# Supersaturated Aqueous Magnesium Borate Solutions, a Structural Study by Difference FT—Raman and $^{11}$B NMR Spectroscopy

LI Jun, LI Bing*
(Xi'an Branch, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xi'an, 710043, China)

**Abstract**: Three kinds of supersaturated aqueous magnesium borate solutions were prepared. The differential FT—Raman and $^{11}$B NMR spectra of supersaturated and saturated aqueous magnesium borate solutions were recorded. The $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_5O_6(OH)_4^-$ were detected in supersaturated and saturated $MgB_6O_{10}\cdot 7.5H_2O$, $MgB_4O_7\cdot 9H_2O$, and $Mg_2B_6O_{11}\cdot 15H_2O$ solutions. There were no simple crystallization mechanisms for these magnesium borates, complicated dynamic equilibria among the boron species in solutions existed during the precipitation of magnesium borates.

**Key words**: Magnesium borate; Supersaturated solutions; Differential FT—Raman spectra; $^{11}$B NMR spectra
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## 1 Introduction

Aqueous borate solutions are important in chemistry, geochemistry, and industry. The speciation of aqueous borate solutions have been studied by using indirect and direct methods[1—3] for long time because of their complexity and importance. The above studies have shown that the nature of aqueous borate solutions depends strongly on the pH values and boron concentrations of aqueous solutions, as well astemperature. The $B(OH)_3$, $B(OH)_4^-$, $B_2O(OH)_5^-$, $B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{2-}$, $B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4^-$ species were suggested to be present in concentrated borate solutions, but the structural studies[2] favored $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4^{2-}$ at room temperature. In our recent study on the speciation of aqueous borate solutions, these five boron species were found to be the main species in' solutions, there was no evidence found for presence of higher polymeric boron species.

It is known that aqueous borate solutions become easily supersaturated with respect to borates at given conditions. The observations by Gao et al.[4—7] on the behavior of magnesium borates in salt lake brines have shown that magnesium borates could exist in solution to high concentrations, the brines were highly supersaturated with respect to magnesium borates. Dilution of these brines accelerated the precipitation of magnesium borates. Lehmann and Rietz[8] found that several magnesium borates could be crystallized from the supersaturated magnesium borate solutions at room and at high temperatures.

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Reburn and Gale[9] prepared highly supersaturated lithium tetraborate solutions that maintained long time without precipitation. A method to prepare supersaturated solution with respect to borax was patented.[10] Understanding of structures of supersaturated aluminate and silicate solutions,[11] important both for aluminum and silicate industries, is good, however very little is known about the structures of supersaturated borate solutions. The understanding of the structur al mechanisms of supersaturated borate solutions is not only scientifically interesting, but serves industrial interests. The understanding provides us the information of structural changes in aqueous solutions, and enables us to develop more feasible chemical technologies. As a continuing study on the speciation of aqueous borate solutions, we caried out the structural study of supersaturated magnesium boratesolutions. We will propose structural mechanisms of supersaturated aqueousmagnesium borate solutions, and crystallization mechanisms of magnesium borates from supersaturated borate solutions.

