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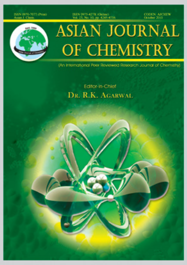

Polyborates in Aqueous Sodium Borate Solution at 298.15 K

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pH of aqueous sodium metaborate and pentaborate solutions were precisely measured as functions of concentration from dilute to super-saturation at 298.15 K. Coupling with Raman spectra of some super-saturation samples, a clear picture of the main polyborates and their equilibria was presented. At least five polyborates $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$ exist in aqueous sodium borate solutions. In supersaturated aqueous sodium pentaborate solutions $B_5O_6(OH)_4^-$, $B_3O_3(OH)_4^-$ and $B(OH)_3$ are the main polyborates, $B(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ present in a minor concentration. While, in aqueous sodium metaborate solutions, covering all the concentration range, $B(OH)_4^-$ is the most important species other polyborate anions are less than 5 %. Relevant interactions mechanisms among polyborates were also suggested.

Key Words: Polyborstes, FT-Raman spectra, Aqueous sodium borate solutions, pH, Distribution.

INTRODUCTION

Borate is of considerable practical importance as it is high effective boron fertilizer[1], high quality flame retardant[2], fine performance polycondensation catalyst carrier[3,4] and effective antibiotics for *Streptococcus pneumonia*, *Neisseria gonorrheal*, *Mycobacterium tuberculosis*, *etc*.[5]. Aqueous borate solutions are extremely important for borate crystal preparation and industrial production. Although, many researchers have been performed in this area, but which polyborates exist in aqueous borate solutions and their equilibrium relationships are still controversial because they are affected by temperature, pH, total boron concentration and external cations[6,7]. In order to get a clear picture of the polyborates and their relevant equilibria in aqueous sodium borate solution, pH of aqueous NaB_5O_8 and $NaBO_2$ solutions were precisely measured as functions of concentration from dilute to super-saturation at 298.15 K. FT-Raman spectra of some super-saturation samples recorded. Main polyborates distribution and possible equilibrium were listed out by elaborate deduction.

EXPERIMENTAL

Boric acid, sodium metaborate and borax (Sinopharm chemical reagent Co. Ltd. AR) were recrystallized twice from double-distilled water ($\kappa = 1.056\ \mu S\ cm^{-1}$), sodium pentaborate was synthesized according to the ternary phase diagram of Na_2O-B_2O_3-H_2O[8]. The entire sample solutions were prepared by mass using double-distilled water and the overall relative uncertainty in the solution preparation was 0.3 %. Sample solutions were carefully protected from atmospheric CO_2 and could be used for *ca.* 1 week without concentration changes.

Acidity, pH, of all the solutions was measured using an Orion 310P-01 pH meter (Thermo, USA) with a reproducibility of (0.5 %). The pH meter was calibrated using three pH standard solutions (Phthalate, 4.01; phosphate, 6.86; borate, 9.18) before measurements, a standard solution was measured after per five measurements, if the deviation $\geqq$ 0.5 % the pH meter recalibrated. In all the measurements a thermostat (GDH-1015W, Sayfo analytical instrument factory, Jintan Jiangsu, China) was used to maintain the temperature at 298.15 ± 0.01 K. FT-Raman spectra of some selected solutions (Table-1) were recorded at room temperature from ALMEGA dispersive Raman spectrometer (Thermo Nicolet, USA).

RESULTS AND DISCUSSION

Acidity: Measured pH of aqueous NaB_5O_8 and $NaBO_2$ solutions are collected in Table-1 as functions of concentration at 298.15 K. pH of aqueous NaB_5O_8 solutions were increase with concentration increasing Fig. 2(left). But at different concentration range different increase rate can finding. In low concentration ($m < 0.02\ mol\ kg^{-1}$), pH rapidly increase with concentration increase. This is because of extremely dilute solution of polyborates do not exist to any significant extent

