Structure of aqueous potassium metaborate solution

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HIGHLIGHTS

- Study shows that the main borate species in aqueous $KB(OH)_4$ solutions is $B(OH)_4^-$.
- The average hydration number of the first hydration shells of K^+ is 8.1 and the hydration distance is $\sim$0.294 nm.
- The $B–O(H_2O)$ distance in hydrated anion $B(OH)_4^-$ is about 0.37 nm with an average hydrated number of 2.3.
- Contact ions $KB(OH)_4^0$ exist in $KB(OH)_4$ solutions, the distance of K–B is about 0.34 nm.
- Concentration and temperature also effect the hydration structure of $B(OH)_4$.

ARTICLE INFO

ABSTRACT

The structure of aqueous potassium metaborate solutions has been confirmed by X-ray scattering, Raman spectra and species distribution calculation. The optimized structure of $B(OH)_4^-$ was obtained by density functional theory calculation. The hydration distance and hydration number of K^+ in aqueous potassium metaborate solution were given by X-ray scattering. The $B–O(H_2O)$ distance in hydrated anion $B(OH)_4^-$ were determined to be 0.37 nm with the hydration number of 2.3 per hydroxyl(–OH). The K–B distance of the contact ions $KB(OH)_4^0$ was measured to be 0.34 nm.

Introduction

Borate minerals mainly occur in volcanic fumaroles, salt deposits, and granulites [1,2]. Hydroxy-hydrated borate lacustrine sediments were formed by evaporation of saline lakes in Qinghai-Tibetan Plateau [3]. The structure of the borate crystals is based on triangle BO_3 and Tetrahedron BO_4, which they polymerize to form isolated, chains, sheets and three-dimensional structures [4,5]. The formations of borate anions in solution depend on the mutual effect of the composition, temperature, cation type and pH of the primary parent solutions [1,6]. When borate crystal dissolved in water, six common species H_3BO_3, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{2-}$, $B_4O_5(OH)_4^{2-}$, $B_5O_6(OH)_4^-$ exist generallly in solution [7,8]. According to the study of ours [9], the main species are H_3BO_3 and $B(OH)_4^-$, when the concentration of borate solution is less than 0.01 mol/L; The polymerization process is happened and the six-membered ring anions, such as $B_3O_3(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$, are formed with the increasing of concentration; The major chemical species $B_4O_5(OH)_4^{2-}$ and the minor species $B_3O_3(OH)_4^-$ and $B(OH)_4^-$ appear in highly concentrated aqueous $K_2B_4O_7$ solutions. Additionally, the borate anions $B_5O_6(OH)_4^-$, $B_3O_3(OH)_4^-$ and $B(OH)_3$ are the main polyborate in supersaturated aqueous NaB_5O_8 solutions [10]. On the basic of Maeda [11], the main species are H_3BO_3, $B_3O_3(OH)_4^-$, $B_5O_6(OH)_4^-$ in the solution with pH < 8.0; The main species are $B_4O_5(OH)_4^{2-}$ with pH $\sim$ 9.0; $B(OH)_4^-$ is the dominating anion with pH > 10.0. Moreover many chemical reactions, i.e., ionization, hydrolysis, association, polymerization and depolymerization occur with the changing of the concentration and pH in solution [12]. The property study of aqueous borate solution is contributed to making clear the borate species in aqueous solution and their transformation relationship. The structure study is conducive to understanding the information of ionic hydration and association.

Therefore, we report on the structure studies of borate anions, the hydration of cation or anions, and the association between anion and cation, etc., by X-ray scattering and density functional theory (DFT) calculation, acidometry and Raman spectra.

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Experimental

Synthesis and analysis of samples

H_3BO_3 and KOH (all were analytic grade reagent) were commercially available and recrystallized from distilled water. $KBO_2 \cdot 1.33H_2O$ was synthesized according to phase diagram in the ternary system $K_2O–B_2O_3–H_2O$ [13], and verified by element analysis and X-ray powder diffraction. The sample solutions were prepared by weighting with double-distilled water ($\kappa < 1.0$ μS cm^{-1}). The boron composition of the samples was determined by mannitol titration method [14]. The samples were carefully protected from atmospheric CO_2.

pH and density measurement

Acidity of all the solutions was measured using an Orion 310P-01 pH meter (Thermo, USA) with accuracy of ±0.01 pH unit. The pH meter was calibrated using standard solutions (phthalate, 4.01; phosphate, 6.86; and borate, 9.18) before measurements. When the pH value measured was instable, the pH meter was calibrated using a standard solution. Densities of the solutions were measured by pycnometry. In all the measurements a thermostat (GDH-1015W, Sayfo analytical instrument factory, Jintan Jiangsu, China) was used to maintain the constant temperature at 298.15 ± 0.01 K.

Raman experiment and calculation method

ALMEGA-TM Raman spectroscopy was used. The wavelength of laser light source is 532 nm and the minimum power is 25 mW. The solutions were filled in quartz glass tubes with the number of exposures of 32 times.

