Volumetric and Transport Properties of Aqueous NaB(OH)$_4$ Solutions[*]

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Abstract   Density, pH, viscosity, conductivity and the Raman spectra of aqueous NaB(OH)$_4$ solutions precisely measured as functions of concentration at different temperatures (293.15, 298.15, 303.15, 313.15 and 323.15 K) are presented. Polyborate distributions in aqueous NaB(OH)$_4$ solution were calculated, covering all the concentration range, B(OH)$_4^-$ is the most dominant species, other polyborate anions are less than 5.0%. The volumetric and the transport properties were discussed in detail, both of these properties indicate that B(OH)$_4^-$ behaves as a structure-disordered anion.

Keywords   aqueous NaB(OH)$_4$ solution, volumetric property, transport property, polyborate distribution

1   INTRODUCTION

Hydroxy-hydrated borates constitute the bulk of the mineral and optical material kingdom. Especially the tetrahydridoborate (BH$_4^-$), as the reduction product of B(OH)$_4^-$, are versatile reducing agents in various organic and inorganic processes [1]. The percentage of hydrogen presented in NaBH$_4$ and released by hydrolysis are 10.6% and 10.8%, respectively. Therefore, NaBH$_4$ is the most attractive chemical hydride for H$_2$ generation and storage in automotive fuel cell applications [2, 3]. However, the extensive use of NaBH$_4$ fuel would require the disposal of large quantities of the product NaB(OH)$_4$. NaBH$_4$ can be regenerated from NaB(OH)$_4$ chemically [4−7]. Unfortunately, most chemical regeneration syntheses proposed so far involve several reaction steps with high cost. Furthermore, the by-products, wastes, and greenhouse gas emissions have already aroused the growing concern from the public. Luckily, the use of an electrolytic cell to reduce NaB(OH)$_4$ would not create large quantities of by-products, wastes, or emissions. There are a number of patents indicating the possibility of electroreduction of B(OH)$_4^-$ to BH$_4^-$ with 20% to 25% current efficiency and 20% to 80% yield on electrocatalytic hydrogenation cathodes [8−10]. However, reproduction of these claims was facing a number of difficulties, some researchers even got the conclusion that direct electroreduction of NaB(OH)$_4$ into NaBH$_4$ was impossible [11].

Physicochemical properties such as density, electrical conductivity, viscosity, and acidity at moderate temperatures, affect the H$_2$ generation and storage system as well as the electrochemical recyclability of sodium metaborate. The density of NaB(OH)$_4$ solutions has been measured at moderate temperatures by Ward *et al*. [12], Corti *et al*. [13] and Ganopolsky *et al* [14]. The conductivity and viscosity have been studied by Corti *et al*. [13, 15], and Cloutier *et al*. [16] reported the properties (pH, density, conductivity and viscosity) of saturated NaB(OH)$_4$ in aqueous alkaline solutions. However, all those studies were under the concentration of 1.0 mol·L^{-1} or a saturated single point. In the present paper, the density, electrical conductivity, viscosity, acidity and Raman spectra of aqueous NaB(OH)$_4$ solutions were assembled systematically. Not only the volumetric and transport properties of aqueous NaB(OH)$_4$ solution were deliberated, but also the chemical species distribution was given for the first time.

2   EXPERIMENTAL

Commercially available metaborate [NaB(OH)$_4$·2H$_2$O, Sinopharm Chemical Reagent Co., AR] was recrystallized twice from double-distilled water [17] (electrical conductivity, κ<1.0 μS·cm^{-1}). The entire sample solutions were prepared by mass using double-distilled water, and the overall relative uncertainty in the solution preparation was 0.1%. The borate solutions were carefully protected from atmospheric CO$_2$ and can be used about one week without concentration changes.

