N]) by means of differential thermal analysis (DTA) and differential Scanning Calorimetry (DSC) techniques. The heat capacity data was fitted into a linear equations (C_p = k+aT) as a function of temperature range. With the obtained heat capacities of ionic liquids at different temperatures, other thermodynamic properties such as enthalpy, entropy and Gibbs energy change as a function of temperature were derived based on the heat capacity equations for ionic liquid C_4mim[Tf_2N].

EXPERIMENTAL

Materials

1-Butyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide (C_4mim [Tf_2N]) ionic liquid was synthesized according to standard procedures reported in literatures [6, 8]. Starting materials 1-methylimidazole, redistilled, 99+% pure; 1-chlorobutane, 99.5% pure, anhydrous, were obtained from Aldrich (Sigma-Aldrich Chemie GmbH, Germany). Lithium trifluoromethanesulfonimide ($LiN(CF_3SO_2)_2$) was supplied by 3M Fluorad (St. Paul, MN). The synthesized ionic liquid is transparent and liquid at room temperature. It composed of [C_4mim]$^+$ cation and [Tf_2N]$^-$ anion as shown in Figure 1.

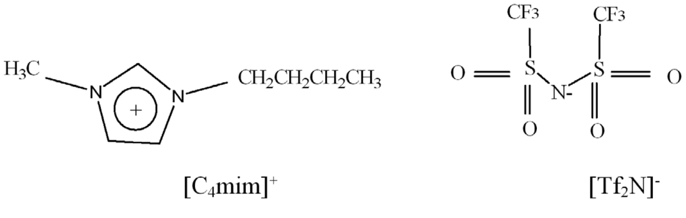

Figure 1: Molecule structures of C_4mim [Tf_2N] ionic liquid

The characterizations of synthesized ionic liquids were performed to ensure the purity using coulometric titration and nuclear magnetic resonance (NMR) analyses. The measurement showed that the water content of dried samples is less than 0.1 wt % after drying. Since the sample without drying contained more water and its water content increases when exposed to humidity environment. All thermal analysis samples were immediately tested after drying and sealed in liquid pans.

Apparatus

TG/DTA - Perkin Elmer Pyris Diamond TG/DTA, which combines both TG and DTA measurements, was used to measure the thermal properties of ionic liquids. It measures simultaneously the enthalpy change and weight loss of the sample. The furnace system comprises of a tubular furnace and two horizontal beams. The outer ends of which are attached with pan holders and inner ends are fixed to internal balance. Thermocouples measuring the sample and reference temperatures are welded to the pan holders. The principal heat transfer mechanism involved is radiation from furnace walls and heat convection from the carrier gases. The apparatus has provisions for introducing carrier gases and collecting outgases for further analysis. It is also provided with a cooling fan for rapid cooling of the furnace system. During the measurement, the heating rate was fixed at 20°C/min, and purging gas was high-purity argon at a flow rate of 100 cc/min at atmospheric pressure. Each ionic liquid sample was dried under vacuum for 2 hours before conducting TG/DTA measurements in platinum pans. The reference material is alumina (Al_2O_3). The standard material used for the calibration was pure α-alumina powders (99.997%).

DSC - DSC differs fundamentally from DTA in that the sample and reference materials are sealed in pans and both maintained at the temperature predetermined by the program. During a thermal event in the sample, the system will transfer heat to or from the sample pan to maintain the same temperature in reference and sample pans. Unlike the measurement of temperature difference in DTA, DSC measures the energy or heat flow difference between the reference (R) and sample (S) materials. Table 1 shows the operating condition for TG/DTA and DSC used in this research.

