Available online at www.sciencedirect.com
ScienceDirect

Thermochimica Acta 448 (2006) 52–55

thermochimica acta

www.elsevier.com/locate/tca

Short communication

Thermochemistry of $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$

Jianguo Zhou[a,*], Fengying Zhao[a], Qian Yang[b], Yan Lu[a], Shuping Xia[c], Shiyang Gao[a,c]

[a] *College of Chemistry and Environmental Science, Henan Normal University, Xinxiang 453007, China*
[b] *Institute of Applied Chemistry, Shaanxi Normal University, Xi'an 710069, China*
[c] *Xi'an Branch, Institute of Salt Lakes, Chinese Academy of Sciences, Xi'an 710043, China*

Received 21 January 2006; received in revised form 26 April 2006; accepted 2 May 2006

Abstract

The enthalpies of solution of $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid and of RbCl in aqueous (hydrochloric acid + boric acid + sodium chloride) were determined. From these results and the enthalpy of solution of H_3BO_3 in approximately 1 mol dm^{-3} HCl(aq) and of sodium chloride in aqueous (hydrochloric acid + boric acid), the standard molar enthalpy of formation of $-(5128.02 \pm 1.94)$ kJ mol^{-1} for $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$ was obtained from the standard molar enthalpies of formation of NaCl(s), RbCl(s), H_3BO_3(s) and H_2O(l). The standard molar entropy of formation of $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$ was calculated from the Gibbs free energy of formation of $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$ computed from a group contribution method.

Keywords: $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$; Standard molar enthalpy of formation; Solution calorimetry; Molar enthalpy of solution

---

1. Introduction

Since the discovery of the promising second harmonic generation properties of β-BaB_2O_4 (BBO) [1] and LiB_3O_5 (LBO) [2], the chemistry of borates has become of great interest to scientists due to their diverse industrial uses and rich structural chemistry. The studies of borate hydrates have been extensively explored in recent years and many new tetraborate hydrates have also been synthesized, the structure and thermal behavior being described [3–8]. All these compounds contain the $[B_4O_5(OH)_4]^{2-}$ tetraborate anion which is the same as that of borax. Recently, Ben Ali et al. [9] synthesized a new hydrated double metals tetraborate $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$ and determined its crystal structure.

In previous work [10–15], the standard molar enthalpies of formation of some hydrated alkali metals borates and hydrated alkali earth metals borates were reported. The thermodynamic properties of some hydrated double metals borates were also studied [16–18]. As part of the systematic study of the thermochemistry of hydrated borates and hydrated double borates of alkali metals and alkali earth metals, this paper reports the standard molar enthalpies of formation as well as the calculated entropy of formation of $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$.

2. Experimental

2.1. Synthesis of $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$

All of the chemical reagents used in synthesis were of analytical grade. Crystals of hydrated sodium rubidium tetraborate were obtained from an aqueous solution of $RbB_5O_6(OH)_4\cdot 2H_2O$ and NaOH in a molar relation of 1/1, by the slow evaporation at room temperature (7 days) [9]. Colourless transparent crystals were filtered and washed with redistilled water and ether, respectively, and dried at room temperature. Composition of the crystal was determined as follows: Na and Cs were analyzed by atomic absorption spectroscopy (Hitachi Z5000 atomic absorption spectrometer); B was determined by titration with a standard solution of NaOH in the presence of mannitol; H_2O content was determined by thermal dehydration. The powder X-ray diffraction data of the synthesized compound was obtained using Bruker D8 advance with Cu Kα radiation. TG -DSC curves were obtained on a Setaram-Labsys^{TM} thermal analyzer with a heating rate of 1 °C/min in flowing N_2. TG-DTA curves were obtained on a Shimadzu DT-40 thermal analyzer in air with a heating rate of 10 °C/min. FT-IR spectra was

---

[*] Corresponding author. Tel.: +86 373 3326335; fax: +86 373 3329115.
E-mail addresses: jgzhou@henannu.edu.cn, zhoujgwj@sina.com (J. Zhou).

doi:10.1016/j.tca.2006.05.001

recorded on a FTS-40 FT-IR spectrometer (Bio-Rad) using KBr pellets.

