Density, Electrical Conductivity, Acidity, Viscosity and Raman Spectra of Aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 Solutions at 298.15 and 323.15K

[1,2]ZHOU YONGQUAN, [1]FANG CHUNHUI*, FANG YAN AND [1,2]ZHU FAYAN
[1]*Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China.*
[2]*Graduate School of Chinese Academy of Science, Beijing 100049, China.*
fangch@isl.ac.cn*

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Summary: Density, electrical conductivity, viscosity and acidity of aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions were preciously measured as functions of concentration from dilute to super-saturation at 298.15 and 323.15 K. The results are in reasonable agreement with literature data where comparisons are possible. Semi-empirical equations for those properties *vs* concentration were also suggested. Coupling with Raman spectra of some concentrated samples, main species and possible equilibria were listed by elaborate deduction. In aqueous sodium borate solutions, at least five polyborate species *i.e.* $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$ exist, and their distribution and relevant mechanism were also suggested.

Introduction

Solubility isotherms of the ternary system Na_2O-B_2O_3-H_2O was determined in the 1960s [1], which indicated many hydrates of sodium metaborate ($NaBO_2{\cdot}4H_2O$, $NaBO_2{\cdot}2H_2O$ and $NaBO_2{\cdot}0.5H_2O$), sodium tetraborate ($Na_2B_4O_7{\cdot}10H_2O$ and $Na_2B_4O_6(OH)_4{\cdot}3H_2O$) and sodium pentaborate ($NaB_5O_8{\cdot}5H_2O$ and NaB_5O_8) exist at 273.15~373.15 K.

Aqueous $NaBO_2$ solution as an important potential raw material was electro-reduced to $NaBH_4$ for H_2 generation and storage in automotive fuel cell applications [2, 3]. The densities of $NaBO_2$ solution were measured at moderate temperatures by Ward *et al.*[4], Corti *et al.*[5] and Ganopolsky *et al.* [6]. The conductivity and viscosity have been studied by Corti *et al.* [5, 7]. Cloutier *et al.* [8] reported the pH, density, conductivity, and viscosity of saturated $NaBO_2$ in alkaline aqueous solutions. But all those studies were under the concentration of 1.0 $mol{\cdot}L^{-1}$ or a single saturated point. Borax ($Na_2B_4O_7{\cdot}10H_2O$) is the commonest sodium borate and an important pH standard substance. Experimental value on the densities of aqueous $Na_2B_4O_7$ solutions is scarce. A few data appear in the International Critical Table. Novotny *et al.* [9] developed a correlation to estimate densities of binary aqueous solutions for a number of inorganic substances including $Na_2B_4O_7$. The density and refractive index for $Na_2B_4O_7$ solutions have also been studied by Galleguillos *et al.* [10]. Unfortunately, only a few sporadic experiment dada of pH value and conductivity can be found in the literature. For example, Samuel *et al.* [11] list the pH of aqueous $NaBO_2$ and NaB_4O_7 solutions at 303.15 K. NaB_5O_8 is used for high quality flame retardant, fine performance polycondensation catalyst carrier and high effective boron fertilizer. The aqueous NaB_5O_8 solution is an effective antibiotic for streptococcus pneumonia, neisseria gonorrheal, and mycobacterium tuberculosis *etc* [12]. To the best of our knowledge, none precise measurements of those properties for any aqueous NaB_5O_8 solution in concentrated range are available.

Basic physicochemical properties such as density, electrical conductivity, pH, and viscosity are extremely important in industrial applications. In the present paper, all the properties of aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions mentioned above were preciously measured from dilute to super-saturation at 298.15 and 323.15 K. Coupling with Raman spectra of some concentrated samples, main species and their possible equilibria in aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions were given by elaborate deduction.

Results and Discussion

Measured density, conductivity, pH and viscosity of aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions as functions of concentration at 298.15 and 323.15 K were collected in Table-1.

