Investigation on Species Distribution and EXAFS Structure of Aqueous Rubidium Pentaborate Solutions

J. T. Miao^{a,b}, C. H. Fang^{a,*}, Y. Fang^{a,*}, F. Y. Zhu^a, H. Y. Liu^{a,b}, Y. Q. Zhou^a,

H. W. Ge^a, P. C. Sun^{a,b}, X. C. Zhao^{a,b}

^a Laboratory of Salt Resources chemistry, Institute of Salt Lakes, Chinese Academy of Sciences, Xining, Qinghai 810008, China

^b Graduate University of Chinese Academy of Sciences, Beijing 100049, China

ABSTRACT

Based on the measured pH data and reported equilibrium constants, the main polyborate species formation existing in solution was investigated using the Newton iteration method at 298 and 333K, and checked by the method of ¹¹B nuclear magnetic resonance (NMR) spectroscopy. The neighboring structure of rubidium ion was studied at room temperature, which the structural parameters, including the coordination number, interatomic distance of Rb-O and Debye-Waller factor, were determined by the synchrotron radiation extended X-ray absorption fine structure (EXAFS). The results show that the average interatomic distance of Rb-O is 2.93 ± 0.004 Å and coordination number is 7.7 ± 0.9 in the first hydration shell around rubidium ion.

Key words: rubidium pentaborate; species distribution; nuclear magnetic resonance spectroscopy; extended X-ray absorption fine structure

Introduction

Recent years, the borate compounds have attracted much research interest for more and more researchers, which the reason is the structural chemistry and diverse applications [1] in many aspects. The structure chemistry can be attributed to the planar triangle BO₃ and tetrahedral BO₄ in the fundamental building blocks. Because planar triangles BO₃ and tetrahedrons BO₄ can link together by oxygen sharing to form all kinds of chains, sheets and networks [2]. Moreover, borate materials can be extensively used in nonlinear optics [3-5], laser light [6], optical communication, signal processing [7] and cathode materials of lithium ion battery [8], etc. In order to better understand borate materials, properties and structure of their solid and solutions must be well understood. Until to now, the structure of many rubidium pentaborate crystals has been researched by X-ray diffraction [9-14], and that of rubidium ion in aqueous rubidium salt (RbBr, RbCl, RbI, RbF, RbCF₃SO₃, etc) solutions has also been investigated by X-ray diffraction [15-18], neutron diffraction [19], EXAFS [20-22], Molecular Dynamics and Monte Carlo (MD/MC) [23-24]. However, the species distribution and the structure of rubidium in aqueous RbB₅O₈ solution have not been reported in the literature. Therefore, the species distribution of polyborates was investigated to know the main species formation existing in solution at different concentrations

* Corresponding Author at: Laboratory of Salt Resources chemistry, Institute of Salt Lakes, Chinese Academy of Sciences, Xining, Qinghai 810008, Tel: +8615202582106
E-mail address: fangch@isl.ac.cn; fangy8@isl.ac.cn

and temperatures. Additionally, EXAFS is used to study the neighboring structure of Rb^+ in solution so that the structural parameters can be obtained. These studies are beneficial to understand the microscopic structure of the aqueous RbB_5O_8 solution.

Therefore, the main polyborate species formation and neighboring structure around Rb^+ are presented in this paper by analyses of polyborate species distribution, ^{11}B NMR and EXAFS.

Experimental

Synthesis and analysis of sample

Rb_2CO_3 and H_3BO_3 (all analytical grade reagent) are commercially available. The crystal of rubidium pentaborate was obtained via slow evaporation from an aqueous solution of rubidium carbonate and boric acid in stoichiometric proportions. After CO_2 complete releases, the evaporation of solution under constant stirring and heating led to the desired compound at 323K. Boron was determined by volumetric method with the standard solution of NaOH in the presence of mannitol, and rubidium was measured by atomic absorption (the Australia GBC Company, GBC 908).

X-ray powder diffraction and thermogravimetry analysis

X-ray powder diffraction was performed on an X' Pert Pro X-ray diffractometer (the Holland PANalytical B.V.), using Cu $\text{K}\alpha$ ($\lambda=0.15418$ nm) radiation at room temperature. The colorless crystal powder was chosen and the hydrated rubidium borate compound $\text{Rb}(\text{B}_5\text{O}_6(\text{OH})_4\cdot 2\text{H}_2\text{O})$ was used as reference substance with a ICSD collection code 29406. The XRD data is in a good agreement with the Inorganic Crystal Structure Database data. The content of water molecules was determined using the thermogravimetric method on the thermal analyzer (the United States thermoelectric company, SDT Q600). The temperature range is from 303 to 1073K, which the heating rate is $5.0\text{K}\cdot\text{min}^{-1}$ under the atmosphere of nitrogen. The weight loss of 21.16% corresponds to a loss of four water molecules from the compound as expected from the $\text{RbB}_5\text{O}_8\cdot 4\text{H}_2\text{O}$ chemical formula (theoretical water loss: 21.22%) [10].