Densities, ρ, of all the solutions were determined using a DMA4500 apparatus (Anton Paar, Austria) with an uncertainty of 0.00003 g·cm^{-3} and temperature was controlled to ±0.03 K. The instrument was calibrated prior to initiation of each series of measurements, using air and double-distilled water as reference substances. Electrical conductivity, κ, was measured with an YSI 3200 conductivity meter (YSI, USA) using black-platinized electrode with a reproducibility of 0.3%. The constant of electrode was calibrated using six NaCl standard solutions (0.0001, 0.001, 0.01, 0.1, 0.5 and 1.0 mol·kg^{-1}). A standard solution was measured every five measurements, the constant recalibrated if the deviation ⩾0.3%. 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 electrode was calibrated using three pH standard solutions (4.003, 6.864 and 9.182), a standard solution was used for checkup after every five measurements, the electrode recalibrated if the deviation ≥0.5%. In all the pH and conductivity measurements, a thermostat (GDH-1015W, Sayfo Analytical Instrument Factory, Ningbo, China) was used to maintain the temperature of the solutions within ±0.01 K uncertainty. Viscosity, η, was measured with a single Ubbelohde viscometer (Jingliang Precise Instrument Co., Shanghai, China), which was placed in a well-stirred constant temperature water bath and the temperature of the solutions was kept within ±0.05K uncertainty. The flow time was measured with an accurate 0.01 s stopwatch and the double-distilled was used for calibration. Measurements were repeated at least 4 times for each solution and temperature. The uncertainty of the viscosity measurements was estimated to be 0.5%. Raman spectra of solid and liquid samples were recorded in the ranges of 300–4000 cm^{-1}, respectively, with a Nicolet Almega Dispersive Raman spectrometer (laser: 532 nm, exposure time: 8 s) at room temperature. The solid samples were put in the microscope slide (number of exposures: 1). The liquid samples were held in a quartz glass tube (number of exposures: 32).

3 RESULTS AND DISCUSSION

3.1 Chemical species in solutions

Measured pH of aqueous NaB(OH)$_4$ solutions were collected in Table 1 as functions of molality (m), at 298.15 and 323.15 K.

pH of aqueous NaB(OH)$_4$ solutions raises with concentration increasing, but at different concentration range different increasing rate can be found. In extreme low concentration ($m<0.07$ mol·kg^{-1}), pH rises sharply with concentration increase. This maybe because the polyborates do not show any significant extent of polymerization, and the dominant species are B(OH)$_4^-$ and B(OH)$_3$ in the extremely dilute solution. The dehydration and polymerization make pH changes complicated with concentration increase in moderate concentration ($0.07<m<1.46$ mol·kg^{-1}). A good linear relationship between pH and concentration can be seen in high concentration ($m>1.46$ mol·kg^{-1}), which may be due to the low acidity makes B(OH)$_4^-$ become the dominant borate.

Raman spectrum is an effective method for polyborate study [18]. In order to get a clear picture of the main polyborates and their equilibria in aqueous NaB(OH)$_4$ solutions, Raman spectra of the labeled solutions in Table 1 were recorded and displayed in Fig. 1. Range of 500–1200 cm^{-1} is the most favorable zone for the investigation of borate solution, which might be considered as the characteristic absorption bands of polyborates [19–21]. The only obvious band near 741 cm^{-1} in Raman spectra of aqueous NaB(OH)$_4$ solutions is the characteristic peak of the B(OH)$_4^-$.

Table 1 pH of aqueous NaB(OH)$_4$ solutions as functions of concentration at 298.15 and 323.15 K

| m/mol·kg^{-1}	pH	
	298.15 K	323.15 K
0.0010	9.733	9.425
0.0040	10.123	9.792
0.0063	10.283	9.914
0.0101	10.349	9.926
0.0725	10.852	10.362
0.1715	11.084	10.576
0.4003	11.352	10.771
0.6102	11.507	10.903
0.8159	11.621	11.008
1.0520	11.734	11.070
1.4565	11.916	11.249
1.9218	11.982	11.348
2.3792	12.107	11.395
2.8476	12.231	11.492
3.3676	12.323	11.55
3.8549	12.412	11.624
4.3318	12.489	11.721
*4.9404	12.589	11.768
*5.4909	12.678	11.810
*6.0737	12.783	11.904