Density

Fig. 1 displays the experiment and empirical fitting density of aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions *vs* concentration at 298.15 and 323.15 K. An equation suggested by Connaughton [13] which has been used in many brine salts, is useful for density fitting over wide concentration ranges [14].

*To whom all correspondence should be addressed.

Table-1: Density, Conductivity, pH and Viscosity of aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions at as function of concentration at 298.15 and 323.15K.

molality	ρ /g.cm^{-3}		pH		η/mPa.s		κ/ms.cm^{-1}	
mol/kg^{-}	298.15K	323.15K	298.15K	232.15K	298.15K	323.15K	298.15K	323.15K
				$NaBO_2$				
9.99E-04	0.99773	0.99058	9.733	9.425	0.8980	0.5859	0.0956	0.1651
0.004	0.99812	0.98905	10.123	9.792	0.8989	0.5867	0.3753	0.5852
0.00632	0.99789	0.98857	10.283	9.914	0.8996	0.5873	0.5844	0.891
0.01006	0.99775	0.9889	10.349	9.926	0.9008	0.5882	0.8992	1.358
0.07235	1.00314	0.99318	10.852	10.362	0.9203	0.6043	5.377	7.713
0.17049	1.01038	1.00042	11.084	10.576	0.9523	0.6306	10.34	16.14
0.39457	1.02776	1.01724	11.352	10.771	1.0314	0.6948	19.16	31.57
0.59706	1.04089	1.02973	11.507	10.903	1.1106	0.7585	26	42.61
0.79259	1.05147	1.04288	11.621	11.008	1.1950	0.8254	31.58	51.7
1.01359	1.06894	1.05656	11.734	11.070	1.3010	0.9081	36.52	60.45
1.38391	1.09519	1.08201	11.916	11.299	1.5075	1.0656	43.35	73.01
1.79733	1.11939	1.11129	11.982	11.348	1.7904	1.2734	47.25	83.31
2.19135	1.14682	1.13245	12.107	11.395	2.1247	1.5089	49.55	90.31
2.58262	1.17070	1.15498	12.231	11.492	2.5363	1.7853	51.7	94.44
3.00318	1.19539	1.17909	12.323	11.550	3.0923	2.1385	52.31	97.54
3.38481	1.21850	1.20202	12.412	11.624	3.7277	2.5187	51.92	100.43
3.74696	1.23777	1.22073	12.489	11.721	4.4787	2.9411	50.99	99.22
4.19389	1.26624	1.24817	12.589	11.768	5.6642	3.5604	48.42	99.73
4.58402	1.28725	1.27013	12.678	11.811	7.0052	4.2056	44.57	98.52
4.98316	1.30931	1.29398	12.783	11.954	8.7696	4.9857	42.01	95.64
				$Na_2B_4O_7$				
0.01012	0.99916	0.98933	9.177	9.017	0.8998	0.5555	1.654	2.618
0.01937	1.00045	0.99161	9.166	9.010	0.9058	0.5605	2.604	4.297
0.02899	1.00239	0.99284	9.164	9.015	0.9138	0.5649	3.825	6.347
0.04009	1.00417	0.99495	9.163	9.016	0.9276	0.5706	5.142	8.332
0.04994	1.00625	0.99712	9.167	9.012	0.9293	0.5738	6.278	10.21
0.06013	1.00801	0.99905	9.173	9.008	0.9358	0.5812	7.454	11.68
0.0697	1.01041	1.00088	9.178	9.010	0.9483	0.5830	8.326	13.47
0.07979	1.01162	1.00217	9.184	9.018	0.9599	0.5871	9.390	15.15
0.08953	1.01399	1.00464	9.190	9.021	0.9623	0.5921	10.33	16.47
0.10011	1.01569	1.00696	9.199	9.034	0.9720	0.5948	11.26	17.80
0.10982	1.01794	1.00804	9.206	9.045	0.9788	0.5996	11.98	19.07
0.1199	1.01977	1.01007	9.213	9.057	0.9935	0.6084	13.21	20.49
0.12985	1.02073	1.01192	9.218	9.073	1.0101	0.6100	13.93	22.03
0.13986	1.02292	1.01339	9.229	9.082	1.0173	0.6142	14.73	23.37
0.15039	1.02467	1.0147	9.244	9.088	1.0271	0.6183	15.49	24.52
0.15776	1.02539	1.01571	9.256	9.097	1.0336	0.6248	15.85	25.11
				NaB_5O_8				
0.010000	0.99940	0.98980	8.487	8.401	0.9126	0.5593	0.6842	0.7500
0.019943	1.00042	0.99250	8.461	8.390	0.9150	0.5624	1.355	1.479
0.029978	1.00166	0.99416	8.385	8.342	0.9171	0.5652	1.961	2.166
0.039872	1.00360	0.99470	8.315	8.288	0.9254	0.5676	2.527	2.783
0.049915	1.00545	0.99800	8.247	8.252	0.9324	0.5732	3.072	3.361
0.059977	1.00574	0.99761	8.227	8.179	0.9372	0.5756	3.53	3.940
0.069882	1.00759	0.99839	8.165	8.124	0.9495	0.5776	4.053	4.403
0.079934	1.00868	1.00170	8.114	8.079	0.9516	0.5826	4.564	4.942
0.089786	1.01131	1.00199	8.061	8.037	0.9548	0.5846	5.036	5.579
0.10000	1.01180	1.00518	8.014	7.997	0.9615	0.5876	5.491	6.063
0.19967	1.02408	1.01556	7.65	7.661	1.014	0.6179	8.985	9.750
0.29593	1.03651	1.02874	7.381	7.407	1.079	0.6502	11.04	13.10
0.39945	1.04924	1.04132	7.157	7.196	1.149	0.6900	14.48	15.97
0.49564	1.06057	1.05127	7.001	7.041	1.211	0.7296	16.05	17.98
0.59847	1.07386	1.06445	6.815	6.869	1.305	0.7751	17.53	20.06
0.70000	1.08551	1.07445	6.677	6.734	1.394	0.8268	19.12	21.71
0.79308	1.10175	1.09011	6.485	6.582	/	/	19.9	23.48
0.92526	1.11897	1.10660	6.395	6.406	/	/	21.65	25.45
1.11031	1.13918	1.12882	6.125	6.162	/	/	22.74	28.31

