

THERMODYNAMIC INVESTIGATION OF ROOM TEMPERATURE IONIC LIQUID

Heat capacity and thermodynamic functions of BMIBF₄

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The molar heat capacities of the room temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF₄) were measured by an adiabatic calorimeter in temperature range from 80 to 390 K. The dependence of the molar heat capacity on temperature is given as a function of the reduced temperature X by polynomial equations, $C_{p,m}$ (J K⁻¹ mol⁻¹) = $195.55 + 47.230 X - 3.1533 X^2 + 4.0733 X^3 + 3.9126 X^4$ [$X = (T - 125.5)/45.5$] for the solid phase (80~171 K), and $C_{p,m}$ (J K⁻¹ mol⁻¹) = $378.62 + 43.929 X + 16.456 X^2 - 4.6684 X^3 - 5.5876 X^4$ [$X = (T - 285.5)/104.5$] for the liquid phase (181~390 K), respectively. According to the polynomial equations and thermodynamic relationship, the values of thermodynamic function of the BMIBF₄ relative to 298.15 K were calculated in temperature range from 80 to 390 K with an interval of 5 K. The glass transition of BMIBF₄ was observed at 176.24 K. Using oxygen-bomb combustion calorimeter, the molar enthalpy of combustion of BMIBF₄ was determined to be $\Delta_c H_m^\circ = -5335 \pm 17$ kJ mol⁻¹. The standard molar enthalpy of formation of BMIBF₄ was evaluated to be $\Delta_f H_m^\circ = -1221.8 \pm 4.0$ kJ mol⁻¹ at $T = 298.150 \pm 0.001$ K.

Keywords: adiabatic calorimetry, BMIBF₄, combustion calorimetry, glass transition, heat capacity, room temperature ionic liquid, standard enthalpy of formation, thermodynamic function

Introduction

Room temperature ionic liquids (RTILs) have emerged as a new kind of media alternative to the conventionally used organic solvents, which are generally volatile, flammable and hazardous chemicals [1–3]. Even though ionic liquids such as [EtNH₃][NO₃], which has a melting point of 285 K, have been known since 1914 [4], it is only very recently that the usefulness of these systems as a new kind of media for synthetic electrochemical and catalytic applications are being explored [5–11]. Some of the properties that make the room temperature ionic liquids attractive media for various applications are the wide liquid range, nonvolatility (negligible vapor pressure), non-flammable nature, less reactivity, and the ability to dissolve a large variety of organic and inorganic substances including even the polymer materials in high concentration. Many of these properties have made the room temperature ionic liquids a nature-friendly ‘Green Solvent’ [12]. The room temperature ionic liquids that are currently the focus of extensive investigation are generally a substituted imidazolium or a pyridinium salt. Even though the solvent properties of different halogenoaluminate(III) ionic liquids (ILs) were studied as early as in 1986 [13], very little is known about the various properties of the contempo-

rary ionic liquids despite their extensive usage in synthetic applications. We refer, for instance, to that data of heat capacity, standard enthalpy of formation, thermodynamic functions and so on, which are paramount for the design of any technological processes, are even scarcer [14].

As a continuation of our previous investigations of RTILs [15–17], in the present study the molar heat capacities of RTIL, BMIBF₄ were measured by an adiabatic calorimeter in temperature range from 80 to 390 K. Based on the measured heat capacity data and thermodynamic relationship, the values of thermodynamic function of the BMIBF₄ relative to 298.15 K were calculated. The glass transition of BMIBF₄ was observed at 176.24 K. Through oxygen-bomb combustion calorimetry, the molar enthalpies of combustion of BMIBF₄ were determined. The standard molar enthalpy of formation was further evaluated.

Experimental

Chemicals

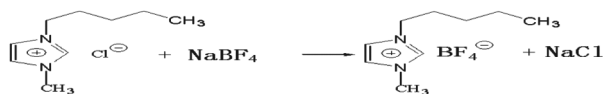
We purchased ethylacetate (AR), acetone (AR), acetonitrile (AR) and sodium tetrafluoroborate (AR), respectively. 1-methylimidazole was vacuum distilled

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prior to use. 1-chlorobutane (AR) was purified by standard method.