The hydration structure and Raman shift of $B(OH)_4^-$ were calculated using DFT. To make a search for the optimized structure and the characteristic frequencies of $B(OH)_4^-$, 6-311++G(df,p) bases were employed for all the atoms. Geometry optimization of $B(OH)_4^-(H_2O)_n$ were done at B3LYP/6-311++G(df,p) level. The vibrational frequency was calculated at the same level in order to ascertaining the nature of the stationary points (no virtual frequency). Z-matrix coordinates constrained to the appropriate symmetry were used to speed up the optimizations. All the geometry optimization and frequency analysis were performed with the Gaussian 03 software package [15].

X-ray scattering experiment and data treatment

X-ray scattering experiment

X-ray scattering experiments of the solution samples with a salt-water molar ratio of 1:5, 1:10 were carried out on an X' pert-Pro $\theta–\theta$ X-ray diffractmeter equipped with a ceramic X-ray tube and with Mo anode of Kα (λ = 0.07107 nm) [16]. The electric current and the voltage were applied at 45 mA and 50 kV, respectively. A thermostatic liquid sample cell designed by ourselves was installed on an infrared remote control positioning stage with motorized z-axial, tilt and θ movements. Diffraction data were collected by an X'celerator detector. Four slits combinations, with 1/8°, 1/4°, 1/2° and 1° DS-ASSX slits for X'celerator detector were employed for different 2θ regions. The intensity collection was performed by free surface diffraction to 1/4° DS-ASS$_X$ slit pair, while a 6 μm Mylar foil was used to window material. The sample solutions were scanned continually at different fixed time range from 200 to 2000 s. Accumulated count was from 10^4 to 5×10^4 photons with the statistical error <1%. The scattering angle ranged from 3° to 150°, corresponding to an s-vector($s = 4\pi\sin\theta/\lambda$) of 4.63–170.8 nm^{-1}. Detailed descriptions of measurement skills and intensity collections have been described elsewhere [16–18].

Data treatment

After subtraction of the Mylar film background radiation and correction of the solution absorption, then conversion of the observed intensity to 1° DS-ASS$_X$ silt pair was carried out. Then, polarization, incoherent scattering, multiple scattering corrections and geometric correction were accomplished, respectively.

The structural function $i(s)$ was calculated by subtracting the independent scattering which is the sum of incoherent and coherent scattering calculated from all the atoms in the solution from the normalized intensity

$$i(s) = KI_P(s) - \sum_{i=1}^{N_{\text{atom}}} x_i \left[f_i^2(s) + (\Delta f_i'')^2 + \text{del}(s) \cdot I_i^{\text{incoh}}(s) \right] \quad (1)$$

Here, K is a normalization factor, $I_p(s)$ the experimental intensity corrected for polarization; x_i is the number of the i th atom in the stoichiometric volume V containing a potassium atom; del(s) indicates the fraction of incoherent radiation reaching the counter; $f_i(s)$ expresses the atomic scattering factor of atom i corrected for the real part of the anomalous dispersion; $\Delta f_i''$ is the imaginary part, taken from the Ref. [19]; $I_i^{\text{inc}}(s)$ presents the incoherent scattering including a Breat–Dirac recoil factor correction for atom i cited from Ref. [19].

The s-weighted structure function $s \cdot i(s)$ was Fourier-transformed into the radial distribution function (RDF)

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{\text{max}} s \cdot i(s) \cdot M(s) \cdot \sin(sr) ds \quad (2)$$

where ρ_0 stands for the average electron density of the sample solution ($\rho_0 = [\Sigma x_i f_i(0)]^2/V$). 0 is the integration lower limit and max the upper limit. The modification function $M(s)$ has the form

$$M(s) = \sum x_i \left[f_i^2(0) + (\Delta f_i'')^2 \right] \Big/ \sum x_i \left[f_i^2(s) + (\Delta f_i'')^2 \right] \cdot \exp(-ks^2) \quad (3)$$

The constant k is a damping factor chosen arbitrarily. The spurious ripples were removed from RDF by calculating the peak shape and performing Fourier transformation again.

A comparison between the experimental and theoretical structure functions was made by a least square refinement procedure of minimizing the error square sum:

$$U = \sum_{s_{\min}}^{s_{\max}} s^2 \left\{ i(s)_{\text{exptl}} - i(s)_{\text{calcd}} \right\}^2 \quad (4)$$

where s is the weighting function, $s_{\max}$ and $s_{\min}$ are the upper and lower range of the function.

The theoretical intensities $i(s)_{\text{calcd}}$ were calculated by the following equation:

$$
\begin{aligned}
i(s)_{\text{calcd}} = & \sum \sum_{pq} n_{pq} f_p(s) f_q(s) \frac{\sin(r_{pq}s)}{r_{pq}s} \exp(-b_{pq}s^2) \\
& - \sum \sum_{pq} n_p n_q f_p(s) f_q(s) \frac{4\pi R_q^3}{V} \\
& \times \frac{\sin(R_q s) - R_q s \cos(R_q s)}{(R_q s)^3} exp(-B_q s^2) \quad (5)
\end{aligned}
$$

The first term of the right-hand-side of Eq. (5) is related to the short-range interactions characterized by the inter-atomic distances r_{pq}, the temperature factor b_{pq}, and the number of interactions n_{pq} for atom pair p–q. The second term arises from the interaction between a spherical hole and the continuum electron