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Low-temperature heat capacity and standard thermodynamic functions of 1-hexyl-3-methyl imidazolium perrhenate ionic liquid

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Abstract
Heat capacity for 1-hexyl-3-methyl imidazolium perrhenate ionic liquid [C_6MIM][ReO_4] in the temperature range from 79 to 396 K has been measured by a fully automated adiabatic calorimeter. For [C_6MIM][ReO_4], glass transition temperature, the melting temperature, standard molar heat capacity, enthalpy and entropy of solid–liquid phase transition were determined to be (202.164 ± 0.405) K, (226.198 ± 0.265) K, (480.702 ± 0.013) J K^{-1} mol^{-1}, (15.665 ± 0.195) kJ mol^{-1} and (69.250 ± 0.780) J K^{-1} mol^{-1}, respectively. In addition, the thermodynamic characteristics and solid–liquid phase change behavior of [C_6MIM][ReO_4] were compared with the ones of [C_7MIM][ReO_4] reported in the literature. The thermodynamic functions ($H_T - H_{298.15}$), ($S_T - S_{298.15}$) and ($G_T - G_{298.15}$), for the compound in the experimental temperature range were calculated.

Keywords Perrhenate · Thermodynamic functions · Heat capacity · Adiabatic calorimeter · Ionic liquids

Introduction

Usually, the melting temperatures of ionic compounds are higher than room temperature due to their strong and long-range interionic interactions. However, it is found that melting temperatures of a series of organic ionic compounds are lower than room temperature, and they are called room-temperature ionic liquids (ILs) [1, 2]. ILs are made up of a bulky organic cation and a counterion and possess special physical and chemical properties, making them attractive for both pure scientific and applied studies [3–7]. In recent years, all kinds of applications, extraction and separation processes, synthetic chemistry, catalysis, materials science and so on have been proposed for ILs; for example, rhenium ionic liquids can be used for epoxidation of olefins due to their excellent activity and selectivity [8–11]. The parameters of fusion of ILs are crucial for their applicability. Many results, such as melting temperature, glass transition temperature, standard molar heat capacity, enthalpy and entropy of solid–liquid phase transition, and other important information about the structure and energetics of the ILs, can be obtained from the experimental heat capacity data. All in all, the low-temperature heat capacity has very significant role in the theoretical research and application development of ILs [12–14].

A report about the preparation and thermodynamic properties of ionic liquid [C_7MIM][ReO_4] has been published in our laboratory [1]; as a continuation of our previous investigation, this paper reports the following: (1) 1-hexyl-3-methyl imidazolium perrhenate ionic liquid [C_6MIM][ReO_4] were prepared and characterized by ^{1}H NMR spectroscopy and Raman spectrum; (2) low-temperature heat capacities of [C_6MIM][ReO_4] were measured by a high-precision automated adiabatic calorimeter over the temperature range from 79 to 396 K; (3) the thermodynamic functions ($H_T - H_{298.15}$), ($S_T - S_{298.15}$) and ($G_T - G_{298.15}$) were also calculated based on the experimental results.

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Experimental

Reagents

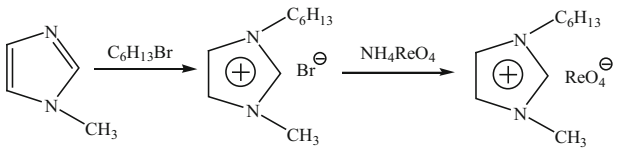
The purities and sources of the reagents are listed in Table 1.

Preparation of IL [C_6MIM][ReO_4]

In this work, [C_6MIM][ReO_4] was synthesized and the scheme 1 shows the synthetic route. The *N*-methylimidazole (1 mol) and the bromohexane (1.2 mol) were placed in a round-bottomed flask and stirred under reflux at 80 °C for 48 h to obtain the [C_6MIM] Br [15, 16]. Then, [C_6MIM] Br and 1.2 equiv. of NH_4ReO_4 were reacted in acetone under argon and stirred at room temperature for 48 h to obtain the target product. In addition, ethyl acetate and acetonitrile were used as an extractant in this experiment. The content of Br^- was determined by dripping the silver nitrate solution; the results reveal that any yellow deposition did not appear. The [C_6MIM][ReO_4] was characterized by ^{1}H NMR spectroscopy and Raman spectrum (see Figure S1 and S2); its purity is more than 99.8%. And the water content was determined by a Karl Fischer moisture titrator (ZSD-2 type), and it is less than 0.3 mass%.

