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Thermochemistry of hydrated lithium monoborates

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Abstract

The enthalpies of solution of two hydrated lithium monoborates in approximately 1 mol dm^{-3} aqueous hydrochloric acid were determined. From these results and the enthalpies of solution of H_3BO_3 in approximately 1 mol dm^{-3} HCl(aq), and of $LiCl\cdot H_2O$ in aqueous(hydrochloric acid + boric acid),combining with the standard molar enthalpies of formation of $LiCl\cdot H_2O(s)$, $H_3BO_3(s)$ and $H_2O(l)$, the standard molar enthalpies of formation of -1627.46 ± 0.90 and -3397.00 ± 0.94 kJ mol^{-1} for $LiBO_2\cdot 2H_2O$ and $LiBO_2\cdot 8H_2O$ were obtained. The standard molar entropies of formation of $LiBO_2\cdot 2H_2O$ and $LiBO_2\cdot 8H_2O$ were calculated from the thermodynamic relation with the standard molar Gibbs free energy of formation of $LiBO_2\cdot 2H_2O$ and $LiBO_2\cdot 8H_2O$ computed from a group contribution method.

Keywords: Hydrated lithium monoborate; Standard molar enthalpy of formation; Solution calorimetry; Molar enthalpy of solution; Aqueous hydrochloric acid solution

1. Introduction

The synthesis, structural, and dehydration studies of borates and especially of hydrated lithium borates have attracted great attention in these past few years. The main reason is that lithium borates have various physical properties like, piezoelectricity for $Li_2B_4O_7$ [1] or non-linear optical behavior of LiB_3O_5 [2]. There exist three hydrated lithium borates, namely monoborate, tetraborate and pentaborate, in Li_2O–B_2O_3–H_2O system [3] at different temperature, among which the standard molar enthalpies of formation of $Li_2B_4O_7\cdot 3H_2O$ and $LiB_5O_8\cdot 5H_2O$ have been reported by Li [4]. There are no reports on the standard molar enthalpies of formation of hydrated lithium monoborates in the literature. As a part of the serial studies [5–9] on the thermochemistry of hydrated borates, in this paper, the standard molar enthalpies of formation $\Delta_f H_m^0$ of hydrated lithium monoborate $LiBO_2\cdot 2H_2O$ and $LiBO_2\cdot 8H_2O$ have been determined by solution calorimetry and other thermochemical parameters have also been calculated.

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2. Experimental

All the reagents used in the synthesis were analytic grade. The $LiBO_2\cdot 2H_2O$ and $LiBO_2\cdot 8H_2O$ were synthesized at laboratory according to thermodynamic equilibrium state phase diagram of Li_2O–B_2O_3–H_2O system at $T = 313$ K [3]. The compounds were characterized by chemical analysis, powder X-ray diffraction, FT-IR spectrum, Raman spectrum and thermal analysis. The powder X-ray diffraction data of the synthesized compounds were obtained using Rigaku D/MAX-2400 with Cu-Kα radiation ($\lambda = 1.5418$ Å)(Fig. 1). Thermogravimetric analysis(TGA) and DSC were conducted on a NETZSCH-Gerätebau STA 449c, in a flow of N_2 with a heating rate of 10 °C min^{-1}. FT-IR spectra were recorded in the 4000–400 cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer using KBr pellets; Raman spectra on a Nicolet Almega Dispersine Raman spectrometer(Fig. 2). All spectroscopic data are in excellent agreement with the literature [10,11]. The analytic data of two compounds are given in Table 1. The data shows that the compounds obtained are pure and have the general formulas $LiBO_2\cdot 2H_2O$ and $LiBO_2\cdot 8H_2O$ and they are suitable for calorimetric experiment.

Thermochemical reaction used for getting the derivation of $\Delta_f H_m^0$ of $LiBO_2\cdot nH_2O$ was:

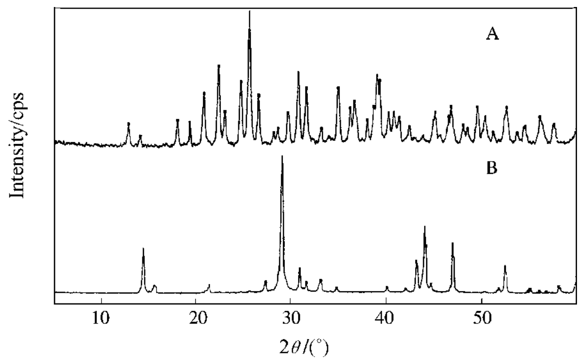

Fig. 1. The XRD of hydrated lituium monoborates (A) $LiBO_2{\cdot}2H_2O$, (B) $LiBO_2{\cdot}8H_2O$.