2.2. Method of calorimetric experiment

Thermochemical reaction used for deriving $\Delta_f H_m^\circ$ of $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$ is

$$NaRb[B_4O_5(OH)_4]\cdot 4H_2O(s) + 2HCl(aq)$$

$$= NaCl(aq) + RbCl(aq) + 4H_3BO_3(aq) + H_2O$$

The standard molar enthalpy of formation of $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of RbCl(s), NaCl(s), $H_3BO_3(s)$ and $H_2O(l)$. The $H_3BO_3(s)$ and $NaRb[B_4O_5(OH)_4]\cdot 4H_2O(s)$ were each dissolved in approximately 1 mol dm^{-3} aqueous hydrochloric acid, the calculated amount of NaCl(s) was dissolved in aqueous $(HCl + H_3BO_3)$ which consisted of approximately 1 mol dm^{-3} HCl(aq) and the calculated amount of H_3BO_3 and then the calculated amount of RbCl was dissolved in the mixed solution $(HCl + H_3BO_3 + NaCl)$.

In the previous paper [21,22], the enthalpy of solution of $H_3BO_3(s)$ in HCl(aq) and NaCl(s) in aqueous $(HCl + H_3BO_3)$ were determined. In this paper, $\Delta_f H_m^\circ$ of $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$ in HCl(aq) and of RbCl in aqueous $(HCl + H_3BO_3 + NaCl)$ are determined. Both RbCl and NaCl (99.99% pure) were heated at 873 K for 3 h and stored in a desiccator. The H_3BO_3 (99.99% pure) was used as obtained. The HCl solvent was prepared from azeotropic hydrochloric acid and redistilled water, and its concentration determined by titration with standard sodium carbonate.

A RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China) was used. The sensitivity of the instrument was measured through electrical calibration and the accuracy and precision were determined by chemical calibration. The calibration was repeated after each experiment and the average calibration constant was used. The temperature of the calorimetric experiments was 298.15 ± 0.005 K. A detailed description is found elsewhere [15,19]. 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.

3. Results and discussion

3.1. Characterization of the synthetic sample

The analytical data of the compound is (calc.): Na_2O 8.39%(8.34%), Rb_2O 25.21%(25.17%), B_2O_3 37.48% (37.45%), H_2O 28.92%(29.04%). The characteristic d values (I/I_0) are presented in Table 1.

The IR spectrum of the compound is shown in Fig. 1. The absorption bands observed at 3584 and 3366 cm^{-1} are assigned to the stretching mode of the OH group. The band at 1631 cm^{-1} is due to the bending mode of this group. Thus, the compound contains crystallization water. The bands observed at 1442, 1349 and 944 cm^{-1} are, respectively, attributed to the antisymmetric and symmetric stretching modes of the group B(3)–O [20]. The bands observed in the region 1269–1135 cm^{-1} are due to the in-plane bending mode of the group B–O–H [20]. The bands at 1064, 1004, 836 and 813 cm^{-1} are assigned to the antisymmetric and symmetric stretching modes of the group B(4)–O [20]. The bands at 711 and 685 cm^{-1} are due to the out-of-plane bending mode of the group B(3)–O [20]. The band observed at 603 cm^{-1} is characteristic for the tetraborate anion and the bands at 522 and 464 cm^{-1} are due to the bending mode of the group B(4)–O [20].

Table 1
The powder X-ray diffraction data for $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$

d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)
8.6021	26.5	3.3564	31.8	2.7077	27.2
6.4285	43.8	3.2361	21.9	2.6532	30.0
5.4956	26.9	3.1912	26.1	2.6323	34.3
4.9569	25.1	3.0653	74.6	2.5589	22.3
4.6850	26.9	3.0281	33.9	2.5328	33.6
4.5552	30.0	2.9507	29.7	2.3901	21.2
4.4385	100.0	2.9174	19.8	2.0692	19.8
4.3794	33.9	2.8077	48.8	1.9161	22.6
4.0081	23.7	2.7848	23.7	1.7397	23.3
3.5557	32.5	2.7349	25.4	1.6892	19.8

TG-DSC curves showed the loss of 19.18% of mass in the range of 30–180 °C temperature range due to the loss of four molecules of crystallization water (calculated, 19.36%). The TG-DTA curves showed that the mass loss is 28.92% in the 30–400 °C temperature range and is due to the loss of six water molecules (calculated, 29.04%).

