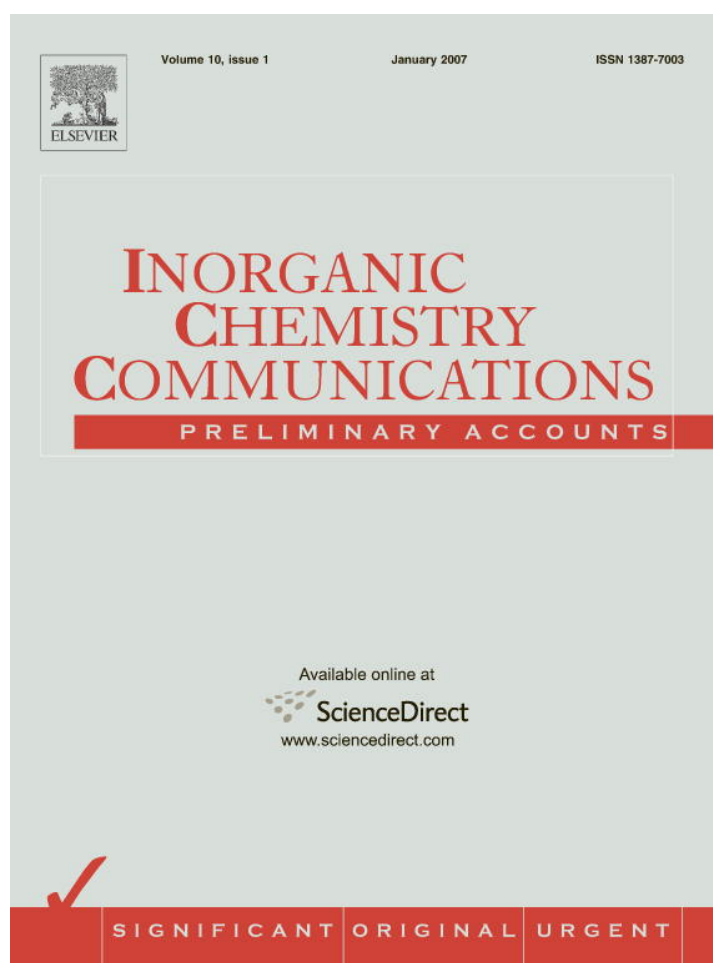


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Preparation of highly concentrated aqueous solution of sodium borate

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Abstract

A highly concentrated aqueous solution of sodium borate with 5.24 mol/kg of boron was prepared at 20 °C by adjusting the Na/B ratio at 0.22 (pH 6.9). This is more than twice more concentrated than the most soluble known borate solution ($\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$, 2.49 mol/kg at 20 °C). Analysis using the Raman spectroscopy and the APCI/MS (atmospheric pressure chemical ionization/mass spectrometry) suggested the formation of polyborate ions such as $\text{B}_9\text{O}_{10}(\text{OH})_9^{2-}$, $\text{B}_{10}\text{O}_{12}(\text{OH})_8^{2-}$, $\text{B}_{11}\text{O}_{14}(\text{OH})_7^{2-}$, $\text{B}_{12}\text{O}_{16}(\text{OH})_6^{2-}$.

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Borax ($\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$) shows fireproofing effect for cellulose-based materials such as wood, paper, cotton, and Gay-Lussac first investigated scientifically the fireproofing properties of borax and boric acid (H_3BO_3) in 1823 [1]. The solubilities of boric acid and borax in water are not sufficiently high at room temperature (4.90 for boric acid, and 5.14 for borax at 20 °C), and thus there are technical difficulties in impregnating sufficient amount of the active constituent into wood. Since their solubilities in hot water are rather high (23.6 for boric acid, 79.60 for borax at 80 °C), some researchers have proposed an impregnation treatment at high temperature (80 °C). However, this causes the precipitation of crystals on surfaces of wood and results in the deterioration of wood. In order to establish effective fireproofing of wood, a highly concentrated aqueous solution of borate at room temperature is desirable. It is known that the sodium borate of the composition $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ [2] showed the highest solubility, 41.9 in water at 20 °C, corresponding to 2.49 mol/kg of boron. In the present study, we have successfully pre-

pared a highly concentrated aqueous solution of sodium borate with 5.24 mol/kg of boron at 20 °C.