$$LiBO_2 \cdot nH_2O(s) + HCl(aq) = LiCl(aq) + H_3BO_3(aq) + (n-1)H_2O(l) \quad (1)$$

The standard molar enthalpies of formation of $LiBO_2{\cdot}2H_2O$ and $LiBO_2{\cdot}8H_2O$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of $LiCl{\cdot}H_2O(s)$, $H_3BO_3(s)$ and $H_2O(l)$. The $H_3BO_3(s)$ and $LiBO_2{\cdot}nH_2O(n = 2$ and $8)(s)$ were dissolved in approximately $1\,mol\,dm^{-3}$ aqueous hydrochloric acid, and the calculated amount of $LiCl{\cdot}H_2O(s)$ was dissolved in aqueous(hydrochloric acid + boric acid) which consisted of approximately $1\,mol\,dm^{-3}$ HCl(aq) and the calculated amount of H_3BO_3. The HCl standard solution was prepared from azeotropic hydrochloric acid and deionized water, and its concentration was determined by titration with standard borax.

An RD496-III microcalorimeter(made in the Southwest Institute of Electronic Engineering, PR China) was used. The sensitivity of the instrument was measured through electrical calibration and the accuracy and precision were determined by chemical calibration. The temperature of the calorimetric experiments was 298.15 ± 0.05 K. The experimental data are saved and processed by using a computer. A detailed description is given elsewhere [12]. A glass ampoule containing a sample to be measured, put in the stainless steel reaction cell of the microcalorimeter and broken after thermal equilibrium was reached for (at least 2 h). The total time required for the complete reaction was about 1 h, depending on the samples. No solid residues were observed in the solution after the calorimetric experiments.

Table 1
The chemical composition of hydrated lithium monoborates (mass%)

Borate	Experimental			Calculated		
	Li_2O	B_2O_3	H_2O[a]	Li_2O	B_2O_3	H_2O
$LiBO_2{\cdot}2H_2O$	17.34	40.68	41.98	17.43	40.59	41.98
$LiBO_2{\cdot}8H_2O$	7.73	18.04	74.23	7.71	17.97	74.32

[a] Determined by thermal analysis method.

3. Results and discussion

To check the performance of the RD496-III microcalorimeter, the enthalpy of solution of KCl in deionized water was measured at $T = 298.15$ K. The experimental value $17.24 \pm 0.06\,kJ\,mol^{-1}$ is in excellent agreement with the value $17.241 \pm 0.018\,kJ\,mol^{-1}$ reported in the literature [13]. This result indicated that the device used in this work was reliable.

Table 2 gives the results of the calorimetric experiments. In this table, m is the mass of the sample, $\Delta_{sol}H_m$ is the molar enthalpy of solution of solute. Tables 3 and 4 give the thermochemical cycles for the derivation of the standard molar enthalpies of formation of $LiBO_2{\cdot}H_2O(n = 2$ and 8). The molar enthalpies of solution of $H_3BO_3(s)$ of $21.83 \pm 0.08\,kJ\,mol^{-1}$ in approximately $1\,mol\,dm^{-3}$ HCl(aq) and of $LiCl{\cdot}H_2O$ (s) of $-14.36 \pm 0.11\,kJ\,mol^{-1}$ in the mixture of HCl and H_3BO_3 were taken from our previous works

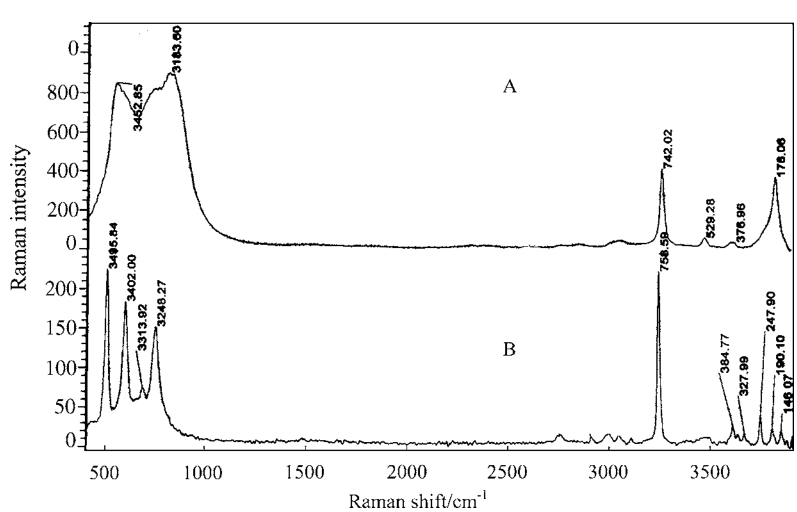

Fig. 2. Raman spectra of hydrated lithium monoborates (A) $LiBO_2{\cdot}2H_2O$, (B) $LiBO_2{\cdot}8H_2O$.