All these results showed that the synthesized compound is pure and has the general formula $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$ and it is suitable for calorimetric measurements.

3.2. Results of calorimetric experiment

The molar enthalpy of solution of RbCl in aqueous $(HCl + H_3BO_3 + NaCl)$ measured at 298.15 K was 18.00 ± 0.09 kJ mol^{-1} (n = 5), where the uncertainty is twice the standard deviation of the mean. The molar enthalpy of solution of $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$ in approximately

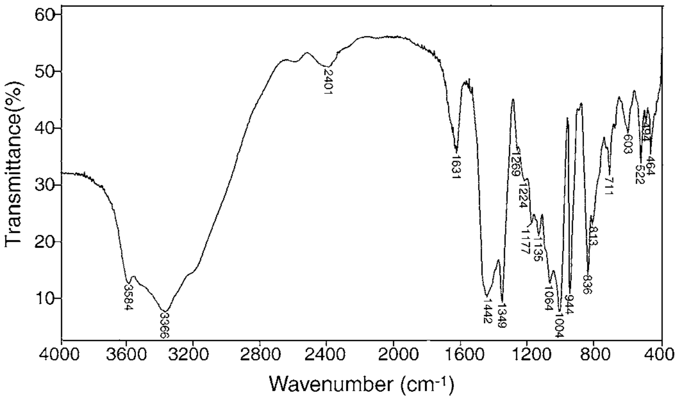

Fig. 1. The FT-IR spectrum of synthetic $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$.

Table 2
Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($NaRbB_4O_7{\cdot}6H_2O$, 298.15 K)

Reaction		$\Delta_r H_m$ (kJ mol^{-1})
$NaRbB_4O_7{\cdot}6H_2O(s) + 81.776(HCl \cdot 53.230H_2O)$ $= Na^+(aq) + Rb^+(aq) + 2Cl^-(aq) + 4H_3BO_3(aq) + 79.776(HCl \cdot 54.577H_2O)$	(1)	55.62 ± 0.25
$4H_3BO_3(aq) + 79.776(HCl \cdot 54.577H_2O) = 4H_3BO_3(s) + 79.776(HCl \cdot 54.577H_2O)$	(2)	−87.32 ± 0.32
$Na^+(aq) + Cl^-(aq) + 4H_3BO_3(aq) + 79.776(HCl \cdot 54.577H_2O)$ $= NaCl(s) + 4H_3BO_3(aq) + 79.776(HCl \cdot 54.577H_2O)$	(3)	−5.14 ± 0.02
$Na^+(aq) + Rb^+(aq) + 2Cl^-(aq) + 4H_3BO_3(aq) + 79.776(HCl \cdot 54.577H_2O)$ $= RbCl(s) + Na^+(aq) + Cl^-(aq) + 4H_3BO_3(aq) + 79.776(HCl \cdot 54.577H_2O)$	(4)	−18.00 ± 0.09
$81.776(HCl \cdot 54.577H_2O) = 81.776(HCl \cdot 53.230H_2O) + 110.154H_2O(l)$	(5)	2.19 ± 0.04
$H_2(g) + Cl_2(g) + 109.154H_2O(l) = 2(HCl \cdot 54.577H_2O)$	(6)	−330.86 ± 0.20
$RbCl(s) = Rb(s) + 1/2Cl_2(g)$	(7)	435.35 ± 0.20
$NaCl(s) = Na(s) + 1/2Cl_2(g)$	(8)	411.15 ± 0.10
$4H_3BO_3(s) = 4B(s) + 6H_2(g) + 6O_2(g)$	(9)	4379.20 ± 3.20
$H_2O(l) = H_2(g) + 1/2O_2(g)$	(10)	285.83 ± 0.04
$NaRbB_4O_7{\cdot}6H_2O(s) = Na(s) + Rb(s) + 4B(s) + 6H_2(g) + 13/2O_2(g)$	(11)	5128.02 ± 1.94[a]

[a] $\Delta_f H_m^\circ = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \Delta_r H_4 + \Delta_r H_5 + \Delta_r H_6 + \Delta_r H_7 + \Delta_r H_8 + \Delta_r H_9 + \Delta_r H_{10}$.