* Samples for Raman spectra measurement
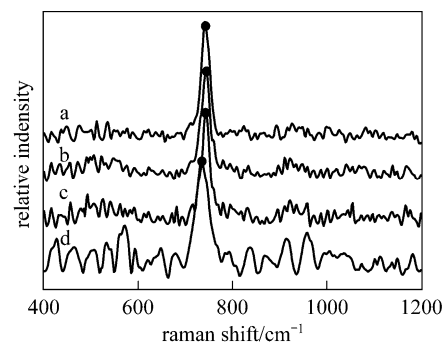
Figure 1 Raman spectra of aqueous NaB(OH)$_4$ solutions and characteristic peak of the B(OH)$_4^-$ at room temperature
a—4.94 mol·L^{-1}; b—5.49 mol·L^{-1}; c—6.07 mol·L^{-1}; d—microcrystals; ● characteristic peak

Polyborate distributions in aqueous NaB(OH)$_4$ solution at 298.15 and 323.15 K were calculated using measured pH values and the literature equilibrium constants [22–24] by Newton iteration algorithm, as Fig. 2 shown. δ is the moles of boron for individual polyborate divided by the moles of total boron. As Fig. 2 shown, the dominating borate anions is B(OH)$_4^-$, the other polyborates (H$_3$BO$_3$, B$_3$O$_3$(OH)$_4^-$, B$_3$O$_3$(OH)$_5^{2-}$, B$_4$O$_5$(OH)$_4^{2-}$ and B$_5$O$_6$(OH)$_4^-$ are less than 5% in NaB(OH)$_4$ solution.
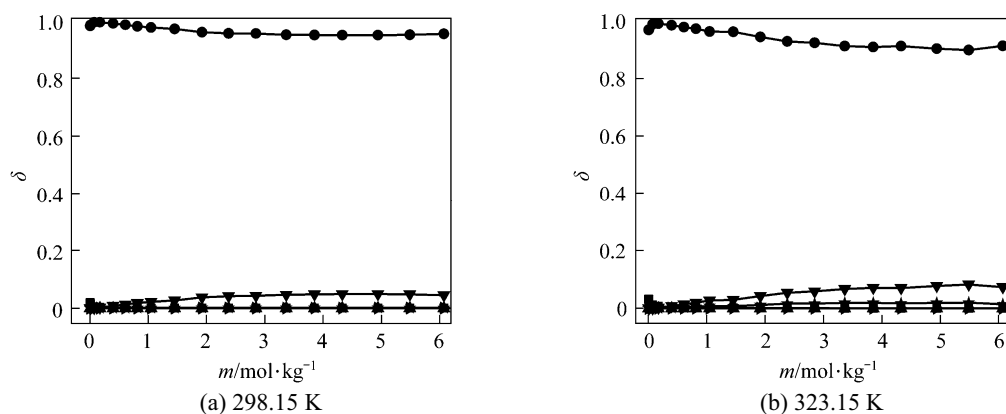
Figure 2   Variation in the distribution of boron species with concentration in aqueous NaB(OH)$_4$ solutions at 298.15 and 323.15 K
■ H$_3$BO$_3$; ● B(OH)$_4^-$; ▲ [B$_3$O$_3$(OH)$_4$]$^-$; ▼ B$_3$O$_3$(OH)$_5^{2-}$; ★ B$_4$O$_5$(OH)$_4^{2-}$; ▶ B$_5$O$_6$(OH)$_4^-$

Table 2   Density and φ_v of aqueous NaB(OH)$_4$ solutions at various temperatures