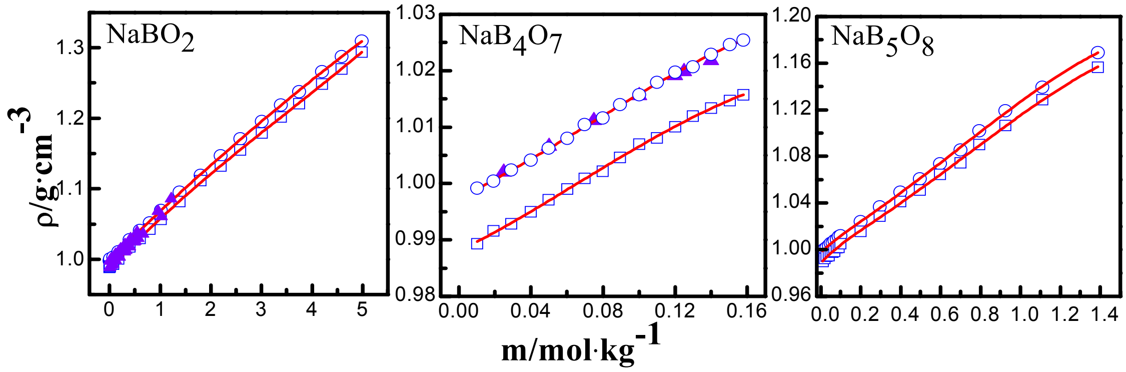


Fig. 1: Density *vs* concentration plots for aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions at 298.15 (○) and 333.15 K (ϒ) . Symbols, experimental; solid curves, calculated; ▲, $NaBO_2$ [4] and $Na_2B_4O_7$ [10].