Table 2
The molar enthalpies of solution $\Delta_{sol}H_m$ of hydrated lithium monoborates in approximately $1\,mol\,dm^{-3}$ HCl(aq) at $T = 298.15\,K$[a]

No	m (mg)	$\Delta_{sol}H_m$ ($kJ\,mol^{-1}$)
$LiBO_2 \cdot 2H_2O(s)$		
1	4.00	−8.16
2	4.03	−8.18
3	4.05	−8.07
4	4.04	−8.19
5	4.06	−8.22
Mean		−8.16 ± 0.11
$LiBO_2 \cdot 8H_2O(s)$		
1	6.17	46.32
2	6.15	46.23
3	6.13	46.44
4	6.16	46.41
5	6.19	46.39
Mean		43.36 ± 0.16

[a] In each experiment, $2.00\,cm^3$ of HCl(aq) was used.

separately [4,5].The standard molar enthalpies of formation of $H_2O(l)$ and $H_3BO_3(s)$ were taken from the CODATA Key Values [14], namely -285.830 ± 0.04 and $-1094.8 \pm 0.8\,kJ\,mol^{-1}$, respectively. The standard molar enthalpy of formation of $LiCl \cdot H_2O(s)$ of $-712.58 \pm 0.36\,kJ\,mol^{-1}$ was taken from NBS tables [15], and that of dilution of HCl(aq) at a given concentration was also calculated from the NBS tables [15]. Therefore, the standard molar enthalpies of formation of $LiBO_2 \cdot 2H_2O$ and $LiBO_2 \cdot 8H_2O(s)$ could be calculated and the results are $-1627.46 \pm 0.90\,kJ\,mol^{-1}$ and $-3397.00 \pm 0.94\,kJ\,mol^{-1}$, respectively. Applying a group contribution method developed by Li [16] for the calculation of thermodynamic properties of hydrated borates, the $\Delta_f H_m^0$ and $\Delta_f G_m^0$ of a hydrated borate should be the sum of the contributions of the corresponding cation in aqueous solution, of the polyborate anion and of liquid water, and could be expressed by Eqs. (2) and (3):

$$\Delta_f H_m^0(LiBO_2 \cdot nH_2O) = \Delta_f H_m^0(Li^+, aq) + \Delta_f H_m^0\{[B(OH)_4]^-\} + (n-2)\Delta_f H_m^0(H_2O, l) \quad (2)$$

$$\Delta_f G_m^0(LiBO_2 \cdot nH_2O) = \Delta_f G_m^0(Li^+, aq) + \Delta_f G_m^0\{[B(OH)_4]^-\} + (n-2)\Delta_f G_m^0(H_2O, l) \quad (3)$$

where $n = 2$ and 8.

we calculated $\Delta_f H_m^0$ of $LiBO_2 \cdot 2H_2O$ and $LiBO_2 \cdot 8H_2O$ to be -1623.94 and $-3366.46\,kJ\,mol^{-1}$, respectively. These values agree with the experimental results. The relative errors are 0.21 and 0.90%, respectively. The $\Delta_f G_m^0$ of $LiBO_2 \cdot 2H_2O$ and $LiBO_2 \cdot 8H_2O$ have also been calculated to be -1453.17 and $-2876.85\,kJ\,mol^{-1}$, respectively. By using experimental standard molar enthalpies of formation of $LiBO_2 \cdot 2H_2O$ and $LiBO_2 \cdot 8H_2O$, the standard molar entropies of formation of $LiBO_2 \cdot 2H_2O(s)$ and $LiBO_2 \cdot 8H_2O(s)$ have been calculated as -584.57 and $-1744.59\,J\,K^{-1}\,mol^{-1}$, according to the following equation:

$$\Delta_f S_m^0 = \frac{(\Delta_f H_m^0 - \Delta_f G_m^0)}{T} \quad (4)$$

Otherwise, the standard molar entropies of $LiBO_2 \cdot 2H_2O(s)$ and $LiBO_2 \cdot 8H_2O(s)$ have been calculated to be 121.68 and

