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Short communication

Thermochemistry of potassium strontium tetraborate decahydrate

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Abstract

The enthalpies of solution of $K_2Sr[B_4O_5(OH)_4]_2\cdot10H_2O(cr)$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid and of $SrCl_2\cdot6H_2O(cr)$ in aqueous solution (hydrochloric acid + boric acid + potassium chloride) were measured by solution calorimetry. From these results and other data, the standard molar enthalpy of formation $\Delta_f H_m^\circ$ of $K_2Sr[B_4O_5(OH)_4]_2\cdot10H_2O(cr)$ has been derived to be $-(10904.47 \pm 6.46)$ kJ mol^{-1} at 298.15 K. According to a group contribution method, the standard molar Gibbs free energy $\Delta_f G_m^\circ$ and the standard molar entropy S_m° of $K_2Sr[B_4O_5(OH)_4]_2\cdot10H_2O(cr)$ were also calculated to be -9690.78 kJ mol^{-1} and 858.31 J K^{-1} mol^{-1} at 298.15 K.

Keywords: $K_2Sr[B_4O_5(OH)_4]_2\cdot10H_2O$; 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 have attracted a great attention in past few years because of their valuable nonlinear optical (NLO) properties [1]. Until now, eight double tetraborates hydrated, namely $K_{1.67}Na_{0.33}[B_4O_5(OH)_4]\cdot3H_2O$ [2], $NaRb[B_4O_5(OH)_4]\cdot4H_2O$ [3], $K_2Ca[B_4O_5(OH)_4]_2\cdot8H_2O$ [4], $Rb_2Ca[B_4O_5(OH)_4]_2\cdot8H_2O$ [5], $Cs_2Ca[B_4O_5(OH)_4]_2\cdot8H_2O$ [6], $(NH_4)_2Ca[B_4O_5(OH)_4]_2\cdot8H_2O$ [7], $Rb_2Sr[B_4O_5(OH)_4]_2\cdot8H_2O$ [8], and $K_2Sr[B_4O_5(OH)_4]_2\cdot10H_2O$ [7] have been synthesized in this laboratory and their crystal structures established. In previous papers, the thermodynamic properties of three double hydrated borates, namely Ulexite ($NaCaB_5O_6(OH)_6\cdot5H_2O$) [9], $K_2Ca[B_4O_5(OH)_4]_2\cdot8H_2O$ [10], $Rb_2Ca[B_4O_5(OH)_4]_2\cdot8H_2O$ [11], and $Cs_2Ca[B_4O_5(OH)_4]_2\cdot8H_2O$ [12] have been studied. In this paper, the standard molar enthalpy of formation of $K_2Sr[B_4O_5(OH)_4]_2\cdot10H_2O$ has been determined by solution calorimetry and other thermochemical parameters have been calculated.

2. Experimental

All the reagents used in the synthesis were analytic grade, 12.5 g of a KOH and 25 g H_3BO_3 were dissolved in approximately 100 ml H_2O at room temperature, the above solution was mixed with 2.66 g of a $SrCl_2\cdot6H_2O$ dissolved in 10 ml H_2O to form an amorphous precipitate, the mixture was stirred during 20 min and brought to room temperature. The crystal hydrated mixed borate $K_2Sr[B_4O_5(OH)_4]_2\cdot10H_2O$ was obtained in a few days. The compound was 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 compound was obtained using Rigaku D/MAX-2400 with Cu Kα radiation ($\lambda = 1.5418$ Å). 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. 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}.

The thermogram indicates a continuous weight loss in the intervals 50–500 °C with a slope change at 79.8 °C. This loss corresponds to the release of the ten free water molecules and four hydroxyl groups. The observed weight loss (34.71%) is in good agreement with the calculated value (34.60%). The DSC curve shows that there are two exothermic peaks (79.8, 857.3 °C) and one endothermic peaks (595.4 °C).

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Both chemical analysis and thermal analysis show that double borate hydrated contains 12.91 (cal. 12.93) wt% K_2O, 14.17 (cal. 14.23) wt% SrO, 38.21 (cal. 38.24) wt% B_2O_3 and 34.71 (cal. 34.60) wt% H_2O. The data shows that the compound obtained is pure and has the general formula $K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O$ and is suitable for calorimetric measurements.

