Thermodynamic Properties of 1-Propyl-3-methylimidazolium Glutamic Acid Salt

Qing-Shan Liu,[†] Jun-Ning Zhao,[‡] Jing Tong,[§] Li-Xian Sun,[‡] Zhi-Cheng Tan,*[,†,‡] and Urs Welz-Biermann*[,†]

China Ionic Liquid Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China, Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China, and Key Laboratory of Green Synthesis and Preparative Chemistry of Advanced Materials, Liaoning University, Shenyang 110036, People's Republic of China

Molar heat capacities ($C_{p,m}$) of the room-temperature ionic liquid (IL) 1-propyl-3-methylimidazolium glutamic acid salt ([C_3mim][Glu]) were measured with a high-precision automated adiabatic calorimeter (AC) in the temperature range of T = (85 to 360) K. A glass transition was observed at 239.861 K. The enthalpy and entropy of the glass transition were determined to be 2.87 kJ·mol^{-1} and 11.97 J·K^{-1}·mol^{-1}, respectively. Two polynomial equations of molar heat capacity as a function of the temperature were fitted before and after the glass transition. The thermodynamic functions ($H_T - H_{298.15}$) and ($S_T - S_{298.15}$) were derived from the molar heat capacity data in the temperature range of T = (85 to 360) K with an interval of 5 K.

Introduction

Ionic liquids (ILs) as organic salts often exhibit interesting properties such as low melting points, good solvation properties, and nonvolatility, which are expected by both industrial and scientific communities to have broad ranges of applications as electrolytes in batteries and supercapacitors,[1] reaction media in nanoscience,[2] physical chemistry,[3,4] and many other areas. Therefore, data on the physicochemical properties of ILs are necessary for their future applications and valuable for insight into the origins of their behavior.

Amino Acid Ionic Liquids (AAILs) as the halogen-free, designable organic molten salts and new "natural ILs" or "bio-ILs" are attracting increasing attention in many fields because they are derived from natural ions.[5−15] AAILs are high-quality functionalized liquids that have chiral centers, biodegradable characteristics, high biocompatibility, etc. The study of AAILs is mainly on the synthesis at present. The thermodynamic properties of AAILs, such as the molar heat capacity, enthalpy, and entropy of phase transitions are significant for their application in many areas, but the data are still lacking.

Recently, the volumetric properties of concentrated aqueous [C_3mim][Glu] were studied and published.[11] As a continuation of the research series of the pure IL [C_3mim][Glu], the molar heat capacities were measured by high-precision adiabatic calorimetry in the temperature range of T = (85 to 360) K in the present study. On the basis of the measured molar heat capacity values and thermodynamic relationships, the values of the thermodynamic functions relative to 298.15 K ($H_T - H_{298.15}$) and ($S_T - S_{298.15}$) were calculated for the compound. The glass transition temperature was obtained from the temperature corresponding to the largest step of the heat capacity jump on the heat capacity curve.

* Corresponding authors. E-mail: tzc@dicp.ac.cn (Zhi-Cheng Tan); uwb@dicp.ac.cn (Urs Welz-Biermann).
[†] China Ionic Liquid Laboratory.
[‡] Thermochemistry Laboratory.
[§] Liaoning University.

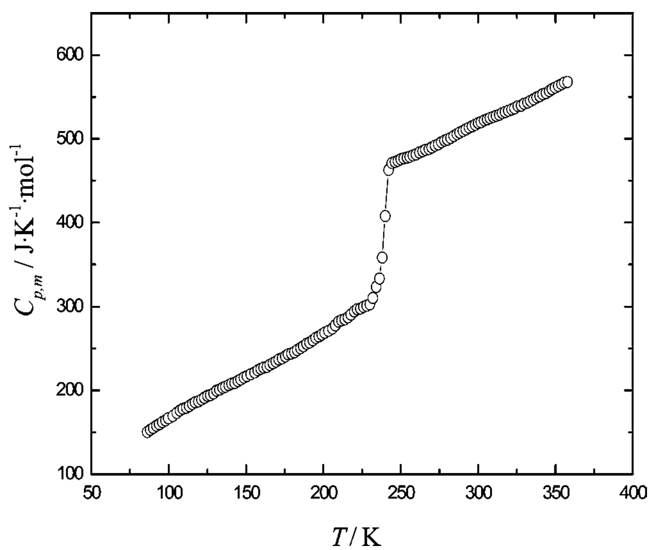

Figure 1. Experimental molar heat capacity ($C_{p,m}$) of [C_3mim][Glu] as a function of temperature.

Experimental Section

Chemical. Preparation and characterization have been described in ref 11. The sample of IL [C_3mim][Glu] was dried in vacuo for 2 days at 353 K before the calorimetric measurement. The content of water was determined to be less than 0.80 % (by mass) by a Cou-Lo Aquamax Karl Fischer Moisture Meter (v.10.06).