Measurement of molar heat capacities of IL [C_6MIM][ReO_4] by adiabatic calorimeter

To verify the dependability of the adiabatic calorimeter, the molar heat capacities for reference standard material, α-Al_2O_3 was measured. The deviations of our experimental results from the recommended values by NIST are within ± 0.5%, while the uncertainty is within ± 0.37%, as compared with the values given by the former National Bureau of Standards [17] in the temperature range of (78–400) K.



Scheme 1 Synthesis of the novel ionic liquid [C_6MIM][ReO_4]

The molar heat capacities of [C_6MIM][ReO_4] (1.74589 g) were repeatedly measured by the adiabatic calorimeter, established by Dalian Institute of Chemical Physics [18–20]. Over the temperature range between 79 and 396 K, the first experimental data are listed in Table 2 and plotted in Fig. 1, and the second experimental data are listed in Table S1 and plotted in Figure S3 in Supporting Information, respectively.

Results and discussion

Heat capacity

From Fig. 1, an endothermic step corresponding to a glass transition occurred at glass transition temperature T_g = 201.760 K. From 210 to 230 K, a sharply endothermic peak was observed with the peak temperature 225.934 K; it corresponds to a melting process. And smooth heat capacity curves without endothermic and exothermic peaks were observed in other experimental temperature regions.

The molar heat capacities are fitted to two following polynomial in reduced temperature (x) by means of the least square fitting.

For the first temperature range (80–196) K:

$$x = (T - 138)/58 \quad (1)$$

$$C_{p,m} = 254.54162 + 76.73522x - 25.34498x^2 + 5.63153x^3 + 25.69092x^4 + 1.67611x^5 - 5.19123x^6. \quad (2)$$

Table 1 The purities and sources of the reagents

Reagent	Purity/%	Source
Deionized water		
N-Methylimidazole	≥ 99.8	ACROS
Bromohexane	99.5	Shanghai Reagent Co. Ltd
Ethyl acetate	99.5	Tianjin Fuyu chemical limited company
Acetonitrile	99.5	Tianjin Fuyu chemical limited company
Ammonium perrhenate	99.9	Jiangxi Copper Industry Company
α-Al_2O_3(s)	> 99.95	National Institute of Standards
Acetone	99.5	Tianjin Fuyu chemical limited company

Table 2 The first series experimental molar heat capacities of $[C_6MIM][ReO_4]$ in the temperature range (79–396) K

T/K	$C_{p,m}$/J K^{-1} mol^{-1}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}
79.847	165.521	186.631	315.379	294.048	479.084
82.171	167.603	189.630	320.004	297.149	480.145
85.489	175.269	192.690	327.105	300.253	481.827
88.308	176.989	195.736	333.939	303.363	482.071
91.167	181.461	198.767	346.877	306.478	484.151
94.026	187.163	201.760	370.199	309.596	486.627
96.896	191.605	204.708	409.994	312.715	487.201
99.765	194.881	207.677	413.112	315.829	489.721
102.650	201.376	210.635	418.281	318.940	492.504
105.555	205.946	213.653	422.586	322.051	493.162
108.476	207.490	216.729	426.548	325.159	495.556
111.417	212.165	219.816	450.574	328.268	497.927
114.348	218.918	222.929	543.826	331.376	503.083
117.269	224.976	225.934	702.589	334.490	505.595
120.213	229.398	228.831	438.340	337.609	507.151
124.263	235.602	231.875	436.097	340.740	509.545
128.265	241.066	234.973	442.837	343.865	512.444
131.159	245.356	237.944	445.658	346.977	516.090
134.130	248.584	240.900	447.247	350.085	522.530
137.126	255.313	244.625	448.292	353.194	524.788
140.098	259.022	248.269	451.607	356.307	528.841
143.045	261.489	251.241	453.704	359.424	531.638
146.023	264.746	254.305	455.820	362.545	536.565
149.028	266.929	257.368	457.209	365.674	540.313
152.015	268.474	260.429	459.765	368.809	541.419
154.981	274.004	263.491	461.608	371.950	544.886
157.933	277.803	266.550	462.297	375.000	549.221
160.916	280.802	269.611	464.743	378.050	552.305
163.931	286.743	272.690	465.772	381.101	557.736
166.933	291.140	275.675	467.945	384.153	559.263
169.922	294.393	278.647	469.106	387.199	563.462
172.897	295.654	281.726	471.806	390.243	567.344
175.908	299.087	284.809	473.688	393.280	568.877
178.952	304.741	287.887	476.739	396.310	573.538
182.814	309.570	290.960	477.476		