To obtain the standard molar enthalpy of formation of hydrated potassium strontium tetraborate, a thermochemical scheme was designed. The enthalpy of solution of $K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O(s)(cr)$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid solution was determined according to the following equation:

$$\begin{aligned}&K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O(cr) + 4HCl(aq)\\&\quad = 2KCl(aq) + SrCl_2(aq) + 8H_3BO_3(aq) + 4H_2O(l)\end{aligned} \tag{1}$$

In addition, the $H_3BO_3(cr)$ were dissolved in approximately 1 mol dm^{-3} aqueous hydrochloric acid, the calculated amount of KCl(cr) was dissolved in aqueous solution (hydrochloric acid + boric acid) which consisted of approximately 1 mol dm^{-3} HCl(aq) and the calculated amount of $H_3BO_3(cr)$, and then the calculated amount $SrCl_2\cdot 6H_2O(cr)$ was dissolved in the former mixed solution (hydrochloric acid + boric acid + potassium chloride). Combining with other auxiliary data, the standard molar enthalpies of $SrCl_2\cdot 6H_2O(cr)$, KCl(cr), $H_3BO_3(cr)$ and $H_2O(l)$, the standard molar enthalpy of $K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O(cr)$ could be derived.

The KCl (mass fraction > 0.9999, PR China), H_3BO_3 (mass fraction > 0.9999, PR China) and $SrCl_2\cdot 6H_2O$ (mass fraction > 0.9999, PR China) were used without further purification. The HCl standard solution was prepared from azeotropic hydrochloric acid and deionized water, and its concentration was determined by titration with standardized sodium carbonate.

An RD496-III microcalorimeter (built in the Southwest Institute of Electronic Engineering, PR China) was used for calorimetric determinations. The instrument was calibrated by Joule effect, and the accuracy and precision were determined by chemical calibration. The enthalpy of solution of KCl in deionized water was measured at $T = 298.15$ K. The experimental value (17.24 ± 0.06) kJ mol^{-1} agrees with the value (17.241 ± 0.018) kJ mol^{-1} reported in the literature [13]. The temperature of the calorimetric experiments was 298.15 ± 0.05 K. A detailed description of procedure is given elsewhere [14]. No solid residues were observed in the solution after the calorimetric experiments.

3. Results and discussion

The results are given in Table 1.

According to the group contribution method [19], the $\Delta_f H_m^\circ$ and $\Delta_f G_m^\circ$ of a hydrated borate should be the sum of contributions of the corresponding cations in an aqueous solution, of the polyborate anions, and of structural water. The $\Delta_f H_m^\circ$ and $\Delta_f G_m^\circ$ of hydrated mixed borate, $K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O$ could be expressed by Eqs. (2) and (3):

$$\begin{aligned}&\Delta_f H_m^\circ(K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O)\\&\quad = 2\Delta_f H_m^\circ(K^+, aq) + \Delta_f H_m^\circ(Sr^{2+}, aq)\\&\qquad + 2\Delta_f H_m^\circ\{[B_4O_5(OH)_4]^{2-}\} + 10\Delta_f H_m^\circ(H_2O, l)\end{aligned} \tag{2}$$

$$\begin{aligned}&\Delta_f G_m^\circ(K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O)\\&\quad = 2\Delta_f G_m^\circ(K^+, aq) + \Delta_f G_m^\circ(Sr^{2+}, aq)\\&\qquad + 2\Delta_f G_m^\circ\{[B_4O_5(OH)_4]^{2-}\} + 10\Delta_f G_m^\circ(H_2O, l)\end{aligned} \tag{3}$$

The thermodynamic parameters are listed in Table 2. We calculated $\Delta_f H_m^\circ$ of the $K_2Sr[B_4O_5(OH)_4]_2\cdot 8H_2O$ to be -10883.68 kJ mol^{-1}. It can be seen that the calculated values are in good agreement with experimental results. The relative error is 0.19%.