TABLE-1
pH OF AQUEOUS NaB_5O_8 AND $NaBO_2$ SOLUTIONS AS FUNCTIONS OF CONCENTRATION AT 298.15 K

Sodium pentaborate solutions				Sodium metaborate solutions			
m/mol kg^{-1}	pH	m/mol kg^{-1}	pH	m/mol kg^{-1}	pH	m/mol kg^{-1}	pH
0.00100	8.209	0.0898	8.061	5.06E-04	9.620	2.1914	12.107
0.00200	8.414	0.1000	8.014	0.00100	9.733	2.5826	12.231
0.00400	8.490	0.1997	7.650	0.00400	10.123	3.0032	12.323
0.00600	8.519	0.2959	7.381	0.006300	10.283	3.3848	12.412
0.00800	8.506	0.3995	7.157	0.01010	10.349	3.7470*	12.489
0.01000	8.487	0.4956	7.001	0.07240	10.852	4.1939*	12.589
0.01990	8.461	0.5985	6.815	0.1705	11.084	4.5840*	12.678
0.03000	8.385	0.7000	6.677	0.3946	11.352	4.9832*	12.783
0.03990	8.315	0.7931*	6.485	0.5971	11.507	–	–
0.04990	8.247	0.9253	6.395	0.7926	11.621	–	–
0.06000	8.227	1.1103	6.125	1.0136	11.734	–	–
0.06990	8.165	1.3879*	5.695	1.3839	11.916	–	–
0.07990	8.114	–	–	1.7973	11.982	–	–

*Samples for Raman.

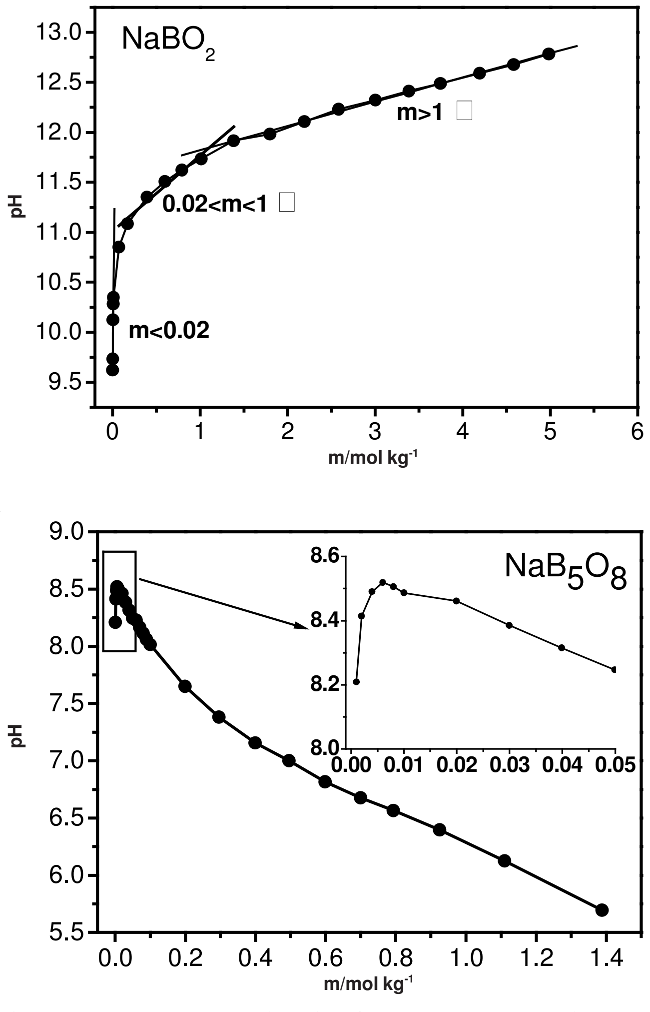


Fig. 1. pH *versus* concentration plots for aqueous NaB_5O_8 and $NaBO_2$ solutions at 298.15 K

polymerization, the dominant species are $B(OH)_4^-$ and $B(OH)_3$; in moderately concentration (0.02 < m < 1 mol kg^{-1}) the dissolution and polymerization make pH changes complicated with concentration increasing; in high concentration (m > 1 mol kg^{-1}), a good linear relationship between pH and concentration in range of m > 1 mol kg^{-1} which may because of the low acidity which makes $B(OH)_4^-$ the upmost polyborate[9,10].

Fig. 2(right) shows the pH of aqueous $NaBO_2$ solutions variation tendency *vs.* concentration. Covering all the concentration range, the pH of aqueous sodium pentaborate solutions were firstly increase and then decreases. This may attribute to the extremely complex dissolution, polymerization and depolymerization equilibria. At extremely dilution concentration region the dissolution and depolymerization of sodium pentaborate makes acid decrease, while acid increased at higher concentration because of H^+ released during polymerization. From the inset picture of Fig. 2(a), it is inferred that the critical total boron concentration for polymerization (CB), at 298.15 K it must be 0.025 mol kg^{-1}, supporting Ingri's conclusion[11]. From moderately to maximum concentration, polymerization becomes the most important effect factors, so the pH keep reducing.

