# FTIR Spectroscopy of Magnesium Tetraborate Solution

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Supersaturated aqueous solution of magnesium tetraborate (MgB<sub>4</sub>O<sub>7</sub> · 9H<sub>2</sub>O), its acidified solutions with azeotropic hydrochloric acid, and its diluted solutions with water have been recorded by differential FTIR spectra. The differential FTIR spectra of borate in solutions are obtained by subtracting FTIR spectrum of water from that of the magnesium borate aqueous solutions. The results showed that various polyborate anions exist in the solutions. The bands of symmetric vibration of the corresponding polyborate anions were indicated and some assignments were tentatively given. Boron concentration and pH of solution are effective on the formations of polyborate anions. The transformations  $B_5O_6(OH)_4^- + OH^- + H_2O \Leftrightarrow B_4O_5(OH)_4^{2-} + B(OH)_3$  and  $B(OH)_3 + OH^- \Leftrightarrow B(OH)_4^-$  are main reactions in these solutions.

Accurate knowledge of species distribution of polyborate ions in solution is fundamental to the understanding of many processes such as characteristic interactions of polyborate ions in brine, formation of borate minerals, and the actions of boron in organisms. For these reasons, a large number of studies have been devoted to explain the formations of polyborate ions in aqueous solution [1-7]. It is necessary to rely on physical measurements, which do not alter the equilibrium position for studying borate aqueous system. Vibration spectroscopy was most applicable to this problem and has been effectively used for the identification and characterization of borates. The solubilities of most magnesium borates are so small that no characteristic IR and Raman peaks can be recorded in their saturated solutions. Little work has been carried out previously about the vibrational spectra of the supersaturated solutions of borates. In previous papers, authors studied vibrational spectra of supersaturated solutions of hexa- and pentaborate [8-11].

In this paper, differential FTIR spectra of supersaturated aqueous solution of magnesium tetraborate, its acidified solutions with azeotropic hydrochloric acid, and its diluted solutions with water have been recorded. The differential FTIR spectra of borate in solutions were described in detail previously [8, 9]. The bands of symmetric vibration of the corresponding polyborate anions were indicated and some assignments were tentatively given. As a part of the serial studies on the spectroscopy of borate solutions [8— 11], we present here the spectra of aqueous solutions of magnesium tetraborate.

### EXPERIMENTAL

 $H_3BO_3$ , anal. grade, produced by Beijing Chemical, China. MgO was obtained according to the method that was described previously in detail [8, 9].

The anal. grade HCl aqueous solution was distilled to obtain azeotropic hydrochloric acid by traditional method. The concentration of the azeotropic hydrochloric acid was analyzed to be 20.20 %.

The supersaturated aqueous solution of magnesium tetraborate (sample 1) was prepared as follows [12]: MgO, H<sub>3</sub>BO<sub>3</sub>, and H<sub>2</sub>O were taken according to the mass ratio  $m(MgO):m(H_3BO_3):m(H_2O) =$ 1:8:66, dissolved at 298 K and stirred for 3 h. At last, the supersaturated solution of magnesium tetraborate was obtained by filtration.

According to the dilution experiment of the concentrated boron-containing brine [6], the magnesium tetraborate supersaturated solution (sample 1) was diluted with water in different mass ratio to give different boron-containing aqueous solutions (samples 2 and 3) at room temperature (298 K). After being mixed thoroughly, the pH value of the diluted solution was determined.

Azeotropic hydrochloric acid was added into the supersaturated aqueous solution of magnesium tetraborate (sample 1) and the acidified solutions (samples 4 and 5) were obtained. After the acidification was completed, the pH value was determined by a pH-meter (PHS-10A model, Zhejiang Instruments, China) with a glass electrode (231 model, Shanghai Instruments, China) and a calomel electrode (232 model,

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5

Sample	$w_{i}$		
	B <sub>2</sub> O <sub>3</sub>	MgO	рн
1	6.07	1.18	7.97
2	3.89	0.76	8.15
3	2.50	0.49	8.30
4	5.63	0.55	6.29

0.02

4.61

2.94

Table 1. Chemical Analyses and pH of Aqueous Solutions of Magnesium Tetraborate

Shanghai Instruments), which was calibrated with the standard pH solutions before use.

The application of infrared spectroscopy to borate aqueous solutions is limited because water absorbs infrared radiation to a very great extent. The FTIR spectra of borate in solution are obtained by difference, subtracting FTIR spectrum of water from that of the magnesium borate supersaturated aqueous solution. Differential FTIR spectra of supersaturated aqueous solution of magnesium tetraborate were recorded in the  $\bar{\nu}$  range of 380—1880 cm<sup>-1</sup> on a NICO-LET 170SX FTIR spectrometer with Ge window.