Synthesis of BMIBF₄

BMIBF₄ was synthesized through alkylation of 1-methylimidazole chlorate (BMIC) with sodium tetrafluoroborate (NaBF₄) in acetone as an inert solvent according to the following reaction scheme.



BMIBF₄ was prepared according to literature procedures [18–25]. We fitted a 500 mL three-necked round-bottom flask with a water condenser, provided it with a teflon-coated magnetic bar, and equipped with a gas inlet, through which we can charged under N₂. 1-methylimidazole (120 mL) and 1-chlorobutane (153 mL) were added into the reaction vessel with continuous magnetic stirring. The reaction mixture was heated under nitrogen N₂ at 353.2 K for 96 h with stirring until two phases formed. The top phase, containing unreacted starting material, was decanted, and ethylacetate (150 mL) was added with through mixing. The ethylacetate was decanted followed by the addition of fresh ethylacetate and this step was repeated twice. After the third decanting of ethylacetate, any remaining ethylacetate was removed by heating to 343 K and stirring while on a vacuum line. The product is slightly yellow and may be crystalline at room temperature, depending on the amount of water present in that phase. The product was recrystallized twice from dry acetonitrile and dried under vacuum at 343 K for 12 h to yield the pure crystalline 1-butyl-3-methylimidazolium chlorate (BMIC). Equimolar sodium tetrafluoroborate was added to the solution of (BMIC) in acetone at room temperature. After 72 h stirring, the resulting NaCl precipitate was then filtered through a plug of celite and the volatiles were removed by rotary evaporation to leave a colorless, clear liquid, and finally *in vacuo* to yield the resulting BMIBF₄. The chemical shifts for ¹H-NMR spectrum (CDCl₃, TMS) of the product appear as follows:

$\delta = 10.567$ (s,H²), $\delta = 7.704$ (d,H⁴), $\delta = 7.543$ (d,H⁵),
 $\delta = 4.347$ (t,NCH²),
 $\delta = 4.136$ (s,NCH³), $\delta = 1.911$ (m,NCH²CH²),
 $\delta = 1.398$ (m,NCH²CH²CH²),
 $\delta = 0.963$ (t,CH³). The ¹H-NMR spectra of the product showed as the same as literature [25].

Heat-capacity measurement

Heat-capacity measurements were carried out in a high-precision automatic adiabatic calorimeter described in detail elsewhere [26, 27]. The principle of the calorimeter is based on the Nernst stepwise heating method. The calorimeter mainly consists of a sample cell, an adiabatic (or inner) shield, a guard (outer) shield, a platinum resistance thermometer, an electric heater, two sets of chromel–copper thermocouples and a high vacuum can. The sample cell was made of gold-plated copper and had an inner volume of 48 cm³. Eight gold-plated copper vanes of 0.2 mm thickness were put into the cell to promote heat distribution between the sample and the cell. The platinum resistance thermometer was inserted into the copper sheath, which was soldered in the middle of the sample cell. The heater wire was wound on the surface of the thermometer. The evacuated can was kept within ca. 1·10⁻³ Pa during the heat-capacity measurements so as to eliminate the heat loss due to gas convection. Liquid nitrogen was used as the cooling medium. One set of chromel–copper thermocouples was used to detect the temperature difference between the sample cell and the inner shield. Likewise, the other set of thermocouples was installed between the inner and outer shields. The temperature difference between them was kept to within 0.5 mK during the whole experimental process. The sample cell was heated by the standard discrete heating method. The temperature of the cell was measured by a platinum resistance thermometer. The thermometer was made by

Table 1 The constant-volume combustion energy of benzoic acid

<i>m</i> /g	<i>Q</i> _{Ni} /J	<i>Q</i> _{HNO₃} /J	ΔT /K	$-\Delta_c U$ /J g ⁻¹
0.9301	43.0534	22.7241	1.8233	26486.25
0.8679	39.2187	19.5872	1.6976	26429.75
0.9134	42.7804	24.5973	1.7912	26491.87

m/g, the mass of the sample; ΔT /K, the corrected temperature rise; $-\Delta_c U$ (J g⁻¹), constant-volume combustion energy