pH measurement

The pH data of the aqueous RbB_5O_8 solutions was determined using an Orion 310P01 pH meter (thermo, USA) at 298 and 333K, and the pH meter has the reproducibility of $\pm 0.5\%$. Before measurement, the pH meter was calibrated using three pH standard solutions [25-26] (phthalate, 4.01; phosphate, 6.86; borax, 9.18). In the process of measurement, a thermostat (GDH-1015W, Sayfo analytical instrument factory, Jintan, Jiangsu, China) was used to control the temperature and the systematic uncertainty is within $\pm 0.01\text{K}$.

NMR spectroscopy

The 160-MHz ^{11}B NMR experiments of aqueous RbB_5O_8 solutions were performed on a Bruker DMX-500 NMR spectrometer, using external $\text{Et}_2\text{O}\cdot\text{BF}_3$ [27] as reference substance at 297K. Before measuring sample solutions, D_2O was used as the NMR solvent and the chemical

shift range $-30\sim 70$ ppm was chosen.

EXAFS measurement

EXAFS experiments were performed with the 1W2B beam line at Beijing Synchrotron Radiation Facility (BSRF), which its energy range is in the $5\sim 18$ keV. The EXAFS spectrum at Rb K-edge (15.2 keV) was all collected at room temperature in the transmission mode using a Si (311) double crystal monochromator [28], and a 50.0% harmonic rejection was achieved by slightly detuning at two crystals from parallel alignment. In the process of experimental measurements, the samples were all kept in a cell with Kapton film windows.

Results and discussion

pH measurement

The experimental pH data at different temperature of 298 and 333K is presented in Table 1 and Fig.1, and the standard uncertainty of data can see the reference [29-30]. By analyses of pH curves, there exists a rising trend with the increase of the RbB_5O_8 solution concentration when it is in a very extreme low concentration range, for which boric acid belongs to the weak electrolyte. Along with the increasing solution concentration, the ionization degree of boric acid and the H^+ concentration decrease, therefore, the pH values increase. However, some very complicated chemical reactions, such as hydrolysis, polymerization, depolymerization and association, etc., exist among different polyborate species in solution. The pH data has a tendency of decrease with the increasing H^+ concentration released into solution. On the same concentration, the experimental pH values fall slowly with the temperature going up.

Table 1

The measured pH data of the RbB_5O_8 solutions ^a

c (mol·L ⁻¹)	298K	c (mol·L ⁻¹)	333K
0.0001	8.701	0.0010	8.601
0.0030	8.710	0.0040	8.621
0.0040	8.706	0.0071	8.598
0.0051	8.698	0.0100	8.578
0.0060	8.688	0.0200	8.552
0.0070	8.680	0.0300	8.502
0.0081	8.674	0.0400	8.441
0.0090	8.664	0.0500	8.390
0.0101	8.652	0.0600	8.345
0.0200	8.584	0.0700	8.296
0.0300	8.518	0.0799	8.241
0.0500	8.390	0.0900	8.182
0.0400	8.454	0.0999	8.136
0.0599	8.343	0.2000	7.767
0.0700	8.278	0.2798	7.582

^a c is the molarity of aqueous RbB_5O_8 solutions. Standard uncertainties u are $u(T) = 0.02\text{K}$, $u(c) = 0.0004$

mol·L⁻¹, and the combined expanded uncertainty U_c is $U_c(\text{pH}) = 0.1$ (confidence level = 0.95).

Fig.1. The pH data of aqueous RbB₅O₈ solutions

Polyborate species distribution

According to the previous studies, it is found that there mainly exist six polyborate species [31] in borate solutions, such as H₃BO₃, B(OH)₄⁻, B₃O₃(OH)₄⁻, B₃O₃(OH)₅²⁻, B₄O₅(OH)₄²⁻ and B₅O₆(OH)₄⁻. It is clearly observed that complex chemical reactions appear in solution, such as hydrolysis, polymerization, depolymerization and association, etc. These existing forms and reactions depend largely on the total boron concentration, temperature, pH and the type of cation. Therefore, the borate solutions are more complex than common salts solutions. On the basis of measured pH data, the polyborate species distribution can be achieved using equilibrium constants [32-33] by the method of Newton iteration [34]. The boric acid B(OH)₃ is assumed as the initial reactant, so the equilibrium constants can be expressed as K_{qp} . Then the general reaction expression [35] and the material balance equation of boron can be written as