$$(\rho-\rho_w^0)(g.cm^{-3}) = Am + B^{1.5} + C^2 + D^{2.5} \quad (1)$$

where ρ_w^0 is the density of water at corresponding temperatures, ρ_w^0 = 0.99707 and 0.98807 g·cm^{-3} at 298.15 and 323.15 K, respectively; A, B, C, and D are coefficients as functions of temperature; m is the concentration in mol.kg^{-1}. The least-squares fitted parameters of Equation (1) are summarized in Table-2. As shows in Fig. 1, our experimental data are good consistent with the literature density for $NaBO_2$ [4] and $Na_2B_4O_7$ [10].

Table-2: Values of A, B, C, D and R^2 for equation (1).

System	T/K	A	B	C	D	R^2
$NaBO_2$	298.15	0.08077	-0.01214	0.00322	-6.33E-04	0.9999
	323.15	0.06403	0.02072	-0.01976	0.00446	0.9999
$Na_2B_4O_7$	298.15	0.23989	-0.81855	3.58189	-4.78444	0.9990
	323.15	0.15548	-0.08449	1.43022	-2.74606	0.9989
NaB_5O_8	298.15	0.21801	-0.34208	0.42992	-0.17603	0.9997
	323.15	0.2548	-0.44443	0.51622	-0.19947	0.9995

Viscosity

The viscosity data of aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions from experiment and nonlinear curve fitting at two temperatures are shown in Fig. 2. A semi-empirical equation [15-17] has been shown to be useful for data fitting over wide concentration ranges.

$$\eta = a_0 \exp(b_0 m + c_0 m^2) \quad (2)$$

where a_0, b_0, and c_0 are the adjustable temperature-dependent parameters. The least-squares fitted parameters of Equation (2) are summarized in Table-3.

Table-3: Values of a_0, b_0, c_0, R^2 for equation (2).

System	T/K	a_0	b_0	c_0	R^2
$NaBO_2$	298.15	0.8977	0.3428	0.02300	1.000
	323.15	0.5857	0.4335	-7.532E-04	1.000
$Na_2B_4O_7$	298.15	0.8936	0.7447	1.2020	0.9946
	323.15	0.5520	0.8006	-0.2057	0.9956
NaB_5O_8	298.15	0.9058	0.5642	0.0725	0.9993
	323.15	0.5574	0.4946	0.09455	0.9998

Electrical Conductivity

The electrical conductivities of aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions from experiment and empirical fitting at two temperatures are plotted in Fig. 3. As Fig. 3 shows that conductivity increases as concentration and temperature rise. The conductivity data over the whole concentration range studied were fitted to the Casteel-Amis equation [17-19].

$$\kappa = k_{max}\left(\frac{m}{u}\right)^a \exp[b(m-\mu)^2 - a(m-\mu)/\mu] \quad (3)$$

where μ is the concentration corresponding to the maximum conductivity κ_{max} at a given temperature; a and b are empirical parameters; m is molality in mol·kg^{-1}. The least-squares fitted values of the parameters of Equation (3) are summarized in Table-4.

Table-4: Values of k_{max}, μ, a, b and R^2 for equation (3).