## 2 Experimental

Preparation of supersaturated aqueous magnesium borate solutions

Three kinds of supersaturated magnesium borate solutions were prepared chemically. The supersaturated $MgB_6O_{10}\cdot 7.5H_2O$, $MgB_4O_7.9H_2O$, and $Mg_2B_6O_{11}\cdot 15H_2O$ solutions were prepared according to the methods presented in literature with a slight modification,[8,12] The $H_3BO_3$ (A. R., Merck) and deionized water were used. The MgO Was decomposed from $Mg(OH)_2\cdot 4MgCO_3\cdot 6H_2O$ (A. R., made in China) in an electric oven at temperature 600 ℃ for 3 hr, and stored in a desiccator. The MgO prepared by this method was of high activity. The mixtures of $H_3BO_3$, MgO, and $H_2O$ (7.067 g $H_3BO_3$, 0.575 g MgO, and 50g $H_2O$ for $MgB_6O_{10}\cdot 7.5H_2O$; 6.060g $H_3BO_3$, 0.757g MgO, and 50g $H_2O$ for $MgB_4O_7\cdot 9H_2O$; 1.185g $H_3BO_3$, 0.232 g MgO, and 50g $H_2O$ for $Mg_2B_6O_{11}\cdot 15H_2O$) were stirred continuously on a magnetic stirrer at room temperature. After half of an hour for $MgB_6O_{10}\cdot 7.5H_2O$, or one and half of an hour for $MgB_4O_7\cdot 9H_2O$ and $Mg_2B_6O_{11}\cdot 15H_2O$, the mixtures became clear. The solutions were filtered to separate the undissolved residue, and the clear solutions were stored in conical flasks with stopper at room temperature. The boron concentrations of the solutions were analyzed, and the pH values were recorded. Two days later, the magnesium borates crystallized from the clear solutions. The solids were separated until the pH values of the solution sremained unchanged. The process of precipitation lasted for half of a month. The dry solids were fully characterized by chemical analysis, FT—IR and FT—Raman spectroscopy, and X-ray powder diffraction. The results shown that the solids were expected magnesium borates. It should be pointed out that the $MgB_4O_7\cdot 9H_2O$ and $MgaB_6O_{11}\cdot 15H_2O$ synthesized according to our improved method are of more pure quality, crystals are of larger size, and to obtain crystals shorter time is needed when the methods by Kesans is used.[12]

Spectroscopy

FT—Raman spectra were recorded on a Nicolet Raman 910 spectrometer. Excitationwavelength of 1064 nm of a Nd: YAG laser at about 1W power was used. The solutions were held in Pyrex tubes. The wavenumber range scanned was from 1600 to 300 $cm^{-1}$. Difference FT—Raman spectra were obtained by subtracting the spectrum of pure water from the spectra of the solutions. $^{11}B$ NMR spectra were recorded at 128.3MHz on a Bruker DPX—400 instrument using a sealed 5 mm tube at 299 K. The NMRsolvent is $H_2O$. All chemical shifts of the signals were relative to $Et_2O\cdot BF_3$ that was used as external reference.

## 3 Results and discussions

The chemical analyses, pH, FT—Raman, and $^{11}$B NMR spectra of the supersaturated and saturated $MgB_6O_{10}\cdot 7.5H_2O$, $MgB_4O_7\cdot 9H_2O$, and $Mg_2B_6O_{11}\cdot 15H_2O$ solutions are given in Tables 1 to 2, and the spectra are illustrated in Figures 1 to 2. The spectra of supersaturated solutions are similar to that of the corresponding saturated solutions. Comparison with corresponding solutions of sodium borate at saturation or nears aturation, no additional bands on the difference FT—Raman spectra and resonance on the $^{11}$B NMR spectra were found. Detailed discussions of the results are given in the following section.

Supersaturated $MgB_6O_{10}\cdot 7.5H_2O$ solution

Based on the assignments in previous papers[2—4] and our new spectral information, $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_5O_6(OH)_4^-$ were found to be present in supersaturated and saturated $MgB_6O_{10}\cdot 7.5H_2O$ solutions. Although the spectra did not show the presence of $B_4O_5(OH)_4^{2-}$, we did not exclude it from the solutions studied. We think that it may be present in the solutions at concentration too low to be detected. The crystallized product $MgB_6O_{10}\cdot 7.5H_2O$ has a hexaborate anion $B_6O_7(OH)_6^{2-}$ which consists of three boron—oxygen six member rings, each ring consists of two B—O tetrahedrons and one B—O triangle. The band 635 $cm^{-1}$ in the Raman spectra of triborates and hexaborates has been attributed to the symmetric pulse vibration[13] of $B_3O_3(OH)_5^{2-}$ and $B_6O_7(OH)_6^{2-}$. $B_6O_7(OH)_6^{2-}$ has three the identical rings as the $B_3O_3(OH)_5^{2-}\cdot B_3O_3(OH)_4^-$ present in solutions differs from $B_3O_3(OH)_5^{2-}$ in the ratio of B—O triangles to B—O tetrahedrons. The $B_3O_3(OH)_4^-$ can easily transform into the $B_3O_3(OH)_5^{2-}$ in aqueous solutions:

$$B_3O_3(OH)_4^- + OH^- = B_3O_3(OH)_5^{2-} \quad (1)$$

The precursor of $MgB_6O_{10}\cdot 7.5H_2O$ crystallized from supersaturated solution may be $B_3O3(OH)_4^-$, but no simple crystallization mechanisms exist. Complicated dynamic equilibria among the boron species in solution must be established at low rate during slow precipitation of $MgB_6O_{10}\cdot 7.5H_2O$.

