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Vibrational Spectroscopic Analysis of Borates in Mother Liquid of Brine after Potassium Separated

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It is well known that boron exists as polyborate anions in aqueous solution. Boron atom can coordinates to three or four oxygen atoms and borate can exist as not only the monomer but also the polymer. The polymerization probably forms a chain, sheer or network by eliminating a water molecule between two hydrated units, thus borate solutions are more complicated than that of general salts (Christ and Clark, 1977). Vibrational spectroscopy is usually a traditional method for the characterization and identification of unknown compounds, thus FT-IR and Raman spectrometry are usually used to study the aqueous solution structure of borates of high boron concentration (Jia et al, 2000; Liu et al, 2003(a); Liu et al, 2003(b); Li et al, 1995). For example, Li et al (Li et al, 1995) had recorder and reexamined 27 hydrated borates by FT-IR and Raman spectra. However, Raman spectrometry is more advantageous to inspect the characteristic peak of borates containing high boron concentration than FT-IR for solvent water has a smaller influence on it. Therefore, in this work, boron existed forms and content in boron-rich brine during acidification and extraction at different acidity by isooctanol + 2-ethyl-1,3-hexanediol + 260[#] sulfonated kerosene system after potassium separating were studied by Raman spectroscopy and ICP-OES.

The original brine was sampled from a salt lake located in Qaidam Basin in Qinghai province. Potassium in brine was previously separated by natural evaporation prior to carry out experiment. Some main components in brine after precipitation are presented in Table 1.

According to the behaviors of borates in brine during acidification, it was found that pH of boron-rich brine presented a trend of decrease → increase → decrease during acidification. It is noted that the trend of decrease is sharply when the pH of brine lower than certain value

(Fig. 1). Meanwhile, boron content obviously decreased for B(OH)₃ gradually form to produce precipitation at low pH range. This result is similar to that carried out by Gao et al (Gao et al, 1989). The decrease for the first step is speculated resulting from the formation of H₂(B_{2n}O_{3n+1}), and H₂(B_{2n}O_{3n+1}) further depolymerizes to generate H₂B₄O₄. The minimal value of pH is correspond with the limiting dissociation acidity of H₂B₄O₄; The increase of pH for the second step is probably caused by the depolymerization of H₂B₄O₄ into B(OH)₃ (dissolved state); The last step of pH decrease sharply main resulting from the largely formation of B(OH)₃ precipitation. Boron was almost completely precipitated at pH approximately 1.4 according to the relationship between pH and boron content, thus the optimum acidity for boron precipitation is about 1.4.

Borates presented slightly change from oligomeric state to high polyborate state at certain pH range based on the change of Raman spectrograms during acidification (Fig. 2). This result is basically in agree with that conducted by Liu et al (Liu et al, 2004), who had investigated the supersaturated aqueous solution of MgO·B₂O₃·32%

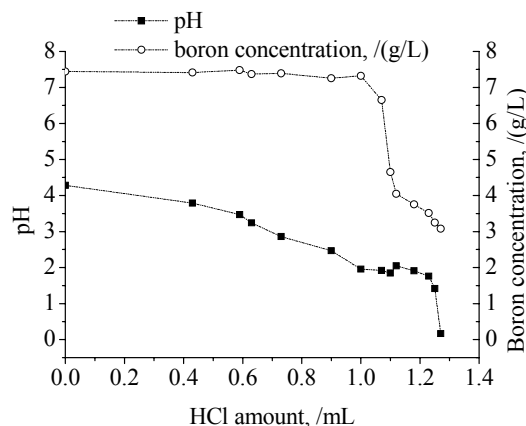


Fig. 1. Relationship between adding HCl in boron-rich brine and pH/boron content.