System	T/K	k_{max}	u	a	b	R^2
$NaBO_2$	298.15	52.34	2.8789	0.79455	-0.01549	0.9995
	323.15	100.1	3.7366	0.8449	-0.00179	0.9999
$Na_2B_4O_7$	298.15	19.87	0.27624	0.85608	-7.71804	0.9995
	323.15	42.38	0.4919	0.89922	-0.94246	0.9995
NaB_5O_8	298.15	22.70	1.35505	0.8112	-0.05234	0.9993
	323.15	27.42	1.3666	0.76012	-0.16746	0.9992

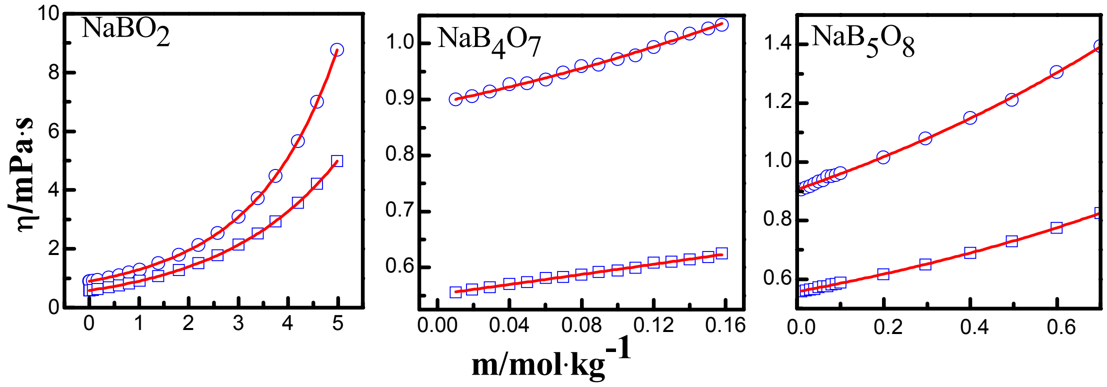


Fig. 2: Viscosity *vs* concentration plots for solutions at 298.15 K (○) and 333.15K (ϒ). Symbols, experimental; solid curves, calculated.

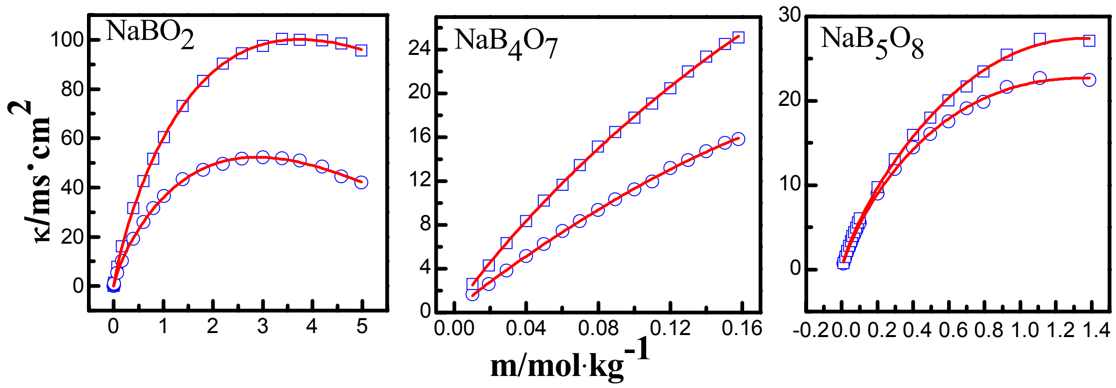


Fig. 3: Conductivity *vs* concentration plots for aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions at 298.15 K (○) and 333.15K (ϒ). Symbols, experimental; solid curves, calculated.

Raman Spectra

Boron exists as polyborate anions in aqueous solution. In order to get a clear picture of the main species and their equilibria, Raman spectra of some concentrated solutions and their corresponding microcrystal were recorded and displayed in Fig. 4.