**Table 1** Chemical analyses and $^{11}$B NMR spectra of supersaturated and saturated magnesium borate solutions

| | Solution | B Conc. /mol·dm$^{-3}$ | pH | Chemical shift/ppm |
|---|---|---|---|---|
| $MgB_6O_{10}\cdot 7.5H_2O$ | Supersatu. | 2.11 | 7.18 | 18.71, 13.17, 1.44 |
| | Satu. | 1.04 | 6.84 | 19.13, 13.34, 1.18 |
| $MgB_4O_7\cdot 9H_2O$ | Supersatu. | 1.81 | 7.94 | 17.06, 12.96, 1.16 |
| | Satu. | 0.81 | 7.12 | 19.09, 13.01, 1.22 |
| $Mg_2B_6O_{10}\cdot 15H_2O$ | Supersatu. | 0.36 | 9.09 | 14.29, 1.16 |
| | Satu. | 0.10 | 8.62 | 14.98 |

**Table 2** Differential FT—Raman spectra (in $cm^{-1}$) of supersaturated and saturated aqueous magnesium borate solutions at room temperature

| $MgB_6O_{10}\cdot 7.5H_2O$ | | $MgB_4O_7\cdot 9H_2O$ | | $Mg_2B_6O_{10}\cdot 15H_2O$ | | Assignments |
|---|---|---|---|---|---|---|
| Supersatu. | Satu. | Supersatu. | Satu. | Supersatu. | Satu. | |
| 876s | 876s | 876s | 876s | 876s | 876m | $\nu_1B(OH)_3$ |
| 745w | | 749w | | 744m | | $\nu_1B(OH)_4^-$ |
| 612m | 609w | 612m | 609w | 609w | | $\nu_pB_3O_3(OH)_4^-$ |
| 529w | 529w | | 528w | | | $\nu_pB_5O_6(OH)_4^-$ |

w—weak, m—medium, s—strong

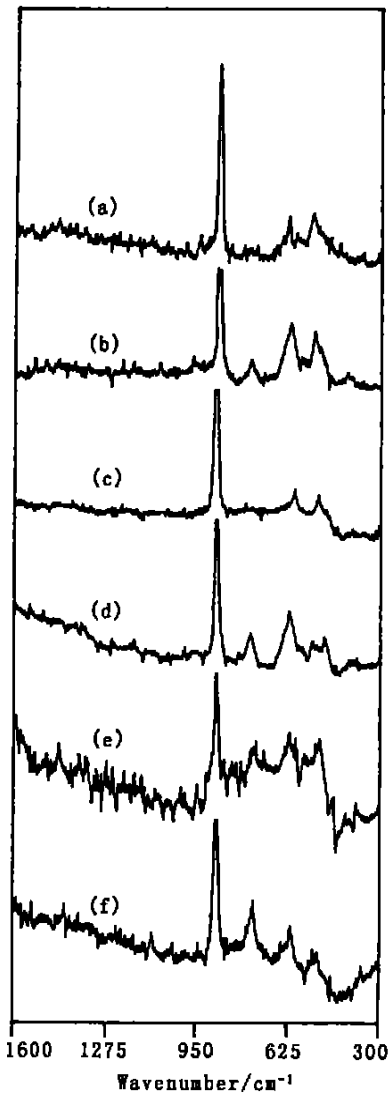


**Fig 1** $^{11}B$ NMR spectra of supersaturated and saturated magnesium borate solutions at room temperature (a) $MgB_6O_{10}\cdot 7.5H_2O$ supersaturated; (b) $MgB_6O_{10}\cdot 7.5H_2O$ saturated; (c) $MgB_4O_7\cdot 9H_2O$ supersaturated; (d) $MgB_4O_7\cdot 9H_2O$ saturated; (e) $Mg_2B_6O_{11}\cdot 15H_2O$ supersaturated; (f) $Mg_2B_6O_{11}\cdot 15H_2O$ saturated