1 mol dm^{-3} HCl(aq) at 298.15 K was 55.62 ± 0.08 kJ mol^{-1} ($n = 5$). Table 2 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $NaRb[B_4O_5(OH)_4]_2{\cdot}4H_2O$. The molar enthalpies of solution of $H_3BO_3(s)$ of (21.83 ± 0.08) kJ mol^{-1} in approximately 1 mol dm^{-3} HCl(aq), and of NaCl(s) of $-(5.14 \pm 0.02)$ kJ mol^{-1} in the mixture of HCl and H_3BO_3 were taken from our previous work [21,22]. The standard molar enthalpies of formation of $H_2O(l)$, NaCl(s), RbCl(s) and $H_3BO_3(s)$ were taken directly from the CODATA Key Values [23], namely $-(285.83 \pm 0.04)$, $-(411.15 \pm 0.10)$, $-(435.35 \pm 0.20)$ and $-(1094.8 \pm 0.80)$ kJ mol^{-1}, respectively. The standard molar enthalpy of formation of HCl(aq) and the enthalpy of dilution of HCl(aq) were calculated from the data in NBS tables [24], respectively. From these data, applying Hess's law, the standard molar enthalpy of formation of $NaRb[B_4O_5(OH)_4]{\cdot}4H_2O$ was calculated to be $-(5128.02 \pm 1.94)$ kJ mol^{-1}, according to the following equation:

$$\Delta_f H_m^\circ = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \Delta_r H_4 + \Delta_r H_5 + \Delta_r H_6 + \Delta_r H_7 + \Delta_r H_8 + \Delta_r H_9 + \Delta_r H_{10}$$

The enthalpy of formation of $NaRb[B_4O_5(OH)_4]{\cdot}4H_2O$ can also be estimated by a group contribution method [25], which can be expressed as shown in following equation:

$$\begin{aligned}\Delta_f H_m^\circ(NaRb[B_4O_5(OH)_4] \cdot 4H_2O, s) &= \Delta_f H_m^\circ(Na^+, aq) + \Delta_f H_m^\circ(Rb^+, aq) \\ &\quad + \Delta_f H_m^\circ([B_4O_5(OH)_4]^{2-}, aq) + 4\Delta_f H_m^\circ(H_2O)\end{aligned}$$

in which, the $\Delta_f H_m^\circ$ for $[B_4O_5(OH)_4]^{2-}$ and H_2O have the values of −3464.46 and −290.42 kJ mol^{-1}, respectively [21]. The $\Delta_f H_m^\circ$ of −240.12 and −251.17 kJ mol^{-1} for Na^+ and Rb^+, respectively, were taken from the NBS tables [24]. The calculated standard molar enthalpy of formation is, by using this scheme, −5117.43 kJ mol^{-1}. The relative error is 0.211%.

We also used a group contribution method to calculate $\Delta_f G_m^\circ$ of $NaRb[B_4O_5(OH)_4]{\cdot}4H_2O$ to be −4591 kJ mol^{-1} according to the following equation:

$$\begin{aligned}\Delta_f G_m^\circ(NaRb[B_4O_5(OH)_4] \cdot 4H_2O, s) &= \Delta_f G_m^\circ(Na^+, aq) + \Delta_f G_m^\circ(Rb^+, aq) \\ &\quad + \Delta_f G_m^\circ([B_4O_5(OH)_4]^{2-}, aq) + 4\Delta_f G_m^\circ(H_2O)\end{aligned}$$

in which the values −3095.99 and −237.28 kJ mol^{-1} for the $\Delta_f G_m^\circ$ of $[B_4O_5(OH)_4]^{2-}$ and H_2O, respectively, were taken from the literature [24], and the $\Delta_f G_m^\circ$ of −261.91 and −283.98 kJ mol^{-1} for Na^+ and Rb^+, respectively, were taken from the NBS tables [24]. Combining the $\Delta_f H_m^\circ$ of $NaRb[B_4O_5(OH)_4]{\cdot}4H_2O$, the standard molar entropy of formation of $NaRb[B_4O_5(OH)_4]{\cdot}4H_2O$ has been calculated to be −1801.174 J mol^{-1} K^{-1} according to following equation:

$$\Delta_f S_m^\circ = \frac{\Delta_f H_m^\circ - \Delta_f G_m^\circ}{T}$$

Finally, the standard molar entropy of $NaRb[B_4O_5(OH)_4]{\cdot}4H_2O$ was calculated to be 467.757 J mol^{-1} K^{-1} according to reaction (11) in Table 2. The standard molar entropies of the elements were taken from the NBS tables [24] to be (51.21, 76.78, 5.86, 130.68 and 205.14 J mol^{-1} K^{-1}) for Na(s), Rb(s), B(s), $H_2(g)$ and $O_2(g)$, respectively.