m/mol·kg^{-1}	293.15 K		298.15 K		303.15 K		313.15 K		323.15 K	
	ρ	φ_v	ρ	φ_v	ρ	φ_v	ρ	φ_v	ρ	φ_v
0.0307	1.00067	22.1884	0.99947	23.4299	0.99805	24.3370	0.99461	24.4818	0.99041	24.9200
0.0612	1.00305	22.8853	1.00183	23.8027	1.00038	24.7124	0.99688	25.6877	0.99259	27.3060
0.0921	1.00546	23.0420	1.00418	24.2819	1.00273	24.8619	0.99915	26.3281	0.99479	28.1111
0.1232	1.00788	23.1695	1.00654	24.5656	1.00508	25.0620	1.00140	26.9320	0.99698	28.7116
0.1545	1.01030	23.3013	1.0089	24.7881	1.0074	25.4286	1.00355	27.9945	0.99908	29.7095
0.3170	1.02210	25.8230	1.02061	26.7977	1.01912	27.0458	1.01510	28.7478	1.01011	31.1458
0.6504	1.04574	27.4018	1.04366	28.7341	1.04212	28.9026	1.03754	30.5086	1.03199	32.4506
0.9963	1.06938	28.3239	1.06653	29.9166	1.06471	30.2832	1.06012	31.2942	1.05390	33.1696
1.3888	1.09399	29.9393	1.09104	31.1314	1.08885	31.6384	1.08445	32.2011	1.07766	33.9063
1.7200	1.11370	31.0442	1.11084	31.9461	1.10870	32.3193	1.10351	33.1991	1.09681	34.5024
2.2405	1.14357	32.2168	1.14006	33.1724	1.13753	33.6169	1.13183	34.4942	1.12507	35.5012
2.7166	1.16885	33.2884	1.16517	34.1292	1.16254	34.5263	1.15689	35.2225	1.14931	36.3321
2.9647	1.18171	33.7061	1.17765	34.5941	1.17511	34.9278	1.16870	35.8063	1.16139	36.7332
3.7917	1.22073	35.2605	1.21667	35.9524	1.21369	36.3209	1.20724	37.0145	1.19934	37.8847
4.4038	1.24758	36.1549	1.24333	36.7914	1.23992	37.2010	1.23336	37.8235	1.22533	38.6030

Note: The densities are in units of g·cm^{-3}, and φ_v are in units of cm^3·mol^{-1}.

So the sodium metaborate [NaB(OH)$_4$·2H$_2$O] was assumed to dissociate in aqueous NaB(OH)$_4$ solution as follows:

$$\text{NaB(OH)}_4 \cdot 2\text{H}_2\text{O} \Longrightarrow \text{Na}^+ + \text{B(OH)}_4^- + 2\text{H}_2\text{O} \quad (1)$$
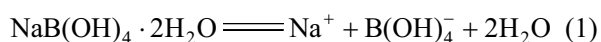
Therefore, all our results reported for sodium metaborate were denoted as NaB(OH)$_4$ which dissociates into Na$^+$ and B(OH)$_4^-$ in aqueous solution.

3.2   Volumetric properties

3.2.1   *Density*

The densities of aqueous NaB(OH)$_4$ solutions were measured at 293.15, 298.15, 303.15, 313.15 and 323.15 K. The density and apparent molar volume of the solution, as a function of concentration and temperature are shown in Table 2.

The apparent molar volumes φ_v for these solutions, given in Table 2 were calculated from the equation

$$\varphi_v = \frac{1000}{m}\left(\frac{1}{\rho^0} - \frac{1}{\rho}\right) + \frac{M_2}{\rho} \quad (2)$$

where ρ^0 is the density of water at corresponding temperatures, $\rho^0 = 0.99823, 0.99707, 0.99568, 0.99225$ and 0.98807 g·cm^{-3} at 293.15, 298.15, 303.15, 313.15 and 323.15 K, respectively; m is the molality (mol·kg^{-1}) of solution and M_2 is the molecular weight of the compounds, 101.828 for NaB(OH)$_4$ here.

Most of the equations reported in the literature [25] with only two variables, *i.e.* the density and the

concentration or temperature. Here we proposed a new expression, Eq. (3), which takes the density as a function of both concentration and temperature.

$$\rho = A + Bm + Cmt + Dmt^2 + Em^{1.5} + Fm^{1.5}t + Gm^{1.5}t^2 \quad (3)$$

where A, B, C, D, E, F, G are empirical constant determined by least-squares fit; m is the concentration in units of $mol \cdot kg^{-1}$; t is the temperature in units of °C. Herein, for the aqueous $NaB(OH)_4$ solution, an empirical equation

$$\rho = 0.99618 + 0.07451m - 2.0135 \times 10^{-4}mt - 2.2871 \times 10^{-6}mt^2 - 0.00158m^{1.5} + 5.50018 \times 10^{-6}m^{1.5}t + 2.46203 \times 10^{-7}m^{1.5}t^2$$