The standard uncertainty (0.68 level of confidence): $u(T) = 0.001$ K. $u(p) = 0.001$ MPa. The expanded uncertainties U_c (0.95 level of confidence): $U_c(C_{p,m}) = 0.005$

The correlation coefficient of the fitting $R^2 = 0.9992$.

For the second temperature range (205–217) K:

$$x = (T - 211)/6 \tag{3}$$

$$C_{p,m} = 418.57120 + 9.91126x - 0.11770x^2 - 1.64125x^3. \tag{4}$$

The correlation coefficient of the fitting $R^2 = 0.9958$.

For the third temperature range (229–396) K:

$$x = (T - 312.5)/83.5 \tag{5}$$

$$C_{p,m} = 487.88856 + 52.43944x + 38.07827x^2 + 31.55308x^3 - 31.39746x^4 - 16.69594x^5 + 10.47850x^6. \tag{6}$$

The correlation coefficient of the fitting $R^2 = 0.9991$.

Where x is the reduced temperature, $x = [T - (T_{max} + T_{min})/2]/[(T_{max} - T_{min})/2]$, T is the experimental temperature.

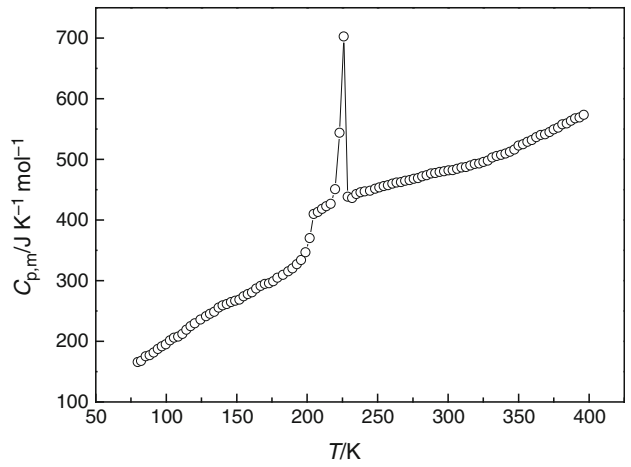


Fig. 1 The first series experimental molar heat capacities of [C_6-MIM][ReO_4] in the temperature range (79–396) K

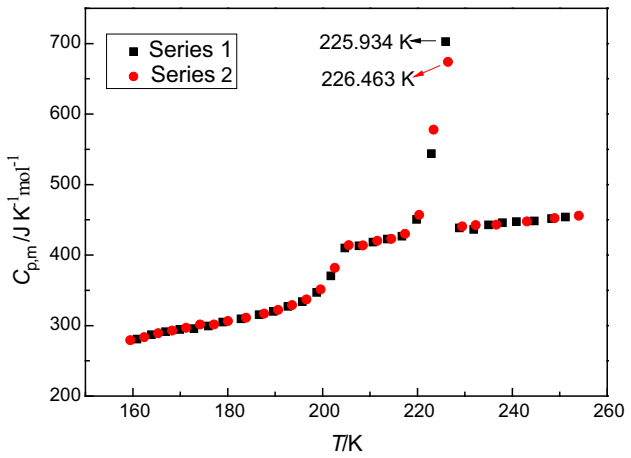


Fig. 2 Both series of experimental molar heat capacities of [C_6-MIM][ReO_4] in the glass transition and fusion region

Both series of heat capacity measurements of the sample in the fusion region are carried out and shown in Fig. 2; from the figure, not only is verified the almost perfect reversibility and repeatability of the fusion process, but also the repeated heat capacity measurements of the both series. And the melting temperature is obtained to be (226.198 ± 0.265) K, and it is listed in Table 4. Compared with [C_7MIM][ReO_4] [1], the melting temperature of [C_6-MIM][ReO_4] is higher, which is possibly due to the more carbonyl group in the cation, the more the steric hindrance strengthened, which leads to the melting temperature decrease with increasing the number of methylene group in the alkyl chains of the ILs, and the change trend is agreement with Tan's work, that is mainly reported that the heat capacities and melting points of ionic liquids 1-ethylpyridinium bromide (EPBr) and 1-propylpyridinium bromide (PPBr) [16].