$$\begin{aligned}
 p\text{B(OH)}_3 + n\text{H}_2\text{O} &= \text{B}_p(\text{OH})_{3p+q}(\text{H}_2\text{O})_{n-q}^{q-} + q\text{H}^+ \\
 K_{qp} &= a(\text{B}_p(\text{OH})_{3p+q}(\text{H}_2\text{O})_{n-q}^{q-}) \cdot a(\text{H}^+)^q / (a(\text{B(OH)}_3)^p \cdot a(\text{H}_2\text{O})^n) \\
 \text{Total boron} &= [\text{B(OH)}_3] + [\text{B(OH)}_4^-] + 3[\text{B}_3\text{O}_3(\text{OH})_4^-] + 3[\text{B}_3\text{O}_3(\text{OH})_5^{2-}] \\
 &\quad + 4[\text{B}_4\text{O}_5(\text{OH})_4^{2-}] + 5[\text{B}_5\text{O}_6(\text{OH})_4^-] \\
 &= [\text{B(OH)}_3] + K_{11}[\text{B(OH)}_3]/[\text{H}^+] + 3K_{31}[\text{B(OH)}_3]^3/[\text{H}^+] + 3K_{32}[\text{B(OH)}_3]^3/[\text{H}^+]^2 \\
 &\quad + 4K_{42}[\text{B(OH)}_3]^4/[\text{H}^+]^2 + 5K_{51}[\text{B(OH)}_3]^5/[\text{H}^+]
 \end{aligned}$$

By solving the above material balance equation of boron, the equilibrium concentration of [B(OH)₃] can be firstly calculated. After that, the other polyborate species existing in solution were calculated in turn. The mole fraction involved in Fig.2 is the moles of boron for a certain polyborate species divided by that of the total boron.

Fig.2 shows the polyborate species distribution in the investigated aqueous RbB₅O₈ solution concentrations at the temperature of 298 and 333K. Firstly the polyborate species distribution at 298K is chosen as an example to study the existing species formation in solution. It is clearly seen that there exist six curves representing six different polyborate species, but the mole fraction of B₃O₃(OH)₅²⁻ is almost close to zero. Therefore, the mole fraction of B₃O₃(OH)₅²⁻ will be neglected in the following discuss. In other words, there are five kinds of polyborate species existing in solution, but their mole fractions vary with the concentrations of borate solution. At the starting point O, there are only two species B(OH)₃ and B(OH)₄⁻ existing in solution, and their mole fractions are 0.8 and 0.2, respectively. However, the mole fractions of other polyborate species, such as B₃O₃(OH)₅²⁻, B₄O₅(OH)₄²⁻ and B₅O₆(OH)₄⁻ are all close to zero. Because the summation of

the mole fractions of B(OH)_3 and B(OH)_4^- is nearly equal to 1.0, it indicates that these two species B(OH)_3 and B(OH)_4^- can be produced by completely dissolving of $\text{RbB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ compound. Moreover, a very important conclusion is drawn that the mole ratio of B(OH)_3 and B(OH)_4^- is equal to 4:1. Hence, relevant chemical reaction involved at point O can be expressed in the following equation

In the concentration range $0.0 \sim 0.008 \text{ mol} \cdot \text{L}^{-1}$, there are four types of polyborate species occurring in solution, including B(OH)_3 , B(OH)_4^- , $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, while the mole fractions of other species $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$ will be ignored. The mole fractions of these four species in turn are 0.665, 0.155, 0.155, 0.025 at the point R ($0.008 \text{ mol} \cdot \text{L}^{-1}$), respectively. It is obviously found that the mole fractions of B(OH)_3 and B(OH)_4^- decrease gradually, nevertheless, the mole fractions of $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ are on the increase over the above concentration range. By comparison of the mole fractions of B(OH)_3 , B(OH)_4^- , $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ between the points of O and R, it is found that the reductions of reactants are 0.135 and 0.045 for the mole fractions of B(OH)_3 , B(OH)_4^- , while the increments of resultants for the mole fractions of $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ are 0.155 and 0.025. These four values indicate that the decreasing mole fractions of reactants are equivalent to the increasing mole fractions of resultants between the concentration range between O and R points. That is to say, there exists main one chemical reaction happening during this concentration range and the polyborate species with high polymerization degree come into being in aqueous RbB_5O_8 solutions. Therefore, the chemical reaction may be represented like this

When $c > 0.008 \text{ mol} \cdot \text{L}^{-1}$, it is clearly found that in solution there mainly exist five polyborate species, involving B(OH)_3 , B(OH)_4^- , $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$, while the mole fraction of $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$ is also ignored. The mole fractions of these three polyborate species $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$ rise gradually with the concentration increasing, while the mole fractions of B(OH)_3 , B(OH)_4^- decrease. It manifests that the B(OH)_3 , B(OH)_4^- act as reactants, and these species $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$ serve as resultants. It is worth noting that the species $\text{B}_5\text{O}_6(\text{OH})_4^-$ comes into being, whose mole fraction has a rising trend with the increase of solution concentration. As a consequence, a conclusion is drawn that these five polyborate species B(OH)_3 , B(OH)_4^- , $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$ mainly exist in aqueous RbB_5O_8 solution at 298K.