with $R^2 = 0.9988$ was deduced in temperature range from 20 to 50 °C. Fig. 3 displays the measurements and the empirical density correlation of aqueous $NaB(OH)_4$ solutions vs. concentration at 293.15, 298.15, 303.15, 313.15 and 323.15 K. As shown in Fig. 3, our experimental data are also in good agreement with the literature [12].
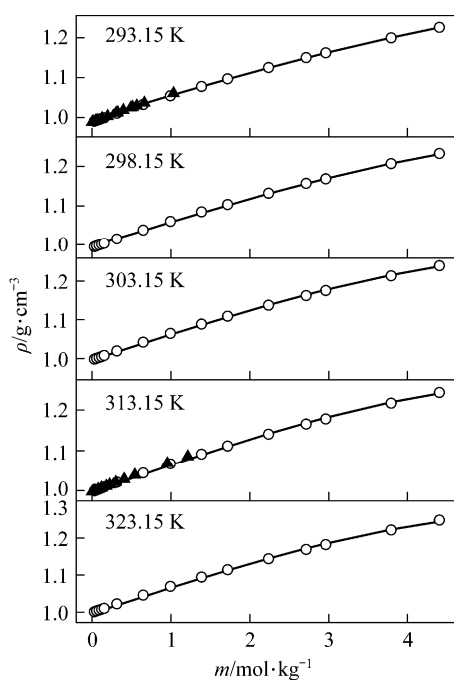

Figure 3   Density vs. concentration plots for aqueous NaB(OH)$_4$ solutions at various temperatures
○ experimental values; ▲ literature data for NaB(OH)$_4$ [12]; —— calculated data from nonlinear fitting

3.2.2 Apparent molar volumes

The concentration dependence of the φ_v of $NaB(OH)_4$ is shown in Fig. 4. Correspondingly, we fitted the experimental data to a three constant polynomial of concentration ($mol \cdot kg^{-1}$)

$$\varphi_v = A_1(= \bar{v}_2^\infty) + A_2m^{0.5} + A_3m \quad (4)$$

where $A_1(= \bar{v}_2^\infty)$, A_2, and A_3 are empirical constant determined by least-squares fit, $\bar{v}_2^\infty$ is the apparent molar volume at infinite dilution which is also equal to the limited partial molar volume. The least-squares parameters together with the correlation coefficient of the fits are reported in Table 4.
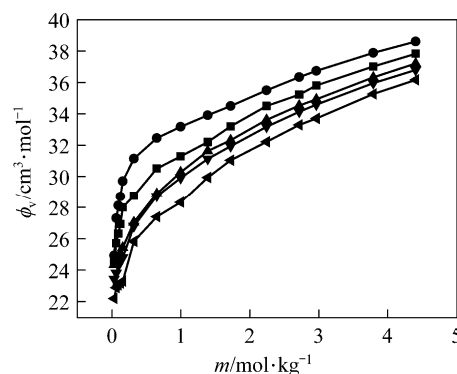

Figure 4   Plot of apparent molar volume (φ_v) against molality of aqueous NaB(OH)$_4$ solutions at different temperatures
■ 313.15 K; ● 323.15 K; ▲ 303.15 K; ▼ 298.15 K; ◄ 293.15 K

The temperature dependence of the $\bar{v}_2^\infty$ of $NaB(OH)_4$, shown in Fig. 5, can be expressed by the equation

$$\bar{v}_2^\infty = -2909.71 + 27.65T - 0.087T^2 + 9.21 \times 10^{-5}T^3 \quad (5)$$

with an average deviation of 0.4 $cm^{-3} \cdot mol^{-1}$. The increase in the $\bar{v}_2^\infty$ of $NaB(OH)_4$ with increasing of temperature (Table 3) could be attributed to the form of a tight hydration sphere, and the behavior of the first layer hydrated water molecules interacting with bulk water region. The apparent molar expansibilities, $\phi_E^0 = \partial \bar{v}_2^\infty / \partial T$, calculated from Eq. (5) between 293.15 and 323.15 K (Table 3) indicate that $NaB(OH)_4$ behaves like most common electrolytes with decreasing ϕ_E^0 with increasing temperature.