Thermodynamic functions

The thermodynamic functions related to the reference temperature 298.15 K were calculated in the temperature range (80–400) K with an interval of 5 K, using the polynomial equation for heat capacity and thermodynamic relationships as follows:

$$H_T - H_{298.15} = \int_{298.15}^{T} C_{p,} dT \quad (7)$$

$$S_T - S_{298.15} = \int_{298.15}^{T} (C_p/T) dT \quad (8)$$

$$G_T - G_{298.15} = \int_{298.15}^{T} C_{p,} \quad dT - T \int_{298.15}^{T} (C_p/T) dT. \quad (9)$$

The calculated values of thermodynamic functions ($H_T - H_{298.15}$), ($S_T - S_{298.15}$) and ($G_T - G_{298.15}$) are listed in Table 3.

From Table 3, standard molar heat capacity at T = 298.15 K is 480.715 J K^{-1} mol^{-1}, which is lower than the value of [C_7MIM][ReO_4] [1], that is, it can be seen that the values of the standard molar heat capacity increase along with increasing the number of methylene group in the alkyl chains of the ILs, and it is also consistent with Tan's [16].

The molar enthalpy $\Delta_{fus}H_m$ and entropy $\Delta_{fus}S_m$ of fusion of the compound were calculated from the following equations:

$$\Delta_{fus}H_m = \frac{Q - n\int_{T_i}^{T_m} Cp(S)dT - n\int_{T_m}^{T_f} Cp(L)dT - \int_{T_i}^{T_f} C0dT}{n} \quad (10)$$

$$\Delta_{fus}S_m = \frac{\Delta_{fus}H_m}{T_m} \quad (11)$$

where T_i is the temperature at the initial melting temperature, T_f is the temperature at the final melting temperature, Q is the total energy introduced to the sample cell from T_i to T_f, $C_{p(S)}$ is the heat capacity of the sample in the solid phase at T_i, $C_{p(L)}$ is the heat capacity of the sample in liquid

Table 3 The calculated values of thermodynamic functions data for $[C_6MIM][ReO_4]$ in the temperature range (80–400) K

T/K	$C_{p,m}$/J K^{-1} mol^{-1}	$H_T - H_{298.15}$/kJ mol^{-1}	$S_T - S_{298.15}$/J mol^{-1} K^{-1}	$-(G_T - G_{298.15})$/kJ mol^{-1}
80	165.402	− 75.698	− 404.008	− 43.377
85	174.468	− 74.775	− 393.446	− 41.332
90	179.236	− 73.850	− 383.166	− 39.365
95	188.902	− 72.917	− 373.135	− 37.469
100	195.301	− 71.971	− 363.322	− 35.639
105	205.410	− 71.007	− 353.699	− 33.869
110	209.448	− 70.019	− 344.237	− 32.153
115	220.404	− 69.004	− 334.911	− 30.489
120	229.087	− 67.955	− 325.696	− 28.871
125	236.619	− 66.871	− 316.571	− 27.300
130	243.802	− 65.746	− 307.513	− 25.769
135	250.355	− 64.578	− 298.504	− 24.280
140	258.941	− 63.364	− 289.525	− 22.831
145	263.631	− 62.100	− 280.561	− 21.419
150	267.211	− 60.785	− 271.597	− 20.045
155	274.039	− 59.416	− 262.620	− 18.710
160	279.619	− 57.993	− 253.619	− 17.414
165	288.534	− 56.512	− 244.585	− 16.155
170	294.444	− 54.974	− 235.508	− 14.938
175	297.698	− 53.378	− 226.383	− 13.761
180	306.245	− 51.723	− 217.206	− 12.626
185	312.849	− 50.009	− 207.972	− 11.534
190	320.775	− 48.237	− 198.681	− 10.488
195	331.924	− 46.406	− 189.331	− 9.486
200	353.849	− 44.519	− 179.927	− 8.534
205	411.956	− 42.576	− 170.470	− 7.630
210	416.681	− 40.579	− 160.966	− 6.776
215	423.020	− 38.530	− 151.421	− 5.974
220	452.516	− 36.430	− 141.843	− 5.225
225	692.993	− 34.234	− 132.243	− 4.479
230	402.480	− 32.092	− 122.632	− 3.887
235	442.765	− 29.860	− 113.023	− 3.300
240	447.245	− 27.589	− 103.430	− 2.766
245	448.568	− 25.285	− 93.831	− 2.296
250	452.873	− 22.951	− 84.362	− 1.861
255	456.145	− 20.593	− 74.925	− 1.487
260	459.389	− 18.213	− 65.579	− 1.162
265	461.840	− 15.819	− 56.348	− 0.887
270	464.939	− 13.415	− 47.256	− 0.656
275	467.499	− 11.008	− 38.330	− 0.467
280	470.227	− 8.602	− 29.597	− 0.315
285	473.859	− 6.206	− 21.087	− 0.196
290	477.301	− 3.827	− 12.830	− 0.106
295	479.433	− 1.470	− 4.859	− 0.037
298.15	480.715			
300	481.744	0.889	3.010	0.014
305	482.905	3.301	10.909	0.026
310	486.761	5.728	18.786	0.096