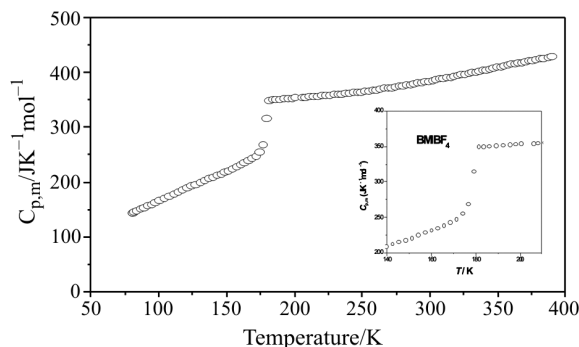


Fig. 1 The experimental molar heat capacities of ionic liquid BMIBF₄

Table 2 The experimental molar heat capacities of ionic liquid BMIBF₄

<i>T</i> /K	<i>C_p</i> /J K ⁻¹ mol ⁻¹	<i>T</i> /K	<i>C_p</i> /J K ⁻¹ mol ⁻¹	<i>T</i> /K	<i>C_p</i> /J K ⁻¹ mol ⁻¹
79.91	144.6	185.90	351.2	293.18	381.8
80.67	145.6	189.01	351.8	295.89	382.8
81.43	146.9	192.11	352.3	298.59	384.3
83.22	148.5	195.24	352.9	301.29	385.7
86.04	152.0	197.97	353.8	303.98	387.0
88.81	155.1	200.35	354.2	306.66	388.3
91.53	158.3	205.79	354.8	309.34	389.7
94.20	161.1	207.75	355.4	312.01	390.8
96.84	163.7	210.83	356.0	314.67	391.8
99.95	167.7	213.89	356.6	317.32	393.3
103.52	172.2	216.93	357.1	319.98	394.3
107.04	175.5	219.93	357.9	322.63	395.9
110.48	179.3	222.91	358.5	325.27	397.8
113.88	183.3	225.85	359.0	327.91	398.6
117.22	186.8	228.78	359.8	330.55	400.2
120.51	190.4	231.64	360.6	333.19	401.5
123.75	193.6	234.55	361.2	335.84	402.9
126.95	196.9	237.43	361.9	338.45	404.4
130.10	200.1	240.30	362.8	341.15	405.2
133.21	203.5	243.10	363.7	343.78	406.5
136.29	207.3	245.90	364.5	346.37	408.2
139.34	209.8	248.75	365.3	349.02	409.5
142.34	213.1	251.58	365.9	351.67	411.0
145.32	216.2	254.40	366.7	354.29	412.3
148.28	218.8	257.21	367.6	356.95	413.7
151.20	221.9	260.02	368.5	359.55	415.2
154.10	225.5	262.82	369.9	362.14	416.5
156.98	229.5	265.63	371.1	364.71	417.9
159.85	232.7	268.45	372.1	367.27	418.7
162.71	235.8	271.24	372.9	369.83	419.7
165.56	239.6	274.01	374.2	372.38	421.0
168.40	243.5	276.77	375.3	374.92	421.9
171.23	248.4	279.52	376.2	377.44	423.4
174.02	256.3	282.27	377.8	380.44	424.8
176.74	269.6	285.01	378.6	383.13	425.9
179.15	315.7	287.74	379.7	386.39	427.4
181.25	349.8	290.46	380.9	389.46	428.7
183.31	350.5				

the Instrument Manufactory of Yunnan, China, and calibrated at the National Institute of Metrology in terms of the IPTS-90. The temperature increment in a heating period was 2–4 K, and temperature drift was maintained at about 10⁻⁴ K min⁻¹ in equilibrium period. All the data were automatically acquired through a data acquisition/switch unit (Model: 34970A, Aglient, USA) and processed online by a computer.

The sample mass used for the heat capacity measurement was 48.7349 g. To verify the reliability of the adiabatic calorimeter, molar heat capacities for the reference standard material, α-Al₂O₃, were measured. The deviations of our experimental results from the values reported by NIST [28] were within ±0.2% in the temperature range of 80–400 K.