Fig. 4: Raman spectra of $NaBO_2$ (a, 4.19 mol·L^{-1}; b, 4.58 mol·L^{-1}; c, 4.98 mol·L^{-1}; d, microcrystals), $Na_2B_4O_7$ (a, 0.100 mol·L^{-1}; b, 0.119 mol·L^{-1}; c, 0.139 mol·L^{-1}; d, 0.159 mol·L^{-1}; e, microcrystals) and NaB_5O_8 (a, 1.39 mol·L^{-1}; b, 0.79 mol·L^{-1}; c, microcrystals) at room temperature

■,H_3BO_3 ; ●, $B(OH)_4^-$;▲, $[B_3O_3(OH)_4]^-$;▼, $B_3O_3(OH)_5^{2-}$;★, $B_4O_5(OH)_4^{2-}$; ►, $B_5O_6(OH)_4^-$

Raman spectrum of the range 400~1200 cm^{-1} is the most favorable zone for the investigation of borate solution, which might be considered as the characteristic absorption bands of polyborates [20-23]. The obvious band near 740 cm^{-1} in Raman spectra of aqueous $NaBO_2$ solutions is the characteristic peak of $B(OH)_4^-$. Four obvious bands can be seen in Raman spectra of aqueous $Na_2B_4O_7$ solution, which can be assigned to the characteristic vibration of $B_4O_5(OH)_4^{2-}$ (564cm^{-1}), $B_3O_3(OH)_4^-$ (614cm^{-1}), $B(OH)_4^-$ (741cm^{-1}),and $B(OH)_3$ (873cm^{-1}), respectively.

The higher solubility and the suitable pH of aqueous NaB_5O_8 solution make it a typical sample for polyborate study. The Raman shifts close to 613 and 530 cm^{-1} are the pulse vibration of $B_3O_3(OH)_4^-$ and $B_5O_6(OH)_4^-$, respectively. The band near 740 cm^{-1} in Raman spectra is the characteristic peak of $B(OH)_4^-$, and the most intensive Raman spectra peak at 875 cm^{-1} is assigned to $B(OH)_3$.

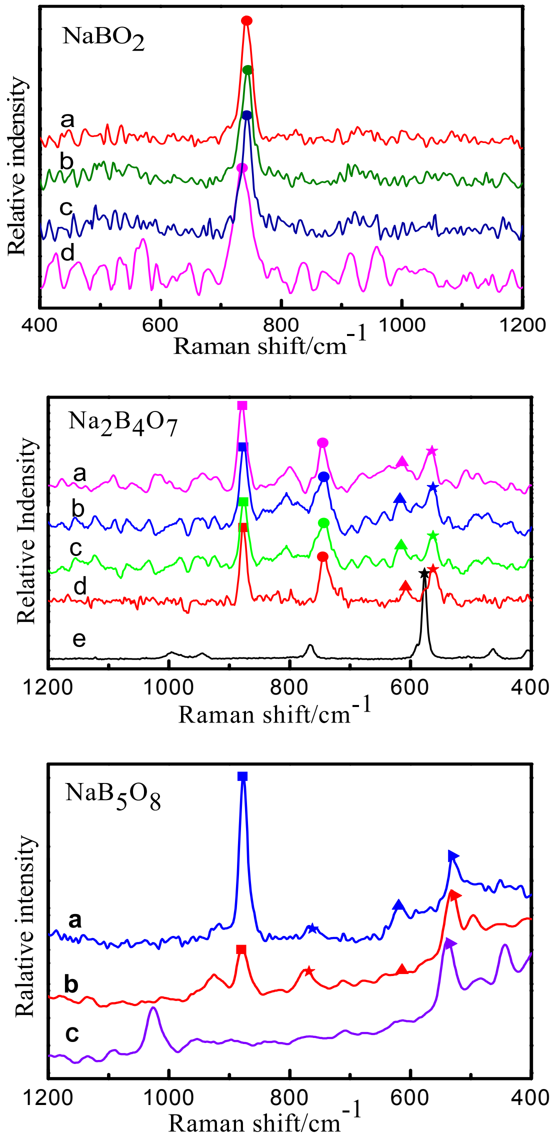


Fig. 4: Raman spectra of $NaBO_2$ (a, 4.19 mol·L^{-1}; b, 4.58 mol·L^{-1}; c, 4.98 mol·L^{-1}; d, microcrystals), $Na_2B_4O_7$ (a, 0.100 mol·L^{-1}; b, 0.119 mol·L^{-1}; c, 0.139 mol·L^{-1}; d, 0.159mol·L^{-1}; e, microcrystals) and NaB_5O_8 (a, 1.39 mol·L^{-1}; b, 0.79 mol·L^{-1}; c, microcrystals) at room temperature.