Adiabatic Calorimetry. The high-precision automated adiabatic calorimeter was established by the Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences in P.R. China. The principle and structure of the adiabatic calorimeter have been described in detail elsewhere.[16−21] The reliability of the adiabatic calorimeter apparatus was verified through the measurement of the molar heat capacities of the reference standard material, α-Al_2O_3. The deviations of our calibration results from those of the smoothed curve lie within ± 0.1 %,[21] as compared with the recommended

10.1021/je100131c
Published on Web 07/15/2010

Table 1. Experimental Values of the Molar Heat Capacities of IL [C_3mim][Glu]

T	$C_{p,m}$	T	$C_{p,m}$	T	$C_{p,m}$
K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$
86.074	150.25	179.170	243.70	272.094	491.51
88.048	152.63	181.114	245.51	274.115	493.23
90.009	154.90	183.047	248.04	276.131	495.70
91.965	157.50	185.030	250.20	278.148	497.67
93.946	159.49	187.051	252.70	280.158	498.94
95.918	162.14	189.061	255.28	282.164	501.05
97.887	164.13	191.064	257.14	284.166	503.38
99.854	166.66	193.052	259.68	286.162	505.39
102.593	169.25	195.034	262.63	288.124	507.35
105.331	173.04	197.011	264.18	290.056	509.26
107.277	175.80	198.971	266.54	292.083	511.23
109.244	177.98	200.930	268.59	294.050	513.10
111.235	179.21	203.311	271.02	296.009	514.91
113.197	181.07	205.670	273.69	297.970	516.83
115.139	183.75	207.647	277.76	299.926	518.67
117.103	185.58	209.690	281.69	301.875	520.07
119.091	186.96	211.733	283.31	303.825	521.96
121.056	188.82	213.765	284.60	305.766	523.25
123.004	191.13	215.799	286.92	307.705	524.77
124.974	193.29	217.825	290.11	309.643	526.25
126.970	194.36	219.853	294.21	311.570	527.31
128.941	196.26	221.880	296.62	313.504	528.82
130.895	199.43	223.909	297.46	315.426	530.52
132.836	200.78	225.943	299.66	317.412	531.97
134.792	203.07	227.970	300.73	319.471	533.47
136.778	204.43	229.985	302.48	321.522	534.99
138.747	206.24	231.961	310.06	323.566	536.53
140.703	207.69	234.002	323.45	325.605	538.93
142.645	208.89	236.070	333.04	327.646	539.74
144.607	211.05	238.024	358.09	329.680	541.83
146.596	212.89	239.861	407.73	331.706	543.17
148.567	215.15	242.007	462.82	333.728	544.98
150.535	216.91	244.243	471.00	335.749	546.87
153.036	219.16	246.181	472.35	337.759	549.25
155.557	221.42	248.116	473.61	339.767	550.76
157.531	223.77	250.045	475.54	341.770	553.01
159.493	225.64	251.972	476.41	343.770	554.52
161.440	227.00	253.896	477.37	345.764	557.00
163.376	228.24	255.887	478.45	347.755	559.26
165.298	230.30	257.873	480.19	349.744	561.22
167.266	232.18	259.860	481.42	351.732	563.15
169.282	234.10	261.908	483.73	353.717	565.12
171.285	236.74	263.957	485.28	355.702	566.91
173.274	237.97	265.995	486.86	357.682	568.06
175.247	240.31	268.035	487.89		
177.213	242.87	270.066	489.67		

values reported by Archer of NIST[22] in the temperature range of $T = (80$ to $400)$ K. The uncertainty of the measurement for molar heat capacity of the sample is 0.3 %. The sample mass used for the heat capacity measurement was 3.68061 g which is equivalent to 0.01357 mol based on the molar mass, $M = 271.1532\ g \cdot mol^{-1}$. The temperature increment was 2 K in a heating period, and the drift of the temperature was maintained at about 1 $mK \cdot min^{-1}$ during the equilibrium period.

Results and Discussion

Molar Heat Capacity. The experimental values of the molar heat capacities of IL [C_3mim][Glu] over the experimental temperature range are listed in Table 1 and plotted in Figure 1, respectively.

From Figure 1, a heat capacity step jump was observed from (229.985 to 244.243) K on the heat capacity curve, which indicated that the IL glass transition process occurred in this temperature range. The glass transition temperature, $T_g = 239.861$ K, was obtained from the temperature corresponding to the largest step of the heat capacity jump on the heat capacity curve. In general, three types of thermal behavior are observed for the imidazolium-based ionic liquids.[23] The first type has a distinct freezing point on cooling and a melting point on heating. The second type shows only glass transition with neither melting nor freezing points. The third one is characterized by a cold crystallization. Upon heating, the compound passes from the glass to a subcooled liquid phase, and then a cold crystallization occurs, followed by a melting transition. In our case, the thermal behavior of [C_3mim][Glu] is similar to the second type. Two smooth heat capacity curves were observed before and after the glass transition process.