Table 1: Parameters used in DTA and DSC measurement

Parameters	DTA	DSC
Heating rate, °C/min	20	20
Purging gas flow rate, cc/min	High-purity Argon, 100	High-purity Argon, 100
Pressure	Atmospheric	Atmospheric
Sample pan	Platinum (without cover)	Volatile Aluminum (sealed with cover)
Standard calibration Materials	Pure graphite powders, 99.997%	Biphenyl, Indium, Zinc
Reference sample	α-Al_2O_3	α-Al_2O_3

RESULTS AND DISCUSSION

Measurement of Enthalpy and Heat Capacity by TG/DTA

Using mass-difference baseline method in DTA can diminish the asymmetric heat transfer influence by means of subtracting a baseline that is constructed in a new way [5, 9]. It greatly improves the linearity between the DTA signal and the enthalpy change. In this work, the enthalpy change of pure graphite was measured over temperature range (30-550°C). The measured heat capacity of graphite was compared with the standard values to determine the conversion factors between DTA signal and enthalpy change.

The follow ing equation was used to calculate the enthalpy change from a DTA curve:

$$\frac{dH}{dt}=\frac{K_2}{K_2'}\frac{(dH/dt)'}{DTA'}DTA \tag{1}$$

where DTA´/(dH/dt)´ is the ratio of the DTA signal and the enthalpy change of the measured materials at a certain temperature. K_2/K_2' is a function of temperature. The correlation, $K_2/K_2' = f(t)$, can be determined for a standard material. It is identical for all the DTA tests of other materials.

DTA measurements were conducted for two different sample mass using same reference material Al_2O_3. During the measurement, the DTA curve for small sample mass was used as the baseline for the larger mass sample. By utilizing mass-difference method, as shown in Figure 2, Curve a (m = 24.8 mg) is used as the baseline for curve b (m = 41.5 mg). Both DTA curves increase in the same manner with increasing temperature. The magnitude difference in DTA signal results from the difference in the sample mass. The enthalpy change of a sample mass equal to the mass difference (16.7 mg) can be calculated by subtracting these two curves, as indicated by curve c. In Figure 2, curves a and b are always positive, indicating that heat transfer on the sample side is larger than the reference side, besides they are varying nonlinearly with temperature implying a complex relationship between the heat transfer and the environmental conditions. Obviously, the subtracted DTA curve shows a nearly linear relationship with temperature as a result of the eliminating of heat transfer influences between sample side and reference side.

One of the significant advantages of ionic liquids is their high thermal stability, which enable their use over a wide operating temperature range. Zhang and Reddy [5, 7, 11] have reported the thermal stability of several common ionic liquids. Their results show that C_4mim[Tf_2N] begin to degrade at 398 K and 711 K, respectively. C_4mim[Tf_2N] are virtually stable up to 508 K and their degradation proceeds very rapidly after 673 K. From the simultaneous thermogravimetric and differential thermal analysis (TG/DTA) measurements in this work, the wide range of thermal stability of C4mim[Tf_2N] was confirmed by the stable increase of their DTA curves. For each ionic liquid, DTA measurements were conducted for two different sample weights from 298 K to 623 K to eliminate the *instrument effect*.

The DTA peaks area were determined by the Muse Standard Analysis Software (Version 2.5U) provided by Seiko Instruments Inc. These areas represent the enthalpy changes during the transformations, which can be calculated with known conversion factors determined previously using α-alumina as standard material. The calculated enthalpy changes of C_4mim [Tf_2N] is shown in Table 2. This result was consistence with the work done by Zhang and Reddy [11], their results show C4mim [Tf_2N] has higher thermal decomposition temperature than C_4mim [Cl]. The long term thermal stability study also found that C_4mim[Tf_2N] is virtually stable up to 508 K.