When we prepare a saturated solution at high temperature by dissolving boric acid or borax into hot water and then cool it to a room temperature, the solution recrystallizes and becomes a saturated solution at room temperature. However, when the mixture of boric acid and borax was dissolved at a certain ratio in hot water, we found that the solution did not show recrystallization after cooling to room temperature. This was not oversaturation because the solutions remained transparent without any precipitation. The Na/B ratio at which the solutions more concentrated than the known borate were formed was in the range of 0.19–0.40. The most concentrated sodium borate solutions were formed in the range 0.22–0.27 (pH 6.9–6.5). For example, the solution prepared by dissolving 20 g of boric acid and 25 g of borax into 100 g of hot water over 80 °C did not recrystallize at 20 °C. This corresponds to the Na/B ratio 0.22 and 5.24 mol/kg of boron. Similarly, the solution prepared by dissolving 25 g of boric acid and 35 g of borax into 100 g of hot water did not recrystallize at 20 °C. This corresponds to the Na/B ratio 0.27 and 6.62 mol/kg of boron. The properties of the former solution (Na/B 0.22, 5.24 mol/kg) at 20 °C are surface tension,

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67.5 mN/m; viscosity, 4.5 mPa s; density, 1.13 g/cm³; and pH, 6.86. These solutions were transparent and showed the Tyndall phenomenon when irradiated by laser light. This indicates that the solute forms colloidal dispersion consisting of polyborate ions.

Evaporation of the solution (5.24 mol/kg) by heating yielded the residue which appeared to be solid foam with the density 0.1–0.3 g/cm³. The XRD pattern of the residue showed that it is an amorphous phase of sodium borate (Fig. 1). When the solution was dried extremely slowly in the air at room temperature, Na₂B₁₈O₂₈ precipitated in a small quantity. The resultant amorphous sodium borate was easily soluble in water at room temperature, and its concentration reached that of the original solution before evaporation. It should be noted that the mixture of boric acid and borax does not dissolve into water at room temperature to the level of the highly concentrated solution. This is considered to be due to the problem of kinetics.

The Raman spectrum for the present highly concentrated borate solution is shown in Fig. 2 along with those of the saturated borax solution (Na₂[B₄O₅(OH)₄]·8H₂O, 4.9 wt%), and the saturated boric acid solution (H₃BO₃, 4.7 wt%). The present borate solution showed a broad peak centered around 910 cm⁻¹, whereas the borax and boric acid solutions showed broad peaks around 1350 cm⁻¹ and 1450 cm⁻¹, respectively. The mixed solution of borax and boric acid showed a broad peak around 1400 cm⁻¹,

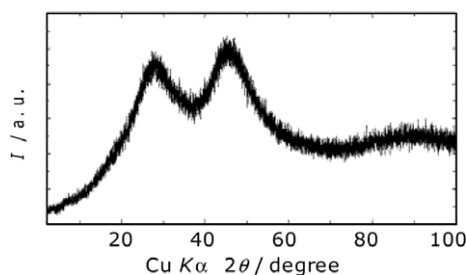


Fig. 1. Powder XRD pattern of the residue obtained by heating the polyborate solution (5.24 kg/mol of boron).

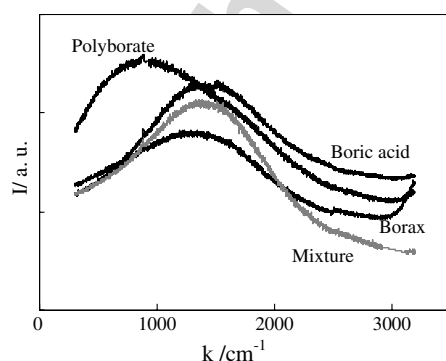


Fig. 2. Raman spectra of the highly concentrated polyborate solution (5.24 kg/mol of boron), the saturated borax solution (Na₂[B₄O₅(OH)₄]·8H₂O, 4.7 wt%), the saturated boric acid solution (H₃BO₃, 4.7 wt%), and the mixture of the saturated boric acid and borax solutions.