■,H_3BO_3 ; ●, $B(OH)_4^-$;▲, $[B_3O_3(OH)_4]^-$;▼, $B_3O_3(OH)_5^{2-}$;★, $B_4O_5(OH)_4^{2-}$; ►, $B_5O_6(OH)_4^-$

Acidity and Polyborate Distribution

Dozens of polyborates exist in aqueous borate solutions at ambient temperature and pressure. Their existing forms and interactions among these different polyborate anions mainly depend on the pH, temperatures, and concentration of boron in solution [24, 25], which makes borate solutions become more complicated than those of common salts. The distribution and equilibria in aqueous borate solution are not substantially understood. Acidity is the most important property of aqueous borate solution, the experimental pH of aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions are listed in Table-1. Polyborate distribution in aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions at 298.15 K was calculated using measured pH value and literature equilibrium constant [26, 27] by Newton iteration method, as shown in Fig. 5. The percentage (*w* %) is the moles of boron for individual polyborate divided by the moles of total boron.

Based on the Raman spectra and polyborate distribution of aqueous $NaBO_2$, $Na_2B_4O_7$ and NaB_5O_8 solutions, we can concluded that at least five ployborate species $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$ exist in aqueous sodium borate solution. In addition, at least five equilibra can be deduced [28]:

$$B_5O_6(OH)_4^- + 2H_2O \rightleftharpoons B_3O_3(OH)_4^- + B_2O(OH)_4 \quad (A)$$

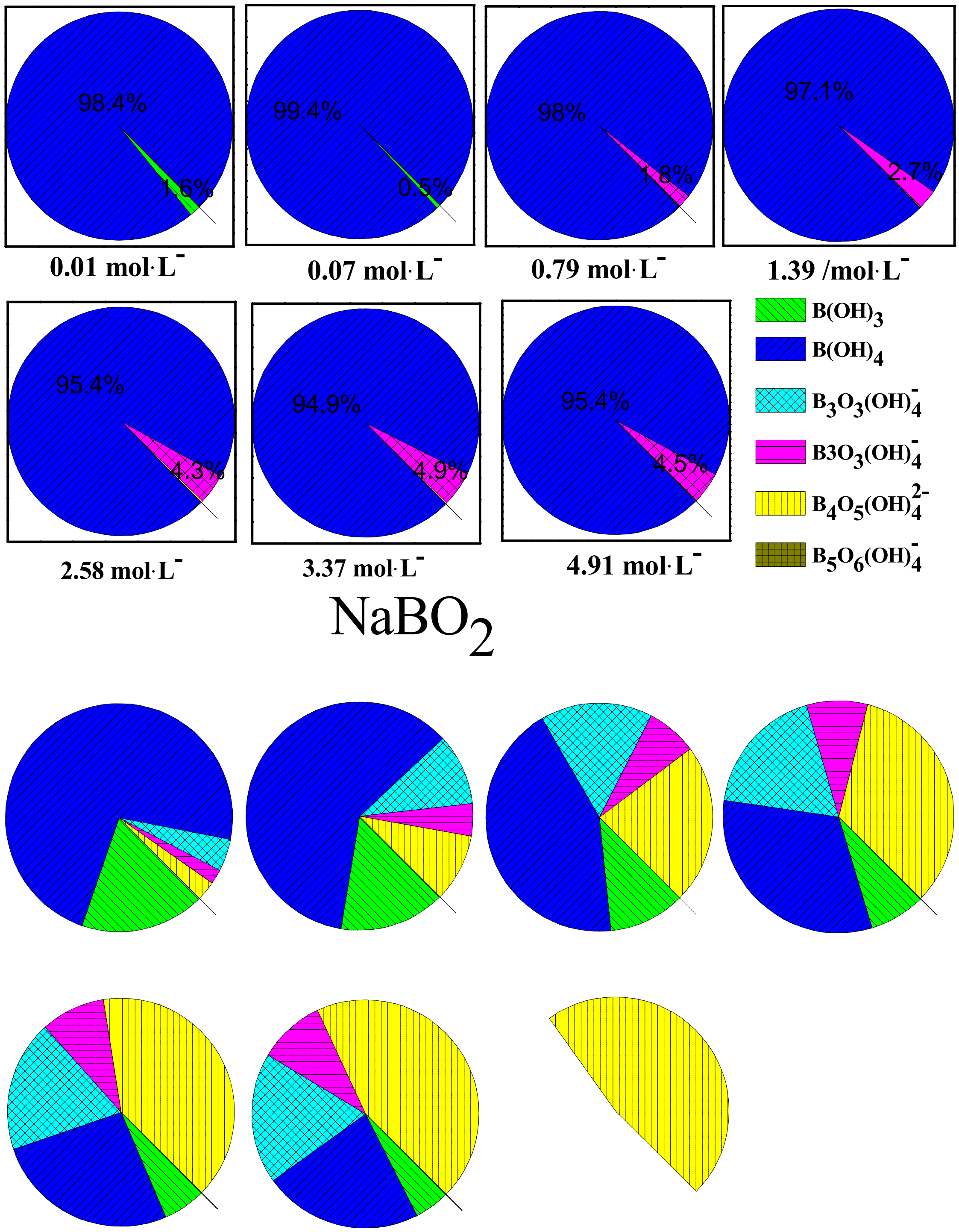
$$B_2O(OH)_4 + H_2O \rightleftharpoons 2B(OH)_3 \quad (B)$$