Furthermore, the polyborate species distribution in solution over a wide concentration range is also studied at 333K. By comparing polyborate species distribution at different temperature, the effect of temperature on the chemical species distribution is also investigated. Though these species, such as B(OH)_3 , B(OH)_4^- , $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$, also exist in aqueous RbB_5O_8 solution at 333K, the mole fractions for these polyborate species have some changes in a certain concentration range. As shown in Fig.2, the mole fractions of $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$ at 298K are higher than theirs at 333K, however, the mole fractions of B(OH)_3 and B(OH)_4^- are higher at 333K than that of their at 298K under the same concentration. The reason for this change may be possible that higher temperature is beneficial to the formation of borate species with lower polymerization degree, such as B(OH)_3 and B(OH)_4^- . Similarly, the lower temperature is conducive to the formation of borate species with higher polymerization

degree in aqueous RbB_5O_8 solution, such as $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$.

Fig.2. Polyborate species distribution in aqueous RbB_5O_8 solutions: ●, $\text{B}(\text{OH})_3$; ■, $\text{B}(\text{OH})_4^-$; ▲, $\text{B}_3\text{O}_3(\text{OH})_4^-$; ▼, $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$; ◆, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$; ►, $\text{B}_5\text{O}_6(\text{OH})_4^-$ (the standard uncertainties u are $u(T) = 0.02\text{K}$, $u(c) = 0.0004\text{mol}\cdot\text{L}^{-1}$, and the combined expanded uncertainty of mole fraction is 0.04 (confidence level = 0.95))

NMR spectroscopy

As shown in Fig.3, there exist mainly three peaks over the chemical shift range in our research solutions, whose resonances are around 1, 13 and 18 *ppm*, respectively. According to previous studies [36-37], these resonances mentioned above can be assigned to $\text{B}_5\text{O}_6(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$ in turn. Moreover, the position and areas of peaks denoting species have some changes at different solution concentrations. The chemical shifts of main resonance peaks are listed in Table 2. Some discoveries are obtained that the peak areas of these two species $\text{B}_5\text{O}_6(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_4^-$ are broadened with the increase of concentration, while that of $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$ is narrowed. There exist two primary peaks of $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$, nevertheless, the peak of $\text{B}_5\text{O}_6(\text{OH})_4^-$ not exists in solution at the concentration of $0.06\text{mol}\cdot\text{L}^{-1}$. On the basis of these discoveries, hence, the effect of concentration on polyborate formation is also researched. It is because the relevant chemical reactions occur in solution, including hydrolysis, depolymerization and polymerization, etc. When the solution concentration is $0.06\text{mol}\cdot\text{L}^{-1}$, the reason for those aforementioned changes is that $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$ species are generated by dissolving of rubidium pentaborate compound. As concentration continues to increase, the peak of $\text{B}_5\text{O}_6(\text{OH})_4^-$ appears and its peak area becomes gradually increasing. At this moment, the chemical reaction of polymerization happens, which $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$ can polymerize into $\text{B}_5\text{O}_6(\text{OH})_4^-$ in solution. Then, the chemical reactions can be presented in the following way, and these results from NMR spectroscopy are in a good agreement with that of polyborate species distribution at 298K.

Fig.3. ^{11}B NMR of aqueous RbB_5O_8 solutions at 297K

Table 2

The chemical shifts of main resonance peaks of aqueous rubidium pentaborate solutions ^a

$c(\text{mol}\cdot\text{L}^{-1})$	Chemical shift(ppm)		
0.06	17.29	13.25	1.28
0.08	17.66	13.22	1.20
0.10	17.92	13.25	1.22

^a The standard uncertainties u is $u(c) = 0.0004 \text{ mol}\cdot\text{L}^{-1}$, and the combined expanded uncertainty of NMR data is 0.1 (confidence level = 0.95).

EXAFS analysis

Through the EXAFS measurements, the data was performed with the IFEFFIT [38-39] software package, which is based on the theoretical calculation of the X-ray absorption fine spectra signal and a subsequent refinement of the structure parameters. The software of Athena is primarily used to reduce the raw EXAFS experimental data and extract the function of $\chi(k)$, and another software of Artemis is used to fit EXAFS data processed by the Athena software. After repeated fitting until the results are satisfactory, the structural parameters, such as the coordination number, interatomic distance and Debye-Waller factor, can be obtained. The EXAFS oscillation function [40-41], $\chi(k)$, can be expressed as

$$\chi(k) = \sum (N_j / k R_j^2) S_0^2(k) F_j(k) \exp[(-2R_j / \lambda_j) - 2\sigma_j^2 k^2] \sin[2kR_j + \Phi_j(k)]$$