#### **RESULTS AND DISCUSSION**

Chemical analytical results of the aqueous solutions of magnesium tetraborate and their corresponding pH values are listed in Table 1. The sample was analyzed according to the standard methods: magnesium was titrated by a standard solution of Na-EDTA in an alkaline buffer solution of NH<sub>3</sub> + H<sub>2</sub>O + NH<sub>4</sub>Cl, boron by a standard solution of NaOH in the presence of mannitol. The chemical composition of magnesium borates is written as  $B_2O_3$  and MgO.

The prepared supersaturated aqueous solution of magnesium tetraborate could be stable for a few days, and then  $MgB_4O_7 \cdot 9H_2O$  would be precipitated from the solution. Comparing the vibration spectra of  $MgB_4O_7 \cdot 9H_2O$  and other hydrated borates [14] with that of the supersaturated aqueous solution of magnesium borate, the spectra of the polyborate anions in solution are similar to that of the polyborate ions in solid. The observed wavenumbers of FTIR spectrum of magnesium borate supersaturated aqueous solution were indicated and assignments are also given in Table 2.

IR peaks in the 1561—1768 cm<sup>-1</sup> region could be assigned as the H—O—H bending modes and the bending modes of B—O—H are in the 1100—1300 cm<sup>-1</sup> region. The peaks in the 1300—1450 cm<sup>-1</sup> region belong to the asymmetric stretch of B(3)—O. It is shown that various species of polyborate anions exist in the supersaturated aqueous solution. The peaks at about 641 cm<sup>-1</sup>, 569 cm<sup>-1</sup>, and 530 cm<sup>-1</sup> are the

Table 2. Observed Wavenumbers of FTIR Spectra of  $MgB_4O_7$  $\cdot 9H_2O$  and its Supersaturated Aqueous Solution

$\tilde{\nu}(MgB_4O_7 \cdot 9H_2O)_i/cm^{-1}$				
Solid [14]	Solution	Assignment		
1690 m	1640 w	δ(H—O—H)		
	1550 w	δ(H—O—H)		
1424 s	1422 s	$\nu_{as}(B(3)-O)$		
	1340 s	$\nu_{as}(B(3)-O)$		
1276 m		$\delta(BO-H)$		
1202 m	1148 s	$\delta(BH)$		
1056 m		$\nu_{as}(B(4)-O)$		
1001 w		$\nu_{as}(B(4)-O)$		
954 m		$\nu_s(B(3)-O)$		
817 m		$\nu_{s}(B(4)-O)$		
764 vw		ν <sub>s</sub> (B(4)—O)		
659 m		γ(B(3)—O)		
	641 m	$\nu_{\rm p}[{\rm B_6O_7(OH)_6}]^{2-}/\nu_{\rm p}[{\rm B_3O_3(OH)_4}]^{-1}$		
	569 s	$\nu_{\rm p}[{\rm B}_4{\rm O}_5({\rm OH})_4]^{2-1}$		
	530 m	$\nu_{p}[B_{5}O_{6}(OH)_{4}]^{-}$		
	512 s	$\nu_{\rm P}({\rm B(OH)}^-)$		
473 m		$\delta(B(4)-O)$		
	438 s	$\nu_{\rm p}[{\rm B}_{3}{\rm O}_{3}({\rm OH})_{4}]^{-1}$		
397 w	43874666-3279 5755	δ(B(4)—O)		

b - broad, m - medium, s - strong, v - very, w - weak. B(3)—O means three-coordinate boron, B(4)—O means four-coordinate boron.

characteristic frequencies of symmetric vibration of hexaborate (or triborate), tetraborate, and pentaborate anion, respectively. Peak at 512 cm<sup>-1</sup> is assigned as the symmetric vibration of  $B(OH)_4^-$ .

Representative spectra of aqueous solutions of magnesium borate during dilution with the  $B_2O_3$  concentration varying from 6.07 % to 2.50 % are presented in Figs. 1 and 2. The IR shifts and relative intensities measured in our experiments are listed in Table 3.