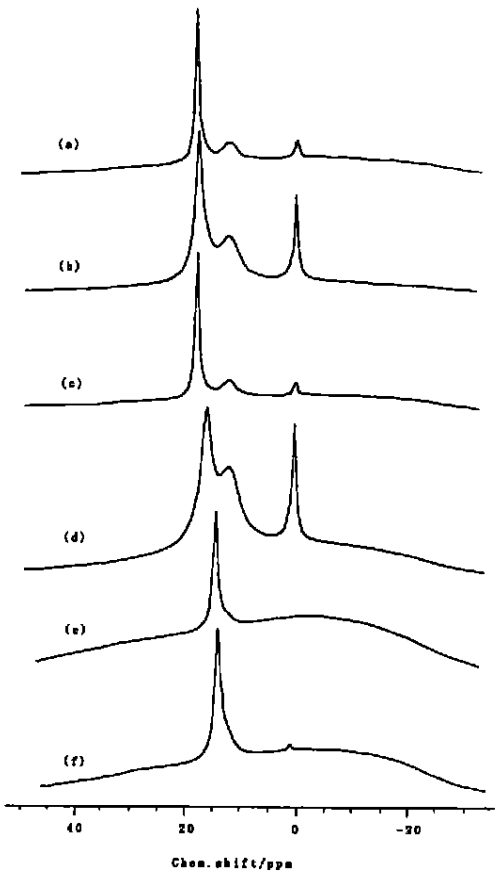


**Fig 2** Differential FT— Raman spectra of supersaturated and saturated magnesium borate solutions at room temperature (a) $MgB_6O_{10}\cdot 7.5H_2O$ supersaturated; (b) $MgB_6O_{10}\cdot 7.5H_2O$ saturated; (c) $MgB_6O_7\cdot 9H_2O$ supersaturated; (d) $MgB_4O_7\cdot 9H_2O$ saturated; (e) $Mg_2B_6O_{11}\cdot 15H_2O$ supersaturated; (f) $Mg_2B_6O_{11}\cdot 15H_2O$ saturated

Supersaturated $MgB_4O_9\cdot 9H_2O$ solution

The difference FT— Raman and $^{11}B$ NMR spectra of supersaturated and saturated $MgB_4O_7\cdot 9H_2O$ solutions were analogous to that of $MgB_6O_{10}\cdot 7.5H_2O$ respectively. The $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_5O_6(OH)_4^-$ are main boron species in solutions. The crystallized product $MgB_4O_7\cdot 9H_2O$ has tetraborate anion $B_4O_5(OH)_4^{2-}$, which is not observable by Raman and $^{11}B$ NMR spectroscopy. Thereare two possibilities that the unobservable $B_4O_5(OH)_4^{2-}$ due to its low concentration is the precursor, or the precursor is formed from complicated equilibria among the boron species in solutions.

Supersaturated $Mg_2B_6O_{11}\cdot 15H_2O$ solution

Because of low boron concentration, the $B(OH)_3$, $B(OH)_4^-$, and $B_3O_3(OH)_4^-$ are only observed in the difference FT— Raman and $^{11}B$ NMR spectra of supersaturated and saturated $Mg_2B_6O_{11}\cdot$

$15H_2O$ solutions. The most possible precursor of $Mg_2B_6O_{11}\cdot 15H_2O$ is $B_3O_3(OH)_4^-$. Just like in case of $MgB_6O_{10}\cdot 7.5H_2O$ and $MgB_4O_7\cdot 9H_2O$, complicated dynamic equilibria among boron species exist in solution.

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# 差示 FT-Raman 和 $^{11}B$ NMR 方法研究过饱和镁硼酸盐的溶液结构


李 军, 李 冰

(中国科学院盐湖研究所西安二部 陕西 西安 710043)



摘 要: 用差示 FT-Raman 和 $^{11}B$ NMR 光谱研究了 $MgB_6O_{10}\cdot 7.5H_2O$、$MgB_4O_7\cdot 9H_2O$、$Mg_2B_6O_{10}\cdot 15H_2O$ 三种镁硼酸盐饱和和过饱和溶液的结构机理, 其结果表明饱和溶液和过饱和溶液中均存在 $B(OH)_3$、$B(OH)_4^-$、$B_3O_3(OH)_4^-$、$B_5O_6(OH)_4^-$ 粒子。镁硼酸盐的结晶过程是一个复杂的动力学平衡过程。



关键词: 镁硼酸盐; 过饱和溶液; 差示 FT-Raman 光谱; $^{11}B$ NMR 光谱