Table 1 Main components of studied brine

Composition	B ₂ O ₃	Li ⁺	K ⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻
Conc./ (g/L)	22.00	5.92	1.15	114.03	325.96	39.13

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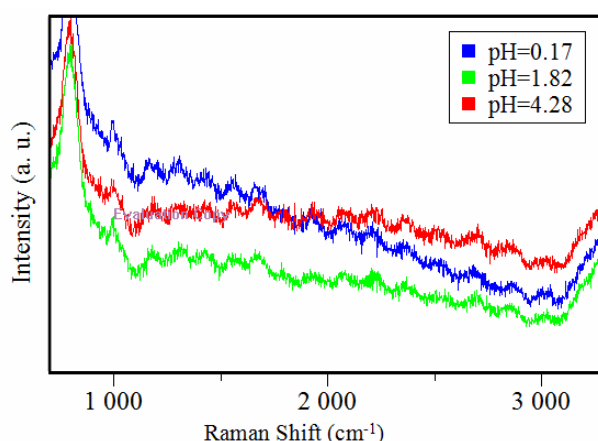


Fig. 2. Raman spectrograms of boron-rich brine at different pH.

MgCl₂-H₂O during acidification and found that higher concentration of cation is beneficial not only to the dissolution of boric acid but also to the polymerization of polyborate anions. Meanwhile, the existing forms and interaction among them depend on the concentration of boron and the pH value in solution. High boron concentration and low pH value of solution are helpful in the formation of polyborate anions with high polymerization degree. However, this phenomenon is not apparent for a relatively low pH as most part of boron was precipitated to form B(OH)₃. Meanwhile, it is noted that Raman spectrometry is not sensitivity for low concentration of borate solution.

According to the ICP-OES analysis, it was found that pH of brine had slightly effects on extraction rates of boron at certain pH range. However, the maximum extraction was achieved at lowermost pH (Fig. 3). It is noted that boron in brine can be transformed into B(OH)₃ to form precipitation when it is acidified to a low pH. However, no obvious B(OH)₃ peak was presented in Raman spectrograms of acidified brine with lower pH. It is probable that Raman spectroscopy is only suitable for high concentration of borate solution, and boron content in water phase after extraction is negligible for Raman analysis, even though B(OH)₃ has strong Raman

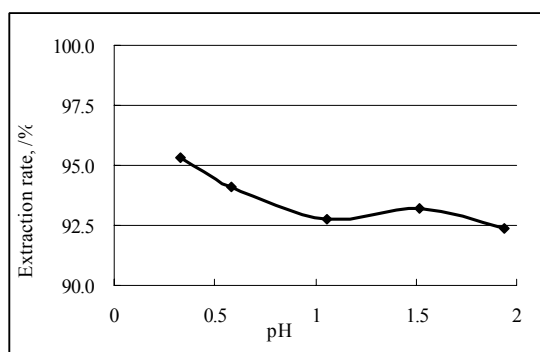


Fig. 3. Extraction rate of boron at different pH

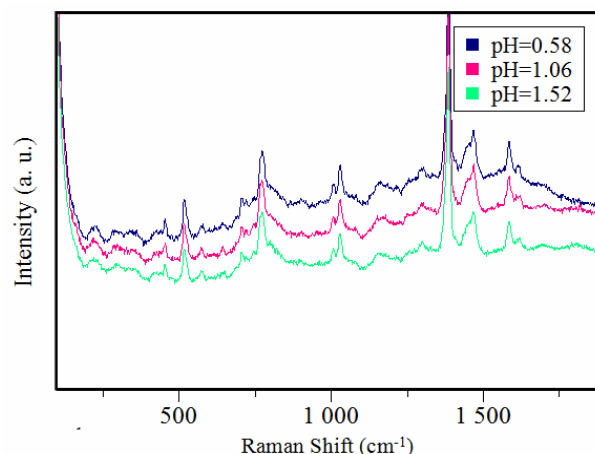


Fig. 4. Raman spectrograms of organic phase after extraction brine at different pH.

scattering. However, as boron was enriched and concentrated into organic phase during extraction, thus obvious [B₅O₆(OH)₄]⁻ peak was presented in Raman spectrograms of organic phase at tested conditions as shown in Figure 4 (in red rectangle).

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