The structure of isolated tetraborate anion is  $[B_4O_5(OH)_4]^{2-}$ , which might be affected by the concentration of OH<sup>-</sup> in solution. It is clear that the H-O-H bending modes lie in the region 1500-1700  $cm^{-1}$ , and they will be more complicated when pH is increased and boron concentration is decreased during dilution. The peak at 1640  $cm^{-1}$  in the spectrum of sample 1 shifts to 1660  $\text{cm}^{-1}$  in the spectrum of 3. Peaks at 1761 cm<sup>-1</sup>, 1724 cm<sup>-1</sup> appear only in the spectrum of 3. The vibration absorption bands and their intensities of the B-O-H bending modes become to be broader and weaker with increasing dilution. The broad and strong peak at 1148  $cm^{-1}$  in IR spectrum of the initial sample 1 shifts to 1139  $cm^{-1}$  in that of the diluted sample 2 and to 1128  $cm^{-1}$  in sample 3. It is clearly indicated that  $OH^{-1}$ is strongly effective on the polyborate anions coexisting in aqueous solution and their absorption bands. At the same time, the intensities of the absorption bands of asymmetric stretch of B(3)—O are weakening from the sample 1 (1422  $\text{cm}^{-1}$  and 1340  $\text{cm}^{-1}$ ) to sample



Fig. 1. FTIR spectra of the 1130—1880 cm<sup>-1</sup> region of magnesium tetraborate solutions during dilution.

2 (1412 cm<sup>-1</sup> and 1328 cm<sup>-1</sup>). Finally, in the sample 3, peaks at 1409 cm<sup>-1</sup> and 1329 cm<sup>-1</sup> become weak and even disappear as the dilution increases. On the other hand, the symmetric stretch of B(4)—O (845 cm<sup>-1</sup>) and symmetric vibration of  $B(OH)_4^-$  (757 cm<sup>-1</sup>) appear. Peak at 515 cm<sup>-1</sup> of symmetric vibration of  $B(OH)_4^-$  becomes stronger. This implied that the amount of  $B(OH)_4^-$  in the diluted solutions would be increased with decreasing of boron concentration and these results are mainly due to the dilution effect. The following reaction will proceed

$$B(OH)_3 + OH^- \Rightarrow B(OH)_4^-$$
 (A)

The low-frequency region  $500-750 \text{ cm}^{-1}$  corresponds to the polyborate anion absorption bands.  $[B_6O_7(OH)_6]^{2-}$  consists of three six-member rings in which the structure is the same as  $[B_3O_3(OH)_4]^{-}$ . Peak at 641 cm<sup>-1</sup> of the vibration of hexaborate anion or triborate anion becomes clear and stronger as the dilution increases, and the depolymerization reactions of pentaborate and tetraborate anions will proceed as follows

$$B_4O_5(OH)_4^{2-} + 2H_2O \Rightarrow B_3O_3(OH)_4^{-} + B(OH)_4^{-} (B)$$

$$B_5O_6(OH)_4^- + 3H_2O \Rightarrow B_3O_3(OH)_4^- + 2B(OH)_3 (C)$$



Fig. 2. FTIR spectra of the 380—1130 cm<sup>-1</sup> region of magnesium tetraborate solutions during dilution.

The characteristic peak of tetraborate anion at 569  $\rm cm^{-1}$  coming from the transformation of pentaborate anion becomes to be stronger, while the pentaborate anion peak at 530 cm<sup>-1</sup> is weak and even disappears in the spectrum of sample 3.

$$B_5O_6(OH)_4^- + OH^- + H_2O \Rightarrow B_4O_5(OH)_4^{2-} + B(OH)_3$$
  
(D)

Fig. 3 shows the hydrochloric acid-pH titration curve of 40 cm<sup>3</sup> magnesium tetraborate supersaturated solution (sample 1), which has been titrated by azeotropic hydrochloric acid at room temperature of 298 K. It shows that in the pH titration curve the pH value varies from 7.97 to 0.80. The shape of the pHhydrochloric acid titration curve for the magnesium tetraborate supersaturated aqueous solution is similar to that for the strong acid with strong base, and it is much different from the result in Ref. [13]. It is clearly divided into four parts. The first part, AB, shows that the polyborate anions in the solution react with HCl and the corresponding polyboric acid is formed and pH changes from 7.97 to 5.80. The second part, BC, shows that the pH of the solution varies slowly and changes little. At this time one can observe that the