Table 3 (continued)

T/K	$C_{p,m}$/J K^{-1} mol^{-1}	$H_T - H_{298.15}$/kJ mol^{-1}	$S_T - S_{298.15}$/J mol^{-1} K^{-1}	$-(G_T - G_{298.15})$/kJ mol^{-1}
315	488.862	8.170	26.596	0.208
320	492.783	10.629	34.343	0.361
325	495.439	13.106	42.030	0.554
330	500.780	15.603	49.661	0.785
335	505.834	18.121	57.241	1.055
340	508.901	20.660	64.772	1.362
345	513.463	23.224	72.258	1.705
350	522.406	25.812	79.704	2.084
355	527.078	28.426	87.113	2.499
360	532.383	31.068	94.489	2.948
365	539.799	33.738	101.836	3.432
370	542.380	36.439	109.157	3.949
375	549.221	39.171	116.457	4.500
380	556.000	41.936	123.740	5.085
385	560.098	44.735	131.008	5.703
390	567.143	47.570	138.266	6.354
395	570.682	50.441	145.518	7.039
400	593.754	53.350	152.767	7.757

Table 4 Results of phase transition of the $[C_6MIM][ReO_4]$ obtained from both series of heat capacity measurements

Thermodynamic functions	Series 1, x_1	Series 2, x_2	$\bar{x} \pm \sigma_a$
T_m/K	225.93	226.46	226.198 ± 0.265
$\Delta_{fus}H_m$/kJ mol^{-1}	15.47	15.86	15.665 ± 0.195
$\Delta_{fus}S_m$/J K^{-1} mol^{-1}	68.47	70.03	69.250 ± 0.780

$\sigma_a = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n(n-1)}}$, in which n is the experimental number; x_i, a single value in a set of calorimetric measurements; x, the mean value of a set of measurement results

phase at T_f and C_0 is the average heat capacity of the empty sample cell at temperature $(T_i + T_f)/2$.

The results of the melting point, molar enthalpy and entropy of two phase transitions obtained from every series of repeated experiments have been listed in Table 4.

Conclusions

In this paper, the heat capacities of $[C_6MIM][ReO_4]$ were measured in the temperature range (79–396) K by adiabatic calorimeter. And according to heat capacity values, glass transition temperature, the melting temperature, standard molar heat capacity, enthalpy and entropy of solid–liquid phase transition were determined to be (202.164 ± 0.405) K, (226.198 ± 0.265) K, (480.702 ± 0.013) J K^{-1} mol^{-1}, (15.665 ± 0.195) kJ mol^{-1} and (69.250 ± 0.780) J K^{-1} mol^{-1}, respectively. It may due to the fact that the longer carbon chain in imidazolium cation, the more steric hindrance and lattice energy, which results in a decrease in melting temperature but an increase in standard molar heat capacity. And the variation trends of the melting temperature and standard molar heat capacity at 298.15 K are consistent with Tan's.

In addition, the corresponding thermodynamic functions $(H_T - H_{298.15})$, $(S_T - S_{298.15})$ and $(G_T - G_{298.15})$ were calculated in the temperature range from 80 to 400 K.

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