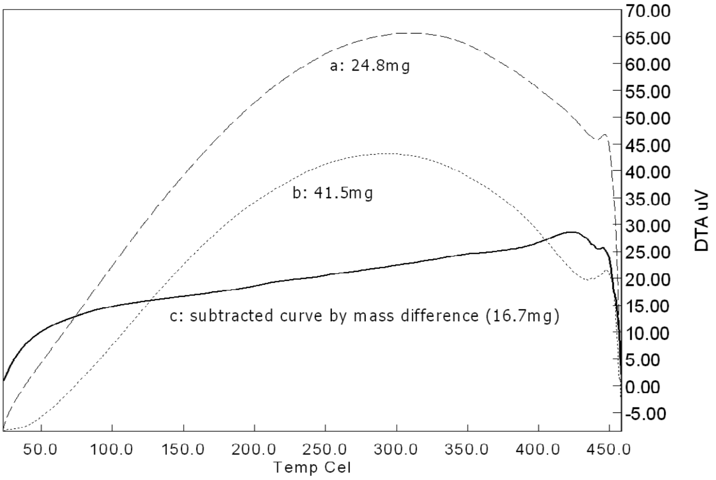

Figure 2: Determination of enthalpy change by mass-difference method

Determination of Heat Capacities by DSC

In DSC, the temperature program represents a linear function of time which can be mathematically expressed as [13]:

$$T_t = T_0 + \beta t \tag{2}$$

where T_t is the temperature at time t, To is the initial temperature and β stands for the heating rate (scan). For $\beta > 0$ the sample is heated, for $\beta < 0$ the sample is cooled and, finally, for the isothermal regime $\beta = 0$. The temperature program is isotherm-heating-isotherm. The initial and final isotherms are measured for setting the zero value of heat flow since if the sample is stable at constant temperature, then the heat flow to the sample is zero.

For reliable results, three measurements are usually carried out: the sample, the baseline and a standard. The baseline is subtracted from the sample record to obtain absolute values of the heat flow to the sample. If one takes into account Equation 2, the heat capacity can be expressed from its definition equation in the form:

$$C_P = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_P = \frac{1}{m}\left(\frac{\partial H/\partial t}{\partial T/\partial t}\right)_P = \frac{1}{m}\frac{\Delta P}{\beta} \tag{3}$$

where m is the sample mass, H is enthalpy and ΔP is the absolute value of the heat flow to the sample, i.e. of the DSC signal. Equation 3 is derived using the equilibrium-thermodynamics definition of heat capacity.

The determined specific heat capacities of ionic liquid within the examined temperature range can be described by the polynomial:

$$C_P(T) = \sum_{i=-1}^{3} A_i T^i \tag{4}$$

where $C_p(T)$ is the specific heat capacity of the examined ionic liquid at temperature T(K) and Ai is the constant. The selection of the polynomial degree (i) depends of the shape of the experimental curve C_p=f(T) obtained for the ionic liquid with precisely defined composition. The interpolated values of C_p at studied temperature ranges are given in Equation 5 and 6. The dependence of the specific heat capacity of the ionic liquid on the temperatures is shown in Figure 3. As seen from the comparison with literature data, the measured curve C_p has similar trend and slope. That is to say, at temperatures from 0 to 200°C, C_4mim[Tf_2N] shows a monotonic increase in the values of specific heat capacities with the increase in temperature. Slight differences in the shape of C_p=f (T) function for the studied temperature range, could be attributed to the differences in purity of prepared ionic liquid samples.

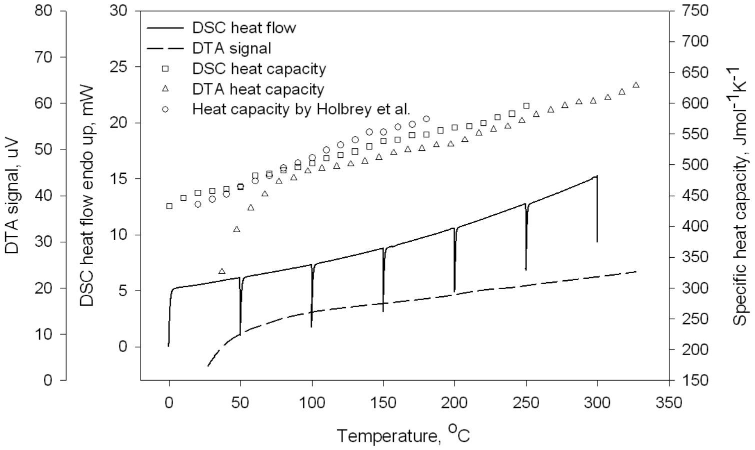

Figure 3: Heat capacity of C_4mim [Tf_2N] ionic liquid as a function of temperature (Determined by DSC and DTA methods and compared with literature data)