Table 3 The thermodynamic functions of BMIBF₄

<i>T</i> /K	<i>C_p</i> /J K ⁻¹ mol ⁻¹	<i>H_T</i> - <i>H</i> _{298.15} /kJ mol ⁻¹	<i>S_T</i> - <i>S</i> _{298.15} /J K ⁻¹ mol ⁻¹
80	145.0	-102.9	-237.2
85	150.6	-101.7	-231.5
90	156.3	-100.5	-225.7
95	162.0	-99.14	-220.0
100	167.8	-97.76	-214.4
105	173.4	-96.32	-208.8
110	179.0	-94.84	-203.2
115	184.4	-93.32	-197.8
120	189.8	-91.76	-192.4
125	195.0	-90.15	-187.1
130	200.2	-88.51	-181.9
135	205.3	-86.81	-176.7
140	210.4	-85.07	-171.6
145	215.7	-83.26	-166.4
150	221.0	-81.38	-161.1
155	226.6	-79.40	-155.5
160	232.6	-77.31	-149.6
165	239.1	-75.09	-143.1
170	246.1	-72.69	-136.0
176.24		glass transition	
185	351.0	-49.61	-35.80
190	351.9	-47.68	-34.83
195	352.8	-45.74	-33.85
200	353.7	-43.78	-32.85
205	354.7	-41.82	-31.83
210	355.7	-39.84	-30.76
215	356.7	-37.83	-29.64
220	357.8	-35.81	-28.46
225	359.0	-33.76	-27.21
230	360.2	-31.69	-25.89
235	361.4	-29.59	-24.50
240	362.8	-27.46	-23.02
245	364.2	-25.30	-21.47
250	365.7	-23.11	-19.82
255	367.3	-20.88	-18.10
260	368.9	-18.61	-16.29
265	370.6	-16.31	-14.40
270	372.5	-13.97	-12.42
275	374.4	-11.58	-10.37
280	376.3	-9.16	-8.25
285	378.4	-6.69	-6.06
290	380.5	-4.18	-3.80
295	382.7	-1.63	-1.48
298.15	384.2	0.00	0.00
300	385.0	0.96	0.88
305	387.3	3.60	3.30
310	389.7	6.28	5.76
315	392.2	9.00	8.25
320	394.7	11.75	10.77
325	397.2	14.55	13.32
330	399.8	17.38	15.87
335	402.3	20.24	18.44
340	404.9	23.13	21.00
345	407.5	26.05	23.55
350	410.1	28.99	26.09
355	412.6	31.95	28.61
360	415.2	34.92	31.11
365	417.6	37.89	33.56
370	420.0	40.87	35.98
375	422.4	43.85	38.36
380	424.6	46.81	40.68
385	426.7	49.75	42.95
390	428.7	52.67	45.17

Combustion enthalpy measurement

Combustion calorimetric experiment was carried out in a precision oxygen-bomb calorimeter described in detail elsewhere [29]. The energy equivalent, ϵ_{calor} , of the calorimeter were determined from 5 combustion experiments using about 0.7 g of NIST 39i benzoic acid with a certified massic energy of combustion under experimental conditions of $\Delta_c U = -26434 \text{ J g}^{-1}$ to be: $\epsilon_{\text{calor}} = 13547.09 \text{ J K}^{-1}$.

The constant-volume combustion energy of the sample can be calculated from the following equation:

$$\Delta_c U / \text{J mol}^{-1} = (\epsilon_{\text{calor}} \Delta T - Q_{\text{Ni}} - Q_{\text{HNO}_3}) \cdot M / W \quad (1)$$

in which $\epsilon_{\text{calor}} / \text{J K}^{-1}$ was the energy equivalent of the oxygen-bomb calorimeter; $\Delta T / \text{K}$, the corrected temperature rise; $M / \text{g mol}^{-1}$, the molar mass of the sample; W / g , the mass of the sample. The calculated results of the constant-volume combustion energy of benzoic acid were listed in Table 1. The uncertainty of the results was the standard deviation of the mean value from the respective measurements

Results and discussion*Molar heat capacity of BMIBF₄*

As a continuation of our previous investigations on thermodynamics for new materials significant in science and technology [30–35], the molar heat capacities of the BMIBF₄ were determined by using the adiabatic calorimeter in temperature range from 80 to 390 K. The results of the molar heat capacities are listed in Table 2 and shown in Fig. 1. No thermal anomaly was observed or no phase transition took place for solid phase from 80 to 171 K, for liquid phase from 181 to 390 K, respectively.