FT-Raman spectra: FT-Raman spectra is an effective method for polyborates study. To get a clear picture of the main polyborates and their equilibria, FT-Raman spectra of the labeled solutions and crystal sodium pentaborate were recorded and displayed in Fig. 2.

Range of 4000-100 cm^{-1} is the most favourable zone for the investigation of borate solution, which might be considered as the characteristic absorption bands of polyborates[12-16]. The Raman shift close to 613, 565 and 530 cm^{-1} are the pulse vibration of triborate [$B_3O_3(OH)_4^-$], tetraborate [$B_4O_5(OH)_4^{2-}$] and pentaborate [$B_5O_6(OH)_4^-$], respectively. The band near 741 cm^{-1} in Raman spectra is the characteristic peak of the monborate [$B(OH)_4^-$] and the intensive Raman spectra peak at 875 cm^{-1} is assigned to boric acid ($B(OH)_3$).

Distribution and interactions mechanisms: From these data, it can be concluded that at least five polyborate $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$ exist in aqueous sodium solutions. In addition, four main equilibriums can be deduced:

$$B_5O_6(OH)_4^- + H_2O \rightleftharpoons B_3O_3(OH)_4^- + B_2O(OH)_4 \quad (A)$$

$$B_2O(OH)_4 + H_2O \rightleftharpoons B(OH)_3 \quad (B)$$

$$B_3O_3(OH)_4^- + OH^- + B(OH)_3 \rightleftharpoons B_4O_5(OH)_4^{2-} + 2H_2O \quad (C)$$

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^- \quad (D)$$

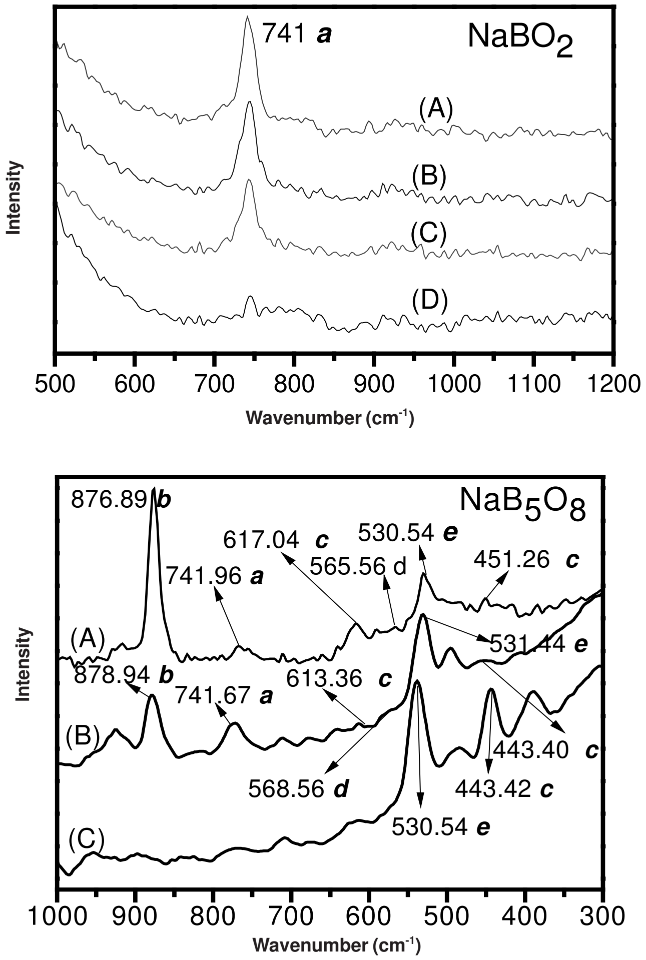


Fig. 2. Raman spectra of $NaBO_2$ (A), 4.98 mol kg^{-1}; (B), 4.58 mol kg^{-1}; (C), 4.19 mol kg^{-1}; (D), 3.75mol kg^{-1}; and NaB_5O_8 (A), 1.39 mol L^{-1}; (B), 0.79 mol L^{-1}; (C), microcrystals; Where a, b, c, d and e are $B(OH)_4^-$, $B(OH)_3$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$, respectively

As Fig. 3 shown, when NaB_5O_8 dissolves in water, the main speciation is pentaborate. Pentaborate may depolymerize into triborate and diborate with cleavage of two bridging oxygen bonds when it's attacked by two water molecules, this process slow and with a large equilibrium constant (A). Diborate can successively depolymerized into two boric acid molecules though attacking of bridging oxygen by another water molecule, this process may be so fast that only a few researchers detected it in solution[17] (B). In alkaline moderately concentration solution, a triborate can couples a boric acid, a hydroxide ion and finally come into tetraborate, so the tetraborate is the main polyborate under this condition (C). In aqueous $NaBO_2$ solution, the concentration of OH^- is high, OH^- attack the boron oxygen triangle makes all the polyborates can't formed, so only the characteristic peak of the monoborate $B(OH)_4^-$ found in their Raman spectra (Fig. 2left).