$$C_p = 1.050 \times 10^{-3} T + 1.051, R^2 = 0.9924 \quad J/(g^oC) \tag{5}$$

$$C_p = 0.61T + 274.53, R^2 = 0.9901 \quad kJ/(mol\ K) \tag{6}$$

Calculation of Thermodynamic Properties

Enthalpy change of ionic liquids is a vital thermal property for their application in thermal storage and heat transfer industry. Based on the heat capacities and enthalpy change data, it is possible to calculate entropy and Gibbs energy change of ionic liquids over temperature range of 0 - 200°C. The thermodynamic properties of C_4mim [Tf_2N] can be calculated by the following equations [14]:

$$S_T^o - S_{298}^o = \int_{298}^{T} (C_p/T)dT \tag{7}$$

$$H_T^o - H_{298}^o = \int_{298}^{T} C_p dT \tag{8}$$

$$G_T^o - G_{298}^o = (H_T^o - H_{298}^o) - T(S_T^o - S_{298}^o) \tag{9}$$

$$H^o - H^o_{273K}\ 274.53T + 0.30\,T^2 - 97618.41 \quad \text{(kJ/mol)} \tag{10}$$

$$S^o - S^o_{273K} = 274.53\ln T + 0.61T - 1706.06 \quad \text{(J/mol K)} \tag{11}$$

$$G^o - G^o_{273K} = 1980.59T - 274.53T\ln T - 0.30T^2 - 97618.41 \quad \text{(kJ/mol)} \tag{12}$$

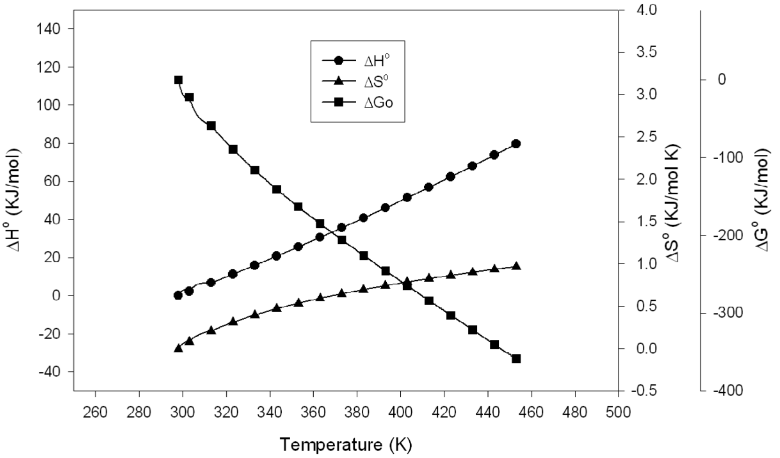

Figure 4: Change of enthalpy, entropy and Gibbs energy of C$_4$mim [Tf$_2$N] with temperature

The heat capacities determined by DTA mass difference method and DSC for C$_4$mim[Tf$_2$N] were compared in Table 2. Unlike the sample and temperature restriction of DSC, using DTA method one can measure the enthalpy changes extended to the decomposition point of ionic liquids. Obviously, there are some discrepancies between the DTA and DSC data. Mainly two reasons accounted for this: One reason is that the physical, chemical and thermodynamic properties are strongly dependent on the purity of ionic liquids. The observed differences could be attributed to varying levels of impurities, primarily the H_2O and Cl^- that might be present in the samples used in this work and those of literature. The water content of the ionic liquid sample used in DSC measurement was < 0.2 wt%, while the water content of the ionic liquids in this work is in the range of 0.7-1.5 wt%, which was confirmed by NMR analysis. The second reason is that DSC measurement requires the sample pan to be covered during heating which may disturb the rate of weight loss, and thus influence the result of the enthalpy measurement. DTA is more suitable to measure the enthalpy changes attributed to phase changes accompanied by weight loss because it uses open sample pans.