$ ilde{ u}_i/\mathrm{cm}^{-1}$			Assimption		
1	2	3	4	5	Assignment
		1761 w			δ(H—O—H)
		1724 w			δ(H—O—H)
1640 w	1640 w	1660 w	1640 w	1660 w	δ(HOH)
1550 w	1568 w				δ(H—O—H)
1422 s	1412 s	1409 w	1426 s	1410 s	$\nu_{as}(B(3)-O)$
		1389 bw			$\nu_{as}(B(3)-O)$
1340 s	1328 s	1329 bw	1340 w		$\nu_{as}(B(3)-O)$
1148 bs	1139 bs	1128 bw	1159 bm	1152 bs	$\delta$ (B—O—H)
			1022 m		
		845 w			$\nu_{s}(B(4)-O)$
		757 w			$\nu_{\rm p}({\rm B(OH)_4^-})$
			738 w		
			708 w		
641 m	638 w	639 s	639 s	639 w	$\nu_{\rm p}[{\rm B_6O_7(OH)_6}]^{2-}/\nu_{\rm p}[{\rm B_3O_3(OH)_4}]^{-}$
569 s	564 m	561 s	565 s	562 m	$\nu_{\rm p}[{\rm B}_4{\rm O}_5({\rm OH})_4]^{2-1}$
530 m	535 m		535 m	536 s	$\nu_{\rm p}[{\rm B}_{\rm 5}{\rm O}_{\rm 6}({\rm OH})_4]^{-1}$
512 s	511 w	515 m	518 s		$\nu_{\rm p}({\rm B(OH)}_{\star})$
438 s	441 s	436 s	454 m	451 m	$\delta(B(4)-O)$
	396 s	394 s			

Table 3. Observed Wavenumbers of FTIR Spectra of Magnesium Tetraborate Solutions during Dilution and during Acidification



Fig. 3. The titration curve of supersaturated aqueous solution of magnesium tetraborate with azeotropic hydrochloric acid.

boric acid will be crystallized out if HCl is dropped any more into the solution. From the point B on the titration curve, boric acid begins to separate out from the titrated solution and all the following titration reactions proceeded at each point on the curve BC.

$$MgB_4O_7 + 2HCl \Rightarrow MgCl_2 + H_2B_4O_7$$
 (E)

$$H_2B_4O_7 + 5H_2O \Rightarrow 4H_3BO_3 \tag{F}$$

In other words, they are under the phase equilibrium of magnesium tetraborate, tetraboric acid, and boric acid. The third part, CD, indicates that the change of pH value will be significant when azeotropic hydrochloric acid is added any more. The fourth part, DE, indicates that all the titration reactions have been completed and ended. The middle point on the CD may be regarded as the end point of the titration.

According to the above titration curve, the magnesium borate supersaturated solution and its titrated solutions with HCl (samples 4 and 5 in Table 3) were recorded by FTIR spectrometer. The observed wavenumbers are listed in Table 3 and Figs. 4 and 5 present the representative spectra of these samples.

In the high wavenumber range,  $1500-1700 \text{ cm}^{-1}$ and  $1200-1400 \text{ cm}^{-1}$ , some peaks which are H-O-H and B-O-H bending modes disappear in the spectrum of sample 5. These changes might be all due to the pH effect. It is noticed that peak at 1340 cm<sup>-1</sup> of the asymmetric stretch of B(3)-O appears clearly in the spectrum of sample 1, weakly in the sample 4, and finally disappears in the spectrum of sample 5. It indicates that the interaction between polyborate anions might proceed in sample 4, but all the reactions are nearly completed in sample 5.

The characteristic peak of tetraborate anion is at 569 cm<sup>-1</sup> in the spectrum of sample 1, at 565 cm<sup>-1</sup> in 4, and at 562 cm<sup>-1</sup> in 5. The peaks of pentaborate anion, at 530 cm<sup>-1</sup> in 1, 535 cm<sup>-1</sup> in 4, and 536 cm<sup>-1</sup> in 5 are strong. While peaks of  $\nu_p[B(OH)_4^-]$ , at 512 cm<sup>-1</sup> in 1 and 518 cm<sup>-1</sup> in 4 are also strong, they disappear in the spectrum of sample 5. This might result from the transformation reactions (D) and (A).

The spectra show that pH could significantly affect the polyborate anion in tetraborate supersaturated solution. At higher pH, polyanions of  $[B(OH)_4]^-$ ,



Fig. 4. FTIR spectra of the 1130—1880 cm<sup>-1</sup> region of magnesium tetraborate solutions during acidification.



Fig. 5. FTIR spectra of the 380—1130 cm<sup>-1</sup> region of magnesium tetraborate solutions during acidification.

 $[B_3O_3(OH)_4]^-$ , and  $[B_4O_5(OH)_4]^{2-}$  are relatively steady in solutions and at lower pH, the depolymerization reaction might proceed and the concentration of boron in solution would be decreased.

In a word, the forms of polyborate anion in solution mainly depend on the boron concentration and pH, which might effectively control the precipitation of magnesium borate minerals. Therefore, the different diluted brines can crystallize out different hydrated magnesium borates with different crystal structure.

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