In the above expression, the equation denotes the summation of the contribution of different coordination shells, including multiple-scattering contributions. The different coordination shells mentioned above refer to a concept that the neighboring atoms to the central atom of rubidium are divided into j shells, which they have same coordination number and distance. The wave vector k is expressed by $k = (2m_e(E - E_0) / (\hbar^2))^{1/2}$, which m_e is the mass of electron, $\hbar$ is Planck's constant divided by 2π and E_0 is the absorption edge energy associated with the ejection of photoelectron. R_j , N_j , σ_j^2 represent the average coordination distance, coordination number and the Debye-Waller factor, respectively. S_0^2 is the amplitude reduction factor and $\Phi_j(k)$ denotes the phase shift. Additionally, λ represents the mean free path of a photoelectron. Based on obtained fitting results, adjusting the Fourier and fit parameters can gain the satisfactory fitting results in the process of fitting. The EXAFS oscillations, $\chi(k)$, was weighted by k using a Hanning window when k is from 2.0 to 8.0 $\text{\AA}^{-1}$. Sometimes, in some literature k begins in less than 2 $\text{\AA}^{-1}$ or equal to 2 $\text{\AA}^{-1}$ [42-45]. The fitting was applied to both the real and imaginary part of $\chi(R)$ in the region of $1.3 < R < 3.2 \text{ \AA}$.

The EXAFS spectrums of rubidium pentaborate are shown in Fig.4 (A). It is the local structure of rubidium ion that can be directly determined using EXAFS spectroscopy. In addition to this, the EXAFS k -space and R -space spectrums by Fourier transform are also described in Fig.4 (B) and Fig.4 (C), respectively. As shown in the EXAFS R -space spectrum for different concentrations of aqueous RbB_5O_8 solutions and its corresponding solid compound, there exists one obvious and independent peak observed. Therefore, the primary peak around $2.93\text{\AA}$ in the EXAFS R -space spectrum is considered in this work, which can be assigned to the Rb-O peak in the first hydration shell of rubidium ion. A long wavelength signal left above $6\text{\AA}^{-1}$ in Fig.4(C) is due to multielectron excitations as references [46-47], which gives rise to low-distance nonstructural peaks in Fourier transform. Besides, the peak below $2\text{\AA}$ in EXAFS R -space spectrum can be found in some literature [48-51]. There are no data reported in the literature about the existence of the second hydration shell of rubidium ion, in other words, rubidium ion is weakly hydrated with only a single shell of water molecules. The reason is that the weakness of hydration of rubidium ion does not favor the formation of the second hydration shell. This information is in a good agreement with the measured experimental results in the EXAFS R -space spectrum.

Fig.4. Experimental EXAFS results of RbB_5O_8 : (A) Rb K-edge spectrum; (B) EXAFS k -space spectrum; (C) EXAFS R -space spectrum

In the process of the EXAFS fitting, the $\text{RbB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ crystal (ICSD collection code 29406) is used as the standard substance. The fitted k -weighted $|\chi(R)|$ plots with phase shift correction applied are described in Fig.5 and the obtained EXAFS structural parameters with error bar based on the k -weighted fits in the R -space spectrum are given in Table 3. It is clearly seen that the experimental and fitting curves are superposed well, which indicates the fitting is satisfactory. k ranges from $2.0 \sim 8.0\text{\AA}^{-1}$ and R range is from 1.3 to $3.2\text{\AA}$ in the EXAFS k -space and R -space spectrum, respectively. The radial distribution function for RbB_5O_8 solutions are shown in Fig.5(C) and the main peak about $2.93 \pm 0.004\text{\AA}$ can be attributed to the Rb-O peak in the first hydration shell around rubidium ion. According to the experimental and EXAFS fitting curves, the $\text{RbB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ crystal (ICSD collection code 29406) used as standard substance is suitable and reasonable for fitting of resultant RbB_5O_8 .

Fig.5. Experimental and fitting spectra of RbB_5O_8 solutions: (B) EXAFS k -space; (C) EXAFS R -space

Table 3

The obtained EXAFS structural parameters of rubidium pentaborate ^a

Sample	Shell	N	R (Å)	S_0^2	σ^2	ΔE_0 (eV)	R-factor
0.03 mol·L ⁻¹	Rb-O	7.8(1.0)	2.92(0.004)	0.97(0.123)	0.022(0.008)	3.58(1.70)	0.009
0.07 mol·L ⁻¹	Rb-O	7.9(0.9)	2.92(0.004)	0.98(0.108)	0.022(0.006)	3.34(1.30)	0.006
0.10 mol·L ⁻¹	Rb-O	7.5(0.9)	2.95(0.004)	0.94(0.107)	0.022(0.008)	4.55(1.68)	0.009
$\text{RbB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ (s)	Rb-O	8.0(1.1)	2.94(0.004)	0.99(0.136)	0.015(0.009)	1.63(1.82)	0.024