Acknowledgements

The authors thank the Henan Train Project for University Innovation Talents, National Natural Science Foundation of China (No. 20271051), Natural Science Foundation of Henan (No. 0111030200) and Henan Education Department (No. 2004150005) for financial support.

References

[1] C.T. Chen, B.C. Wu, A.D. Jiang, C.M. You, Sci. Sin. B28 (1985) 235–239.
[2] C.T. Chen, Y.C. Wu, A.D. Jiang, B.C. Wu, C.M. You, R.K. Li, S.J. Lin, J. Opt. Soc. Am. B6 (1989) 610–616.
[3] N. Penin, L. Seguin, B. Ge'rand, M. Touboul, G. Nowogrocki, J. Alloys Compd. 334 (2002) 97–109.

[4] Y.Z. Jia, S.Y. Gao, K.B. Yu, Acta Chim. Sin. 59 (2001) 544–548.
[5] L.X. Zhu, T. Yue, Sh.Y. Gao, M.C. Hu, K.B. Yu, J. Mol. Struct. 658 (2003) 215–222.
[6] M. Touboul, N. Penin, G. Nowogrocki, J. Solid State Chem. 149 (2000) 197–202.
[7] M. Touboul, N. Penin, G. Nowogrocki, J. Solid State Chem. 143 (1999) 260–265.
[8] J.G. Zhou, F.Y. Zhao, Sh.P. Xia, Sh.Y. Gao, J. Mol. Struct. 688 (2004) 143–148.
[9] A. Ben Ali, L.S. Smiri, V. Maisonneuve, J. Alloys Compd. 322 (2001) 153–159.
[10] L.X. Zhu, T. Yue, Sh.Y. Gao, Sh.P. Xia, Thermochim. Acta 404 (2003) 259–263.
[11] Z.H. Liu, M.C. Hu, Thermochim. Acta 403 (2003) 181–184.
[12] J. Li, B. Li, Sh.Y. Gao, J. Chem. Thermodyn. 30 (1998) 425–430.
[13] J. Li, B. Li, Sh.Y. Gao, J. Chem. Thermodyn. 30 (1998) 681–688.
[14] L.X. Zhu, T. Yue, Sh.Y. Gao, Sh.P. Xia, J. Chem. Thermodyn. 35 (2003) 433–438.
[15] Zh.H. Liu, M.Ch. Hu, Sh.Y. Gao, J. Chem. Thermodyn. 36 (2004) 317–319.
[16] R.Y. Chen, J. Li, Sh.P. Xia, Sh.Y. Gao, Thermochim. Acta 306 (1997) 1–5.
[17] Y.Zh. Jia, J. Li, Sh.Y. Gao, Sh.P. Xia, Thermochim. Acta 335 (1999) 1–4.
[18] L.X. Zhu, T. Yue, Sh.Y. Gao, Zh.H. Liu, Sh.P. Xia, Thermochim. Acta 402 (2003) 241–245.
[19] M. Ji, M.Y. Liu, Sh.L. Gao, Q.Zh. Shi, Instr. Sci. Technol. 29 (1) (2001) 53–57.
[20] J. Li, S.P. Xia, S.Y. Gao, Spectrochim. Acta 51A (1995) 519–523.
[21] J. Li, Sh.Y. Gao, Sh.P. Xia, B. Li, J. Chem. Thermodyn. 29 (1997) 491–497.
[22] J. Li, B. Li, Sh.Y. Gao, J. Chem. Thermodyn. 30 (1998) 425–432.
[23] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989, pp. 2–38.
[24] D.D. Wagman, W.H. Evans, V.B. Parker, et al., The NBS Tables of Chemical Thermodynamic Properties, 1982, pp. 2–48, 2–299, 2–238, 2–358.
[25] J. Li, B. Li, S.Y. Gao, Phys. Chem. Miner. 27 (2000) 342–346.