In order to fit well the heat capacity data to a polynomial equation, the temperature T was replaced by the reduced temperature X which was defined :

$$X = [T - 0.5(T_{\text{max}} + T_{\text{min}})] / [0.5(T_{\text{max}} - T_{\text{min}})] \quad (2)$$

where T is thermodynamic temperature, T_{max} and T_{min} are the maximum and the minimum of the temperature in the experimental temperature range. Then, $-1 \leq X \leq 1$.

Table 4 The constant-volume combustion energy of BMIBF₄

m / g	Q_{Ni} / J	$Q_{\text{HNO}_3} / \text{J}$	$\Delta T / \text{K}$	$-\Delta_c U / \text{J g}^{-1}$
1.1671	37.135	31.058	2.0308	5314.64
0.9405	39.271	29.376	1.6415	5327.61
2.1582	32.592	33.248	3.7828	5359.89

m / g , the mass of the sample; $\Delta T / \text{K}$, the corrected temperature rise; $-\Delta_c U / \text{J g}^{-1}$, constant-volume combustion energy

The values of molar heat capacities of the BMIBF₄ were fitted to the following polynomial expressions by the least square method.

For the solid phase (80~171 K) :

$$C_{P,m} (\text{J K}^{-1} \text{ mol}^{-1}) = 195.55 + 47.230 X - 3.1533 X^2 + 4.0733 X^3 + 3.9126 X^4 \quad (3)$$

where reduced temperature, $X = (T - 125.5) / 45.5$.

The above equation is valid from 80 to 171 K, with an uncertainty of $\pm 0.2\%$. The correlation coefficient of the fitted curve, $R^2 = 0.9999$.

For the liquid phase (181~390 K):

$$C_{P,m} (\text{J K}^{-1} \text{ mol}^{-1}) = 378.62 + 43.929 X + 16.456 X^2 - 4.6684 X^3 - 5.5876 X^4 \quad (4)$$

where reduced temperature $X = (T - 285.5) / 104.5$. The above equation is valid from 181 to 390 K with an uncertainty of $\pm 0.2\%$. The correlation coefficient of the fitted curve, $R^2 = 0.9999$.

Thermodynamic parameters of glass transition

It can be seen from Fig. 1 that the heat capacity jump, corresponding to the glass transition of the BMIBF₄, took place in the range from 171 to 181 K. The temperature of the glass transition, T_g , was determined to be 176.24 K.

Thermodynamic functions of ionic liquid BMIBF₄

Thermodynamic functions of BMIBF₄ were calculated based on the empirical Eqs (2) and (3), and the relationships of the thermodynamic functions:

$$H_T - H_{298.15} = \int_{298.15}^T C_{p,m} dT \quad (5)$$

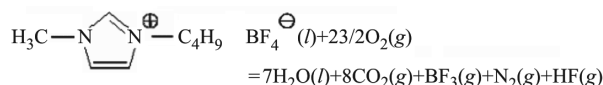
$$S_T - S_{298.15} = \int_{298.15}^T \frac{C_{p,m}}{T} dT \quad (6)$$

The thermodynamic functions relative to the reference temperature (298.15 K) were calculated by Eqs (5) and (6) in the temperature range from 80 to 390 K with an interval of 5 K and listed in Table 3.

The standard molar enthalpy of formation of BMIBF₄

The calculated results of the constant-volume combustion energy of BMIBF₄ were listed in Table 4. The constant-volume combustion energy of BMIBF₄ was determined at $T=298.150\pm 0.001$ K, $\Delta_c U_m = -5334\pm 17$ kJ mol⁻¹.