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

$$B_3O_3(OH)_4^- + OH^- \rightleftharpoons B_3O_3(OH)_5^{2-} \quad (D)$$

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

The possible interaction mechanisms can be described as follows: the main speciation is $B_5O_6(OH)_4^-$ in highly concentrated aqueous NaB_5O_8 solution. The $B_5O_6(OH)_4^-$ depolymerize into $B_3O_3(OH)_4^-$ and $B_2O(OH)_4$ with cleavage of two epoxy bonds when attacked by two water molecules (A); $B_2O(OH)_4$ can successively depolymerizatize into two boric acid molecules through attacking bridged oxygen by another water molecule, and this process is so fast that it was detected in solution by only a few researchers [29] (B); in moderate alkaline solution, the $B_3O_3(OH)_4^-$ couples a $B(OH)_3$ and a OH^- to form $B_4O_5(OH)_4^{2-}$, so the $B_4O_5(OH)_4^{2-}$ is the main species under this condition (C); when the alkalinity increases, the $B_3O_3(OH)_4^-$ combines with a OH^- to form the $B_3O_3(OH)_5^{2-}$(D); Because the high concentrated OH^- tends to attack the boron-oxygen planar triangle to form $B(OH)_4^-$ in the high alkalinity borate solution, all the polyborates can't form (E).


98.4%
1.6%
99.4%
0.5%
98%
1.8%
97.1%
2.7%
0.01 mol·L⁻
0.07 mol·L⁻
0.79 mol·L⁻
1.39 /mol·L⁻
95.4%
4.3%
94.9%
4.9%
95.4%
4.5%
2.58 mol·L⁻
3.37 mol·L⁻
4.91 mol·L⁻
$B(OH)_3$
$B(OH)_4$
$B_3O_3(OH)_4^-$
$B3O_3(OH)_4^-$
$B_4O_5(OH)_4^{2-}$
$B_5O_6(OH)_4^-$
$NaBO_2$