Figure 4 illustrates the enthalpy, entropy and standard Gibbs energy change of C$_4$mim [Tf$_2$N] over the temperature range 298-453 K, respectively. As shown in Figure 4, enthalpy, entropy and Gibbs energy changes exhibit linear like behavior over the studied temperature range due to the stable liquid phase. Unlike C$_4$mim[Cl], at the melting point 330 K, endothermic transformation of solid to liquid take place resulting in an abrupt increase in enthalpy, entropy, consequently in Gibbs energy as reported early [5]. C$_4$mim[Tf$_2$N] typically display thermodynamic property changes in a manner that they can be fitted into the forms of polynomial and logarithmic equations. The measured and calculated data were listed in Table 2. Because the heat capacities of ionic liquids usually change abruptly upon phase transition, fitted equations are only valid for liquid range.

Table 2: Heat Capacities and Thermodynamic Property Changes of C_4mim [Tf_2N] at Selected Temperature in the Liquid Range (273 K-523 K)

T (K)	Thermodynamic properties				
	CP^o(DTA)	CP^o(DSC)	H^o- H^o_{273K}	S^o-S^o_{273K}	G^o-G^o_{273K}
	kJ/mol K	kJ/mol K	kJ/mol	J/mol K	kJ/mol
273	-	432.78	0.000	0.000	0.000
303	146.99	457.52	13.492	46.875	-0.711
323	396.57	463.81	22.792	76.591	-1.947
343	453.61	485.62	32.334	105.252	-3.767
363	480.87	496.10	42.120	132.979	-6.151
383	496.28	511.20	52.149	159.870	-9.081
403	503.36	521.68	62.422	186.012	-12.541
423	514.96	539.30	72.938	211.477	-16.517
443	526.37	548.52	83.697	236.328	-20.996
463	534.12	556.07	94.700	260.618	-25.966
483	542.56	562.78	105.946	284.396	-31.417
503	559.87	577.04	117.436	307.703	-37.339
523	573.89	595.91	129.168	330.575	-43.722
Fitted equations		$\alpha+2\beta T$	$\alpha T+\beta T^2+\lambda$	$\alpha \ln T+2\beta T+\theta$	$(\alpha-\theta)T-\alpha T\ln T-\beta T^2+\lambda$
		$274.53+0.61T$	$274.53T+0.30T^2-97618.41$	$274.53\ln T+0.61T-1706.06$	$1980.59T-274.53T\ln T-0.30T^2-97618.41$

CONCLUSIONS

Specific heat capacity measurement was performed for 1-Butyl-3-Methylimidazolium Bis(trifluoromethylsulfonyl) imide ionic liquid (C_4mim[Tf_2N]) by means of differential thermal analysis (DTA) and differential Scanning Calorimetry (DSC) techniques. It is found the heat capacities of C_4mim[Tf_2N] determined by both methods have a weak temperature dependence over the temperature range 0°C to 200°C. Specific heat capacities of ionic liquid sample increase with increasing in temperature. The calculated heat capacities for C_4mim[Tf_2N] were 1.18 and 1.21 J/g.°C at 25°C and 100°C, respectively. The heat capacity data was fitted into a linear equations (C_p = k+aT) as a function of temperature range. With the obtained heat capacities of ionic liquids at different temperatures, other thermodynamic properties such as enthalpy, entropy and Gibbs energy change as a function of temperature were derived based on the heat capacity equations for ionic liquid C_4mim[Tf_2N].

The enthalpy changes of C_4mim[Tf_2N] ionic liquid are linearly endothermic due to the increase in the heat capacity. The enthalpy changes were fitted to linear regression; the entropy changes were fitted to polynomial quadratic regression and the Gibbs energy changes were fitted to polynomial cubic regression. The evaluation of C_4mim[Tf_2N] ionic liquids indicates that it is a promising candidate for thermal storage and heat transfer media. It has superior physicochemical and thermal properties such as wider liquid temperature range, higher thermal storage density and chemical stability as compared to traditional thermal storage media.

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