Table 3
Thermochemical cycles and results for the derivation of $\Delta_f H_m^0$ ($LiBO_2 \cdot 2H_2O$, $T = 298.15\,K$)

Reaction	$\Delta_r H_m$ ($kJ\,mol^{-1}$)
1. $LiBO_2 \cdot 2H_2O(s) + 41.86(HCl \cdot 54.530H_2O) = Li^+(aq) + Cl^-(aq) + H_3BO_3(aq) + 40.86(HCl \cdot 55.889H_2O)$	−8.16 ± 0.11
2. $H_3BO_3(aq) + 40.86(HCl \cdot 55.864H_2O) = H_3BO_3(s) + 40.86(HCl \cdot 55.864H_2O)$	−21.83 ± 0.08
3. $Li^+(aq) + Cl^-(aq) + H_3BO_3(aq) + 40.86(HCl \cdot 55.889H_2O) = LiCl \cdot H_2O(s) + H_3BO_3(aq) + 40.86(HCl \cdot 55.864H_2O)$	14.36 ± 0.11
4. $41.86(HCl \cdot 55.864H_2O) = 41.86(HCl \cdot 54.530H_2O) + 55.841H_2O(l)$	1.14 ± 0.04
5. $(1/2)H_2(g) + (1/2)Cl_2(g) + 55.864H_2O(l) = (HCl \cdot 55.864H_2O)$	−165.43 ± 0.08
6. $LiCl \cdot H_2O(s) = Li(s) + (1/2)Cl_2(g) + H_2(g) + (1/2)O_2(g)$	712.58 ± 0.36
7. $H_3BO_3(s) = B(s) + (3/2)H_2(g) + (3/2)O_2(g)$	1094.80 ± 0.80
8. $LiBO_2 \cdot 2H_2O(s) = Li(s) + B(s) + 2H_2(g) + 2O_2(g)$	1627.46 ± 0.90

Table 4
Thermochemical cycles and results for the derivation of $\Delta_f H_m^0$ ($LiBO_2 \cdot 8H_2O$, $T = 298.15\,K$)

Reaction	$\Delta_r H_m$ ($kJ\,mol^{-1}$)
1. $LiBO_2 \cdot 8H_2O(s) + 63.033(HCl \cdot 54.530H_2O) = Li^+(aq) + Cl^-(aq) + H_3BO_3(aq) + 62.033(HCl \cdot 55.522H_2O)$	46.36 ± 0.16
2. $H_3BO_3(aq) + 62.033(HCl \cdot 55.506H_2O) = H_3BO_3(s) + 62.033(HCl \cdot 55.506H_2O)$	−21.83 ± 0.08
3. $Li^+(aq) + Cl^-(aq) + H_3BO_3(aq) + 62.033(HCl \cdot 55.522H_2O) = LiCl \cdot H_2O(s) + H_3BO_3(aq) + 62.033(HCl \cdot 55.506H_2O)$	14.36 ± 0.11
4. $63.033(HCl \cdot 55.506H_2O) = 63.033(HCl \cdot 54.530H_2O) + 61.520H_2O(l)$	1.18 ± 0.04
5. $(1/2)H_2(g) + (1/2)Cl_2(g) + 55.506H_2O(l) = (HCl \cdot 55.506H_2O)$	−165.43 ± 0.08
6. $LiCl \cdot H_2O(s) = Li(s) + (1/2)Cl_2(g) + H_2(g) + (1/2)O_2(g)$	712.58 ± 0.36
7. $H_3BO_3(s) = B(s) + (3/2)H_2(g) + (3/2)O_2(g)$	1094.80 ± 0.80
8. $6H_2O(l) = 6H_2(g) + 3O_2(g)$	1714.98 ± 0.24
9. $LiBO_2 \cdot 8H_2O(s) = Li(s) + B(s) + 8H_2(g) + 5O_2(g)$	3397.00 ± 0.94

$360.21\,J\,K^{-1}\,mol^{-1}$, respectively, according to reaction (8) in Table 3 and (9) in Table 4. The standard molar entropies of the elements were taken from CODATA Key Values as 29.12, 5.90, 130.571, and $205.043\,J\,K^{-1}\,mol^{-1}$ for Li(s),B(s), H_2(g), and O_2(g), respectively.

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