in the middle of those of borax and boric acid solutions. This suggests that mixing of the boric acid solution and the borax solution at room temperature does not accompany the reaction of borate anions. On the other hand, the present borate solution prepared by dissolving 20 g of boric acid and 25 g of borax in 100 g of water at 80 °C showed the peak at a much smaller wavenumber than the other three. It has been reported that the peaks of Raman spectrum for vibration of the metaborate ring (B₃O₆³⁻) are in the range 382–778 cm⁻¹ [3]. The peaks for B–O–H bending appears at 1077 cm⁻¹ and 1163 cm⁻¹ [4], and those for B–O stretching at 878 cm⁻¹ and 1365 cm⁻¹ [5]. The reduction of the wavenumber observed for the present borate solution indicates that B–O–H was transformed into the metaborate ring (B₃O₆). Polyborate ions are considered to be formed by condensation of the conventional borate ions such as B(OH)₄⁻, B₃O₃(OH)₄²⁻, B₄O₅(OH)₄²⁻ derived from boric acid and borax.

The APCI/MS (atmospheric pressure chemical ionization/mass spectrometry) [6] spectrum of the present borate solution is shown in Fig. 3. Polyborate ions such as B₇O₈(OH)₇²⁻, B₈O₁₀(OH)₆²⁻, B₈O₈(OH)₁₀²⁻, B₉O₁₀(OH)₉²⁻, B₁₀O₁₂(OH)₈²⁻, B₁₁O₁₄(OH)₇²⁻, B₁₂O₁₆(OH)₆²⁻, B₁₃O₁₈(OH)₅²⁻, B₁₄O₂₀(OH)₄²⁻, B₁₅O₂₂(OH)₃²⁻ were observed along with the conventional ions such as B₄O₅(OH)₃⁻, B₃O₃(OH)₄⁻. This regularity leads to B₁₈O₂₈²⁻ and B₂₀O₃₂⁴⁻, though they have not been clearly observed. It is interesting to note that B₁₈O₂₈²⁻ and B₂₀O₃₂⁴⁻ are considered to form spherical shapes, because they do not have terminal oxygen. B₂₀O₃₂⁴⁻ may form the spherical structure similar to the pentakis dodecahedron having 60 isosceles triangles and 32 vertices. One possible structure for B₁₀O₁₂(OH)₈²⁻

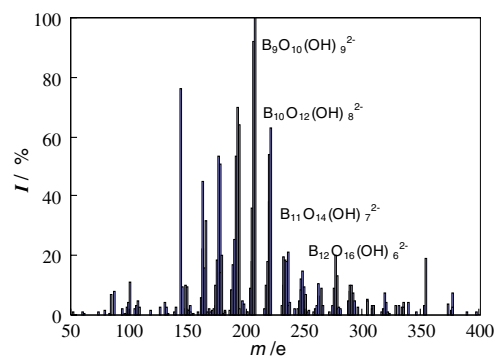


Fig. 3. APCI/MS spectrum of the highly concentrated polyborate solution (5.24 kg/mol of boron).

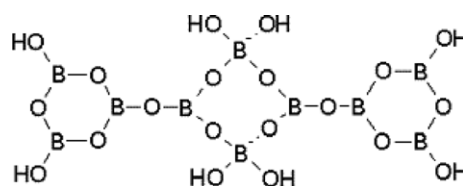


Fig. 4. One possible structure for B₁₀O₁₂(OH)₈²⁻.

is shown in Fig. 4. The Raman and APCI/MS spectra indicate that the drastic increase in the borate concentration is due to formation of the polyborate ions containing more boron atoms.

These concentrated sodium borate solutions are useful as fireproofing agents because of a remarkable fireproofing effect for cellulose-based materials such as wood, paper, cotton, rayon. It is also expected that it will be widely used for new fire retardant for polymers because it contains no hazardous heavy metals.

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