Polyborates distribution in aqueous NaB_5O_8 and $NaBO_2$ solutions as function of concentration at 298.15 K, calculated using measured pH value and equilibrium constant[18-20] (Fig. 4). As (Fig. 4 right) shows, in high concentration aqueous metaborate solutions the main speciation is $B_5O_6(OH)_4^-$, concentration decreaseing makes the main speciation change to $B_3O_3(OH)_4^-$ and $B(OH)_3$; with concentration continue decrease, in alkaline moderately concentration solution the main polyborate become $B_4O_5(OH)_4^{2-}$; in extremely dilute aqueous sodium pentaborate solution, $B(OH)_3$ and $B(OH)_4^-$ are the dominant speciation. In sodium metaborate solution, the upmost borate anions is $B(OH)_4^-$, other polyborates are less than 5 %, which are well consistent with our suggested interactions mechanism between polyborates in aqueous sodium borate solutions (Fig. 4 left).

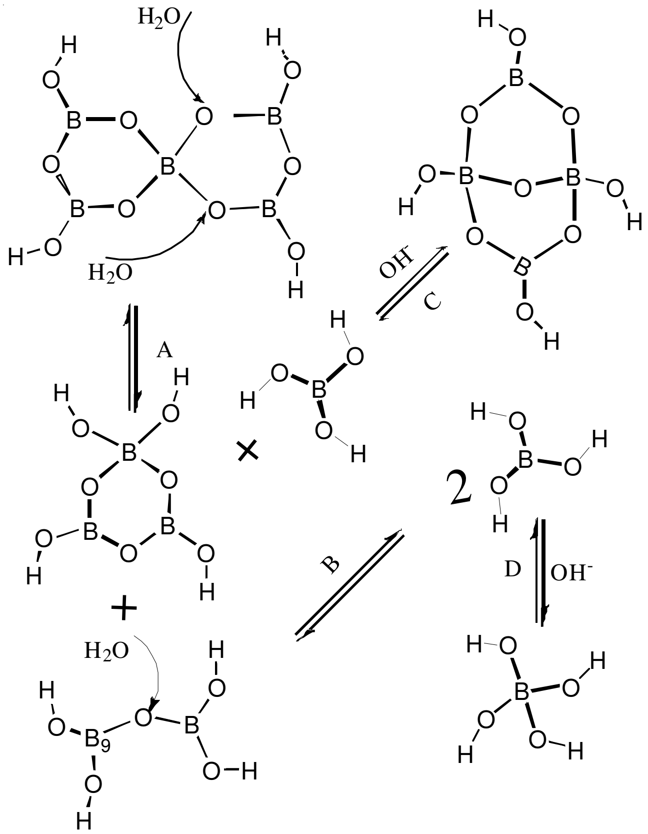
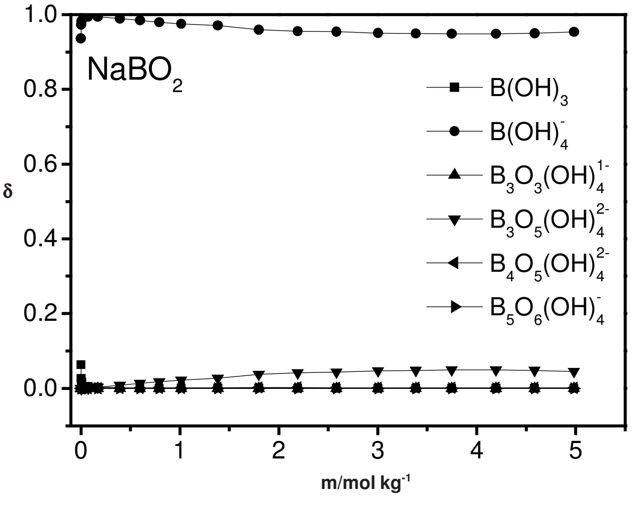


Fig. 3. Interactions between polyborates in aqueous sodium borate solution

Borate usually has extraordinary supersaturation[21], the complex polymerization, depolymerization and association, especially, the interaction between water and ions in aqueous solution needs a long time to reach phase equilibrium. A further study on the structure of aqueous borate solution, especially focus on hydration of polyborate by X-ray.