The standard molar enthalpy of combustion of BMIBF₄, $\Delta_c H_m^\circ$, referred to the combustion enthalpy change of the following reaction at $P^\circ=100$ kPa, based on the definition of the combustion enthalpy about the organic compound [36]:



The standard molar enthalpies of combustion can be derived from the constant-volume combustion energy by means of the following formula:

$$\Delta_c H_m^\circ = \Delta_c U_m + \Delta n RT, \quad (7)$$

in which $\Delta n = \sum n_i$ (products, g) – $\sum n_i$ (reactants, g), where $\sum n_i$ was the total molar amount of the gases in products or reactants. The calculated standard molar enthalpy of combustion of BMIBF₄ was: $\Delta_c H_m^\circ = -5335\pm 17$ kJ mol⁻¹.

The standard molar enthalpy of formation of the BMIBF₄, $\Delta_f H_m^\circ$, was calculated by a designed Hess thermochemical cycle according to the reaction as follows:

$$\Delta_f H_m^\circ = [8\Delta_{f,\text{CO}_2(\text{g})} H_m^\circ + 7\Delta_{f,\text{H}_2\text{O}(\text{l})} H_m^\circ + \Delta_{f,\text{BF}_3(\text{g})} H_m^\circ + \Delta_{f,\text{HF}(\text{g})} H_m^\circ] - \Delta_c H_m^\circ \quad (8)$$

In the above formula, the standard molar enthalpies of formation for CO₂(g) and H₂O(l), were recommended by CODATA [37, 38], $\Delta_f H_m^\circ(\text{CO}_2, \text{g}) = (-393.51\pm 0.13)$ kJ mol⁻¹, $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) = (-285.83\pm 0.04)$ kJ mol⁻¹, and the standard molar enthalpies of formation for (BF₃, g) and (HF, g) were recommended, $\Delta_{f,\text{BF}_3(\text{g})} H_m^\circ = -1135.62$ kJ mol⁻¹, $\Delta_{f,\text{HF}(\text{g})} H_m^\circ = -272.55$ kJ mol⁻¹ [39], were employed in the calculation of $\Delta_f H_m^\circ(\text{BMIBF}_4, \text{l})$ values. The standard molar enthalpy of formation of the BMIBF₄ can be derived based on these values and standard molar enthalpy of combustion of BMIBF₄ to be: $\Delta_f H_m^\circ(\text{BMIBF}_4, \text{l}) = (-1221.8\pm 4.0)$ kJ mol⁻¹.

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References

- 1 C. M. Gordon, J. D. Holbrey, A. R. Kennedy and K. R. Seddon, *J. Mater. Chem.*, 8 (1998) 2627.
- 2 J. Fuller, R. T. Cartin and R. A. Osteryoung, *J. Electrochem. Soc.*, 144 (1997) 3881.
- 3 J. Sun, M. Forsyth and D. R. Macfarlane, *J. Phys. Chem. B.*, 102 (1998) 8858.
- 4 T. Welton, *Chem. Rev.*, 99 (1999) 2071.
- 5 A. J. Carmichael and K. R. Seddon, *J. Phys. Org. Chem.*, 13 (2000) 591.
- 6 C. E. Song, W. H. Shim, E. J. Roh, S. G. Lee and J. H. Choi, *Chem. Commun.*, 12 (2001) 1122.
- 7 P. Wasserscheid, C. M. Gordon, C. Hilgers, M. J. Muldoon and I. R. Dunkin, *Chem. Commun.*, 13 (2001) 1186.
- 8 C. Wheeler, K. N. West, C. L. Liotta and C. A. Eckert, *Chem. Commun.*, 10 (2001) 887.
- 9 F. Endres, *Phys. Chem. Chem. Phys.*, 3 (2001) 3165.
- 10 V. Najdanovic-Visak, J. M. S. S. Esperanca and L. P. N. Rebelo, *Phys. Chem. Chem. Phys.*, 4 (2002) 1701.
- 11 P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.*, 39 (2000) 3772.
- 12 J. D. Holbrey and K. R. Seddon, *Clean Products Processes*, 1 (1999) 223.
- 13 D. Appleby, C. L. Hussey, K. R. Seddon and J. E. Turp, *Nature*, 323 (1986) 614.
- 14 J. L. Anthony, F. J. Maginn and Brennecke, *J. Phys. Chem. B.*, 105 (2001) 10942.
- 15 J. Z. Yang, P. Tian, L. L. He and W. G. Xu, *Fluid Phase Equilib.*, 204 (2003) 295.
- 16 J. Z. Yang, W. G. Xu and Q. G. Zhang, *J. Chem. Thermodyn.*, 35 (2003) 1855.
- 17 J. Z. Yang, P. Tian and W. G. Xu, *Thermochim. Acta*, 412 (2004) 1.
- 18 J. D. Holbrey, W. M. Reichert and R. P. Swatloski, *Green Chem.*, 4 (2002) 407.
- 19 J. Fuller, R. A. Osteryoung and R. T. Carlin, *J. Electrochem. Soc.*, 142 (1995) 3632.
- 20 E. N. Jacobsen, I. Marko and K. B. Sharpless, *J. Am. Chem. Soc.*, 110 (1988) 1986.
- 21 P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Gratzel, *Inorg. Chem.*, 35 (1996) 1168.
- 22 P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. D. Souza and J. Dupnot, *Polyhedron*, 157 (1996) 1217.
- 23 P. J. Dyson, M. C. Grossel, N. Srinivasan, T. Vine, T. Welton, D. J. Williams, A. J. P. White and T. Zigras, *Dalton*, 19 (1997) 3465.
- 24 R. M. Lau, F. van Rantwijk, K. R. Seddon and R. A. Sheldon, *Org. Lett.*, 2 (2000) 4189.
- 25 P. J. Dyson, M. C. Grossel, N. Srinivasan, T. Vine, T. Welton, D. J. Williams, A. J. P. White and T. Zigras, *J. Chem. Soc., Dalton Trans.*, (1997) 3465.