^a σ^2 : Debye-Waller factor; ΔE_0 : energy zero offset; S_0^2 : amplitude reduction factor (the data in brackets: error bar)

It can be seen obviously from the Table 3 that the coordination number for 0.03, 0.07, 0.10 mol·L⁻¹ solutions and its corresponding solid compound vary in a wide range. The gained average interatomic distance of Rb-O and coordination number in the first hydration shell around Rb^+ are $2.93 \pm 0.004 \text{ Å}$ and 7.7 ± 0.9 , respectively. What is noteworthy is that the amplitude reduction factor S_0^2 is directly correlated with coordination number in the first hydration shell around rubidium ion in solution. If a proper background model is used, S_0^2 is expected to be close to 1.0 [20]. The interatomic distance of Rb-O and coordination number in the first hydration shell around rubidium ion by different methods are summarized in Table 4. By beyond that, the average coordination number and hydration distance of other alkali metal ions reported in literature [18] are 4 and 2.10 Å for lithium, 6 and 2.43 Å for sodium, 6-8 and 2.81 Å for potassium, 8 and 3.07 Å for cesium, respectively. It is also found that these average coordination numbers and hydration distances have a rising trend with the increase of ion radius, furthermore, hydration and the ability of forming the second hydration shell become weaker on passing from lithium to cesium ion. That is to say, the ability of hydration for rubidium ion in aqueous solution is weaker and cannot form the second hydration shell, which the information is in a good accordance with the experiment results.

Table 4

The obtained coordination number and distance of Rb-O in aqueous solution by different methods ^a

Substance	c(mol·L ⁻¹)	N	R(Å)	Method	reference
RbBr	1	6.5	2.88	EXAFS	52
RbCl	4	6.4-7.4	3.05	AXD	53,54
RbI	1.51	8	2.99	LAXS	20
RbF	3.01	8	2.96	LAXS	20
RbCF_3SO_3	1.00	8.0	2.98	EXAFS	20
$[\text{Rb}(\text{H}_2\text{O})_n]^+$	-	7.1	2.95	QM/MM MD	16

(n=1-8)

RbBr	1	6	2.83	EXAFS	21
RbBr	0.5	5.6	2.93	XAFS	55
Rb ⁺	-	6	2.90	EXAFS	56
Rb ⁺	-	8	2.98	LAXS	19
RbBr	4.6	-	2.90	DAS	57
RbBr	4.6	-	2.84	EXAFS	57
RbCl	4	6.9	3.10	NDIS	58
RbF	2.22	5.36	3.02	XRISM	59
RbCl	0.22-3.97	~7.7-6.1	3.75	MD	17
Rb-H ₂ O	-	5	2.89	MD	60
RbBr	0.2	6.4	3.65	EXAFS	22
RbBr	2	5.52	3.70 ^d	MD+MC	23
RbB ₅ O ₈	0.10	7.7	2.93	EXAFS	this paper

^a AXD is Anomalous X-ray diffraction, XAFS is fine structure X-ray absorption spectroscopy, EXAFS is extended X-ray absorption fine structure spectroscopy, MD is molecular dynamics, MC is Monte Carlo, LAXS is large-angle X-ray scattering, *ab initio* QM/MM MD is the molecular dynamics method using quantum and molecular mechanical approaches, DAS is differential anomalous scattering, NDIS is neutron diffraction isotopic substitution, XRISM is extended reference interaction site model.

Conclusions

In this paper, by analyses of the polyborate species distribution under different temperatures and concentrations, these five species B(OH)₃, B(OH)₄⁻, B₃O₃(OH)₄⁻, B₄O₅(OH)₄²⁻ and B₅O₆(OH)₄⁻ mainly exist in our researched solution and polyborate species formation is also studied. Furthermore, the higher temperature is beneficial to the formation of B(OH)₃ and B(OH)₄⁻, while the lower temperature is conducive to the formation of B₃O₃(OH)₄⁻, B₄O₅(OH)₄²⁻ and B₅O₆(OH)₄⁻ in solution. Through EXAFS experiment, the interatomic distance of Rb-O is 2.93±0.004 Å and coordination number in the first hydration shell around Rb⁺ is 7.7±0.9.

Acknowledgements

This work was financially supported by National Science Foundation of China (NO. 21373251) and the Main Direction Program of Knowledge Innovation of Chinese Academy of Sciences (NO. KZCX2-EW-307). Tiandou Hu, Jing Zhang, Lirong Zheng are sincerely acknowledged for their support in the process of the EXAFS experiments performed at Beijing Synchrotron Radiation Facility.