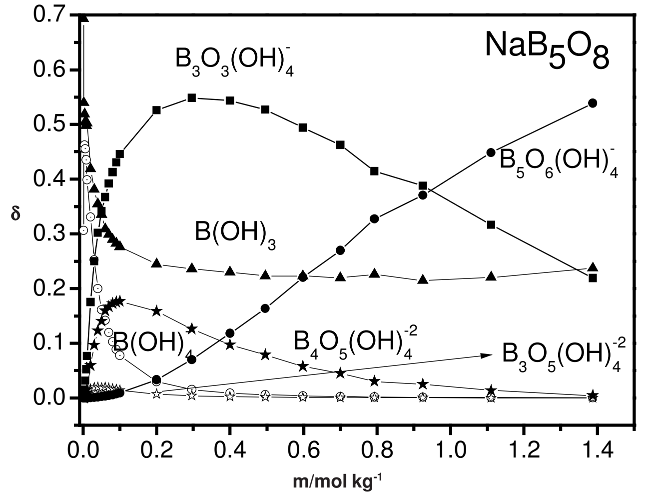


Fig. 4. Speciation of polyborate in aqueous $NaBO_2$ and NaB_5O_8 solutions as a function of concentration at 298.15 K

Conclusion

The pH of aqueous sodium pentaborate and metaborate solutions were precisely measured as functions of concentration from dilute to super-saturation at 298.15 K. Coupling with Raman spectra of some super-saturation samples, main polyborates and possible equilibria were listed by elaborate deduction. At least five polyborates $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$ exist in aqueous sodium borate solutions. While, in aqueous sodium metaborate solutions, $B(OH)_4^-$ is the most important species other polyborate anions are less than 5 %. Relevant interactions mechanisms among polyborates were also suggested which are well consistent with the polyborates distributions in aqueous sodium borate solution.

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REFERENCES

1. A.J. Parr and B.C. Loughman, in eds.: D.A. Robb and W.S. Pierooint Boron and Membrne Function in Plants. In: Metals and Micronutrients: Uptake and Utilization by Plants, Academic Press, New York, pp. 87-107 (1983)
2. K.S. Nami and N.Y. Ayrilmis, *Imamura. Building Environ.*, **42**, 1207 (2007).
3. Teijin Ltd., JPN Patent, JP73039236-B (1973).
4. D.M. Schubert and C.B. Knobler, *Phys. Chem. Glasses-Eur. J. Glass Sci. Technol. B*, **50**, 71 (2009).
5. J.P. Galvan Perez and J.P.G. Perez, International Patent, In200700459-P3 Inmn00459 (2007).
6. J.B. Farmer, *Adv. Inorg. Chem.*, **25**, 187 (1982).
7. S.Y. Gao, P.S. Song, S.P. Xia and M.P. Zheng, Salt Lake Chemistry-New Type Borate Salt Lake, Beijing: Science Press, pp. 179-200 (2007).
8. N.P. Nies and R.W. Hulbert, *J. Chem. Eng. Data*, **12**, 303 (1967).
9. T. Hirao, M. Kotaka and H. Kakihana, *J. Inorg. Nucl. Chem.*, **41**, 1217 (1979).
10. N. Ingri, *Acta Chem. Scand.*, **11**, 1034 (1957).
11. N. Ingri, *Acta Chem. Scand.*, **16**, 439 (1962).
12. G. Heller, R. Janda and J. Mathieu, *Inorg. Chim. Acta*, **40**, X107 (1980).
13. R. Janda and G. Heller, *Spectrochim. Acta A*, **36**, 997 (1980).
14. Y.Z. Jia, S.Y. Gao, S.P. Xia, J. Li and W. Li, *Chem. J. Chin. Univ.*, **22**, 99 (2001).
15. Z.H. Liu, B. Gao, S.N. Li, M.C. Hu and S.P. Xia, *Spectrochim. Acta A*, **60**, 3125 (2004).
16. W.J. Zheng and Z.H. Liu, *Spectrosc. Spectral Anal.*, **23**, 705 (2003).
17. R.E. Mesmer, C.F. Baes and F.H. Sweeton, *Inorg. Chem.*, **11**, 537 (1972).
18. J.E. Spessard, *J. Inorg. Nucl. Chem.*, **32**, 2607 (1970).
19. O. Weres, *J. Solut. Chem.*, **24**, 409 (1995).
20. Y.Q. Zhou, Y. Fang and C.H. Fang, *J. Salt Lake Res.*, **18**, 65 (2010).
21. I. Tsuyumoto, T. Oshio and K. Katayama, *Inorg. Chem. Commun.*, **10**, 20 (2007).