Combining with the standard molar enthalpy of formation of $K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O(cr)$ in this work, and the standard molar Gibbs free energies $\Delta_f G_m^\circ$ of $K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O(cr)$ to be -9690.78 kJ mol^{-1} from a group contribution method, the standard molar entropy of formation $\Delta_f S_m^\circ$ of $K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O(s)$ has also been calculated as -4070.74 J K^{-1} mol^{-1}, according to the

Table 1
Thermochemical cycles and results for the derivation of $\Delta_f H_m^\circ$ ($K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O(cr)$, $T = 298.15$ K

Reaction	$\Delta_r H_m$ (kJ mol^{-1})
(1) $K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O(cr) + 161.39\ (HCl\cdot 54.577H_2O) = 2K^+(aq) + Sr^{2+}(aq) + 4Cl^-(aq) + 8H_3BO_3(aq) + 157.39\ (HCl\cdot 55.989H_2O)$	129.82 ± 0.30
(2) $8H_3BO_3(aq) + 157.39\ (HCl\cdot 55.951H_2O) = 8H_3BO_3(cr) + 157.39\ (HCl\cdot 55.951H_2O)$	−174.64 ± 0.64 [15]
(3) $2K^+(aq) + 2Cl^-(aq) + 8H_3BO_3(aq) + 157.39\ (HCl\cdot 55.951H_2O) = 2KCl(cr) + 8H_3BO_3(aq) + 157.39\ (HCl\cdot 55.951H_2O)$	−35.26 ± 0.22 [16]
(4) $2K^+(aq) + Sr^{2+}(aq) + 4Cl^-(aq) + 8H_3BO_3(aq) + 157.39\ (HCl\cdot 55.989H_2O) = SrCl_2\cdot 6H_2O(cr) + 2K^+(aq) + 2Cl^-(aq) + 8H_3BO_3(aq) + 157.39\ (HCl\cdot 55.951H_2O)$	−41.80 ± 0.11
(5) $157.39\ (HCl\cdot 55.951H_2O) = 157.39\ (HCl\cdot 54.577H_2O) + 216.254H_2O(l)$	4.03 ± 0.16 [17]
(6) $2H_2(g) + 2Cl_2(g) + 218.308H_2O(l) = 4\ (HCl\cdot 54.577H_2O)$	−661.72 ± 0.40 [17]
(7) $SrCl_2\cdot 6H_2O(cr) = Sr(cr) + Cl_2(g) + 6H_2(g) + 3O_2(g)$	2623.80 ± 0.16 [17]
(8) $2KCl(cr) = 2K(cr) + Cl_2(g)$	873.50 ± 0.20 [17]
(9) $2H_2(g) + O_2(g) = 2H_2O(l)$	−571.66 ± 0.08 [18]
(10) $8H_3BO_3(cr) = 8B(cr) + 12H_2(g) + 12O_2(g)$	8758.40 ± 6.40 [18]
(11) $K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O(cr) = 2K(cr) + Sr(cr) + 8B(cr) + 14H_2(g) + 14O_2(g)$	10904.47 ± 6.46

Table 2
Thermodynamic parameters of borate polyanions and the experimental and calculated $\Delta_f H_m^\circ$ and $\Delta_f G_m^\circ$ of $K_2Sr[B_4O_5(OH)_4]_2 \cdot 10H_2O(cr)$ at 295.15 K

Species	$\Delta_f H_m^\circ$ (kJ mol^{-1})	$\Delta_f G_m^\circ$ (kJ mol^{-1})
$K^+(aq)$ [19]	−252.38	−283.26
$Sr^{2+}(aq)$ [18]	−545.80	−559.48
$H_2O(l)$ [19]	−290.42	−237.28
$[B_4O_5(OH)_4]^{2-}$ [19]	−3464.46	−3095.99
$K_2Sr[B_4O_5(OH)_4]_2 \cdot 10H_2O(s)$		
Calc.	−10883.68	−9690.78
Expt.	−10904.47	
Error (%)	0.19	

following equation:

$$\Delta_f S_m^\circ = \frac{\Delta_f H_m^\circ - \Delta_f G_m^\circ}{T} \tag{4}$$

And then, the standard molar entropy of $K_2Sr[B_4O_5(OH)_4]_2 \cdot 10H_2O(cr)$ has been calculated to be 858.31 J K^{-1} mol^{-1}, on the basic of the following reaction:

$$2K(cr) + Sr(cr) + 8B(cr) + 14H_2(g) + 14O_2(g) = K_2Sr[B_4O_5(OH)_4]_2 \cdot 10H_2O(cr)$$

The standard molar entropies of the elements were taken from NBS tables as 64.18, 52.30, 5.86, 130.684, and 205.138 J K^{-1} mol^{-1} for K(cr), Sr(cr), B(cr), H_2(g), and O_2(g), respectively.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.08.004.

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