References

- [1] C. Rong, Z. Yu, Q. Wang, S.-T. Zheng, C.-Y. Pan, F. Deng, G.-Y. Yang, Inorg. Chem. 48 (2009) 3650-3659.
- [2] Y. Yang, S. Pan, J. Han, X. Hou, Z. Zhou, W. Zhao, Z. Chen, M. Zhang, Cryst. Growth Des. 11 (2011) 3912-3916.
- [3] Y. Zhao, S. Pan, F. Li, Y. Wang, X. Fan, X. Dong, D. Jia, J. Guo, Z. Zhou, Solid State Sci. 13 (2011) 82-87.
- [4] J. Luo, S. Pan, H. Li, Z. Zhou, Z. Yang, J. Mater. Sci. 46 (2011) 7443-7448.
- [5] S.A. Rajasekar, K. Thamizharasan, A.J.A. Pragasam, J.P. Julius, P. Sagayaraj, J. Cryst. Growth 247 (2003)

- [6] P. Becker, P.Held, L. Bohatý, Cryst. Res. Technol. 35 (2000) 1251-1262.
- [7] P. Becker, Adv. Mater. 10 (1998) 979-992.
- [8] P. A. Tang, L. H. Liu, G. R. Xu, J. Shen, Y. L. Ling, Chin. J. Applied Chem. 29 (2012) 1221-1230 (in Chinese).
- [9] Yu. E. Anderson, S. K. Filatov, I. G. Polyakova, R. S. Bubnova, Glass Phys. Chem. 30 (2004) 450-460.
- [10] N. Penina, L. Seguína, B. Géranda, M. Touboula, G. Nowogrockib, J. Alloy. Compd. 334 (2002) 97-109.
- [11] N. Penin, L. Seguin, M. Touboul, G. Nowogrocki, J. Solid State Chem. 161 (2001) 205-213.
- [12] M. G. Krzhizhanovskaya, R. S. Bubnova, S. K. Filatov, A. Belger, P. Paufler, Z. Kristallogr. 215 (2000) 740.
- [13] R. Bubnova, I. Polyakova, Y. E. Anderson, S. Filatov, Glass phys. Chem. 25 (1999) 183-194.
- [14] H. Behm, Acta Cryst. 40 (1984) 217-220.
- [15] P. R. Smirnov, V. N. Trostin, Russ. J. Gen. Chem. 77 (2007) 2101-2107.
- [16] T. S. Hofer, B. R. Randolph, B. M. Rode, J. comput. Chem. 26 (2005) 949-956.
- [17] H. Du, J. C. Rasaiah, J.D. Miller, J. Phys. Chem. B 111 (2007) 209-217.
- [18] J. Mähler, I. Persson, Inorg. Chem. 51 (2011) 425-438.
- [19] G. Neilson, P. Mason, S. Ramos, D. Sullivan, Phil. Trans. Soc. Lond. A 359 (2001) 1575-1591.
- [20] P. D'Angelo, I. Persson, Inorg. Chem. 43 (2004) 3543-3549.
- [21] T. Ohkubo, T. Konishi, Y. Hattori, H. Kanoh, T. Fujikawa, K. Kaneko, J. Am. Chem. Soc. 124 (2002) 11860-11861.
- [22] G. Ferlat, A. San Miguel, J. Jal, J. Soetens, P.A. Bopp, I. Daniel, S. Guillot, J. Hazemann, R. Argoud, Phys. Rev. B 63 (2001) 134202-1-134202-9.
- [23] L. Pusztai, H. Dominguez, O. Pizio, S. Sokolowski, J. Mol. Liq. 147 (2009) 52-55.
- [24] M. San-Román, J. Hernández-Cobos, H. Saint-Martin, I. Ortega-Blake, Theor. Chem. Acc. 126 (2010) 197-211.
- [25] F. Y. Zhu, C. H. Fang, Y. Fang, Y. Q. Zhou, H. W. Ge, H. Y. Liu, J. Mol. Struct. 1070 (2014) 80-85.
- [26] C. H. Fang, F. Y. Zhu, Y. Fang, Y. Q. Zhou, S. Tao, S. Xu, Phys. Chem. Liq. 51 (2013) 218-232.
- [27] C. G. Salentine, Inorg. Chem. 22 (1983) 3920-3924.
- [28] J-L. Bantignies, L. Alvarez, R. Aznar, R. Almairac, J-L. Sauvajol, L. Duclaux, F. Villain, Phys. Rev. B 71 (2005) 195419-1-195419-6.
- [29] K. Gregory, G. Bibbo, J. E. Pattison, Australas. Phys. Eng. Sci. Med. 28 (2005) 131-139.
- [30] International Organization for Standardization, Guide to the expression of uncertainty in measurement. International Organization for Standardization, Geneva, 1995.
- [31] Y. Q. Zhou, F. C. Fang, Y. Fang, F. Y. Zhu, Chin. J. Chem. Eng. 21 (2013) 1048-1056.
- [32] O. Weres, J. Solution Chem. 24 (1995) 409-438.
- [33] J. E. Spessard, J. Inorg. Nucl. Chem. 32 (1970) 2607-2613.
- [34] F. Y. Zhu, C. H. Fang, Y. Fang, Y. Q. Zhou, H. W. Ge, H. Y. Liu, J. Mol. Struct. 1083 (2014) 471-479.
- [35] H.W. Ge, Y. Fang, C.H. Fang, Y.Q. Zhou, F.Y. Zhu, H.Y. Liu, Z.X. Yang, Y.L. Tang, J. Chem. Eng. Data 59 (2014) 4039-4048.
- [36] R. K. Momii, N. H. Nachtrieb, Inorg. Chem. 6 (1967) 1189-1192.
- [37] C. G. Salentine, Inorg. Chem. 22 (1983) 3920-3924.
- [38] B. Ravel, M. Newville, J. Synchrotron Radiat. 12 (2005) 537-541.
- [39] B. Ravel, M. Newville, Phys. Scr. 2005 (2005) 1007-1010.
- [40] F. F. Xia, D. Zeng, H. B. Yi, C. H. Fang, J. Phys. Chem. A 117 (2013) 8468-8476.
- [41] H. Y. Liu, C. H. Fang, Y. Fang, Y. Q. Zhou, F. Y. Zhu, H. W. Ge, Z. X. Yang, Y. L. Tang, Acta Phys. -Chim. Sin. 30 (2014) 1979-1986.