- 26 Z. C. Tan, G. Y. Sun, Y. Sun, A. X. Yin, W. B. Wang, J. C. Ye and L. X. Zhou, *J. Thermal Anal.*, 45 (1995) 59.
- 27 Z. C. Tan, L. X. Sun, S. H. Meng, L. Li, F. Xu, P. Y. B. P. Liu and J. B. Zhang, *J. Chem. Thermodyn.*, 34 (2002) 1417.
- 28 G. Archer, *J. Phys. Chem. Ref. Data*, 22 (1993) 1441.
- 29 Y. Y. Di, Z. C. Tan, X. H. Sun, M. H. Wang, F. Xu, Y. F. Liu, L. X. Sun and H. T. Zhang, *J. Chem. Thermodyn.*, 36 (2004) 79.
- 30 S. X. Wang, Z. C. Tan, Y. Y. Di, F. Xu, M. H. Wang, L. X. Sun and T. Zhang, *J. Therm. Anal. Cal.*, 76 (2004) 335.
- 31 F. Xu, L. X. Sun, Z. C. Tan, J. G. Liang, Y. Y. Di, Q. F. Tian and T. Zhang, *J. Therm. Anal. Cal.*, 76 (2004) 481.
- 32 Z. D. Nan and Z. C. Tan, *J. Therm. Anal. Cal.*, 76 (2004) 955.
- 33 B. Xue, J. Y. Wang, Z. C. Tan, S. W. Lu and S. H. Meng, *J. Therm. Anal. Cal.*, 76 (2004) 965.
- 34 Y. J. Song, Z. C. Tan, S. W. Lu and Y. Xue, *J. Therm. Anal. Cal.*, 77 (2004) 873.
- 35 Z. C. Tan, B. Xue, S. W. Lu, S. H. Meng, X. H. Yuan and Y. J. Song, *J. Therm. Anal. Cal.*, 63 (2001) 297.
- 36 H. A. Skinner, *Experimental Thermochemistry*, Vol. 2, John Wiley and Sons, New York, London, 1962.
- 37 J. D. Cox, D. D. Wagman and V. A. Medvedev, *CODATA Key Values for Thermodynamics*. Hemisphere: New York., 1989.
- 38 J. D. Cox, *J. Chem. Thermodyn.*, 10 (1978) 903.
- 39 M. W. Chase, Jr., *NIST-JANAF Thermochemical Tables*, Fourth Edition, *J. Phys. Chem. Ref. Data*, Monograph, 9 (1998) 1–1951.

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