Table 2. Data of the Thermodynamic Functions of IL [C_3mim][Glu]

T	$C_{p,m}$	$H_T - H_{298.15}$	$S_T - S_{298.15}$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
85	148.34	−62.05	−321.96
90	155.03	−61.29	−313.29
95	161.20	−60.50	−304.74
100	167.01	−59.68	−296.33
105	172.55	−58.83	−288.04
110	177.89	−57.95	−279.89
115	183.08	−57.05	−271.87
120	188.13	−56.12	−263.96
125	193.07	−55.17	−256.18
130	197.91	−54.19	−248.52
135	202.65	−53.19	−240.96
140	207.31	−52.16	−233.51
145	211.90	−51.12	−226.15
150	216.45	−50.04	−218.89
155	220.98	−48.95	−211.72
160	225.54	−47.84	−204.64
165	230.16	−46.70	−197.62
170	234.90	−45.53	−190.68
175	239.80	−44.35	−183.80
180	244.91	−43.13	−176.97
185	250.26	−41.90	−170.19
190	255.88	−40.63	−163.44
195	261.78	−39.34	−156.72
200	267.92	−38.01	−150.02
205	274.25	−36.66	−143.33
210	280.68	−35.27	−136.64
215	287.02	−33.85	−129.96
220	293.07	−32.40	−123.29
225	298.51	−30.92	−116.64
230	302.94	−29.42	−110.03
235		glass transition range	
240			
245	471.49	−26.17	−96.54
250	475.10	−23.81	−86.98
255	478.37	−21.42	−77.54
260	481.76	−19.02	−68.22
265	485.54	−16.61	−59.01
270	489.77	−14.17	−49.89
275	494.39	−11.71	−40.86
280	499.27	−9.22	−31.91
285	504.25	−6.72	−23.03
290	509.19	−4.18	−14.22
295	513.94	−1.62	−5.47
298.15	516.79	0.00	0.00
300	518.42	0.96	3.20
305	522.60	3.56	11.81
310	526.52	6.18	20.34
315	530.27	8.83	28.79
320	533.96	11.49	37.17
325	537.76	14.17	45.48
330	541.82	16.86	53.72
335	546.26	19.58	61.90
340	551.10	22.33	70.03
345	556.26	25.10	78.11
350	561.45	27.89	86.15
355	566.16	30.71	94.15
360	569.53	33.55	102.10

The values of the experimental molar heat capacities can be fitted to the following polynomial equations with the least-squares method.[24]

Before the glass transition, T = (86 to 230) K

$$C_{p,\mathrm{m}}/\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1} = 223.710 + 65.674x + 5.011x^2 + 21.866x^3 + 8.996x^4 - 10.931x^5 - 11.387x^6 \quad (1)$$

After the glass transition, T = (244 to 358) K

$$C_{p,\mathrm{m}}/\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1} = 519.278 + 48.722x - 19.472x^2 + 3.396x^3 + 42.667x^4 - 3.244x^5 - 22.932x^6 \quad (2)$$

where x is the reduced temperature; $x = [T - (T_{\max} + T_{\min})/2]/[(T_{\max} - T_{\min})/2]$; T is the experimental temperature; and $T_{\max}$ and $T_{\min}$ are the maximum and minimum of the temperature in the experimental temperature range. The correlation coefficient of the fitting is R = 0.9998 and 0.9999 corresponding to eqs 1 and 2, respectively.

Thermodynamic Functions. The thermodynamic functions $(H_T - H_{298.15})$ and $(S_T - S_{298.15})$ of the IL [C_3mim][Glu] were derived from the molar heat capacity data in the temperature range from (85 to 360) K per 5 K, using the polynomial equation for the molar heat capacity and thermodynamic relationships as follows

$$H_T - H_{298.15} = \int_{298.15}^{T} C_{p,\mathrm{m}}\mathrm{d}T \quad (3)$$

$$S_T - S_{298.15} = \int_{298.15}^{T} (C_{p,\mathrm{m}}/T)\mathrm{d}T \quad (4)$$

The values of the standard thermodynamic functions $(H_T - H_{298.15})$ and $(S_T - S_{298.15})$ are listed in Table 2.

Conclusions

Molar heat capacities ($C_{p,\mathrm{m}}$) of 1-propyl-3-methylimidazolium glutamic acid salt were measured with a high-precision automated adiabatic calorimeter in the temperature range of T = (85 to 360) K. A glass transition took place in the range of T = (229.985 to 244.243) K. Two polynomial equations of molar heat capacity as a function of the temperature were fitted before and after the glass transition. According to the polynomial equations and thermodynamic relationship, the thermodynamic functions $(H_T - H_{298.15})$ and $(S_T - S_{298.15})$ were determined in the temperature range of T = (85 to 360) K with an interval of 5 K.

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Received for review February 6, 2010. Accepted July 2, 2010.

JE100131C