- [42] Y. Kubozono, A. Hirano, H. Maeda, S. Kashino, Zeitschrift fur Naturforschung A-A Journal Physical Sciences 49 (1994) 727-729.
- [43] E. J. Dorskocil, S. V. Bordawekar, R. J. Davis, J. Catal. 169 (1997) 327-337.
- [44] J. L. Fulton, D. M. Pfund, S. L. Wallen, M. Newville, E. A. Stern, Yanjun Ma, J. Chem. Phys. 105 (1996) 2161-2166.
- [45] P. D'Angelo, V. Barone, G. Chillemi, N. Sanna, W. Meyer-Klaucke, N. Viorel Pavel, J. Am. Chem. Soc. 124 (2002) 1958-1967.
- [46] P. D'Angelo, A. Di Nola, E. Giglio, M. Mangoni, N. V. Pavel, EXAFS Study of Micellar Aggregates of Bile Acid Rubidium Salts. J. Phys. Chem. 99 (1995) 5471-5480.
- [47] E. Giglio, S. Loreti, N. V. Pavel, EXAFS: a new approach to the structure of micellar aggregates. J. Phys. Chem. 92 (1988) 2858-2862.
- [48] G. Nowitzke, J. Dumschat, G. Wortmann, Mol. Cryst. Liq. Cryst. 245 (1994) 321-326.
- [49] O. Fussa, S. Kauzlarich, J. L. Dye, J. Am. Chem. Soc. 107 (1985) 3727-3728.
- [50] C. R. A. Catlow, A. V. Chadwick, G. N. Greaves, L. M. Moroney, M. R. Worboys, Solid State Ionics 9&10 (1983) 1107-1114.
- [51] M. Dubiel, S. Brunsch, I. Arcon, R. Frahm, J. Phys. IV 7(1997) C2-1169-C2-1170.
- [52] H. Bertagnolli, T. S. Ertel, M. Hoffmann, R. Frahm, Ber. Bunsenges. Phys. Chem. 95 (1991) 704-709.
- [53] S. Ramos, A.C. Barnes, G.W. Neilson, M.J. Capitan, Chem. Phys. 258 (2000) 171-180.
- [54] S. Ansell, A. Barnes, P. Mason, G. Neilson, S. Ramos, Biophys. Chem. 124 (2006) 171-179.
- [55] M. Newville, J. Fulton, D. Pfund, S. Wallen, E. Stern, Y. Ma, J. Phys. IV France 7 (1997) C2-1007-C2-1008.
- [56] Y. Kubozono, A. Hirano, H. Maeda, S. Kashino, S. Emura, H. Ishida, Z. Naturforsch., A: Phys. Sci. 49 (1994) 727-729.
- [57] K. Ludwig Jr, W. Warburton, A. Fontaine, J. Chem. Phys. 87 (1987) 620-629.
- [58] E. Taskaev, J. Radioanal. Nucl. Chem. 118 (1987) 319-322.
- [59] M. V. Fedotova, Russ. J. Gen. Chem. 81 (2011) 15-23.
- [60] J. Aqvist, J. Chem. Phys. 94 (1990) 8021-8024.