Table 3   Least-squares parameters of Eq. (5) [ϕ_E^0 and $\partial(\bar{v}_2^\infty)^2 / \partial T^2$ for aqueous NaB(OH)$_4$ solutions

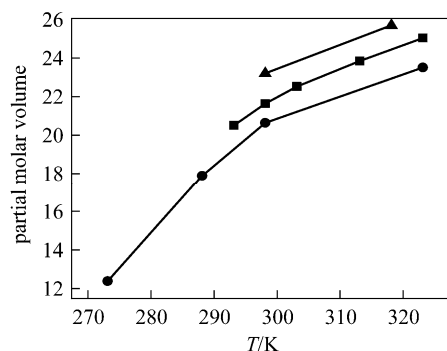| T/K	$A_1(\bar{v}_2^\infty)$	A_2	A_3	R^2	ϕ_E^0	$\partial(\bar{v}_2^\infty)^2 / \partial T^2$
293.15	20.50	8.7662	−0.6211	0.9965	0.2250	−0.00461
298.15	21.63	9.2237	−0.9703	0.9986	0.2020	−0.00696
303.15	22.53	8.3561	−0.6493	0.9984	0.1555	−0.00616
313.15	23.85	8.5864	−0.9613	0.9900	0.1253	−0.00185
323.15	25.03	10.037	−1.8221	0.9661	0.1185	−0.000673

Figure 5   Partial molar volumes at infinite dilution of NaB(OH)$_4$ as a function of temperature
■ present work; ● Ward *et al.*; ▲ Corit *et al.*

Table 4   Viscosity of aqueous NaB(OH)$_4$ solutions at as functions of concentration at 298.15 and 323.15 K

m/mol·kg^{-1}	η/mPa·s	
	298.15 K	323.15 K
0.0010	0.8996	0.5529
0.0050	0.9010	0.5546
0.0105	0.9027	0.5581
0.0498	0.9138	0.5702
0.0972	0.9299	0.5918
0.1965	0.9604	0.6277
0.4032	1.0309	0.7116
0.6117	1.1041	0.7788
0.8214	1.1912	0.8625
1.0318	1.2910	0.9362
1.4639	1.5067	1.1177
1.9061	1.7771	1.2960
2.3861	2.1276	1.5155
2.8709	2.5957	1.7919
3.3606	3.0945	2.1461
3.8623	3.7088	2.4701
4.4012	4.5922	2.9699
5.1494	6.1484	3.8338

As Fig. 5 shown, the agreement among the different data sources is satisfactory. Using Hepler's [26] reasoning, NaB(OH)$_4$ would be classified as a "structure breaking" solute between 298.15 and 323.15 K (that is, if $\partial \overline{v}_2^{\infty} / \partial T > 0$ and $\partial (\overline{v}_2^{\infty})^2 / \partial T^2 < 0$ the solute has the hydrophilic character, while if the behavior shows that $\partial \overline{v}_2^{\infty} / \partial T < 0$ and $\partial (\overline{v}_2^{\infty})^2 / \partial T^2 > 0$ the solute has hydrophobic character) , this may due to the unique structure of B(OH)$_4^-$ anion (four tetrahedrons OH groups) [27].
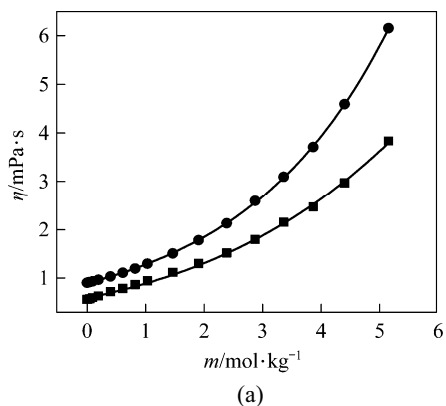
3.3   Transport properties

3.3.1   *Viscosity*

Measured viscosities for aqueous NaB(OH)$_4$ solutions were collected in Table 4. The viscosity data are plotted in Fig. 6 at two temperatures. A semi-empirical equation [28–30]:

$$\eta = a_0 \exp\left(b_0 m + c_0 m^2\right) \tag{6}$$

has been shown to be useful for data fitting over wide concentration range, where a_0, b_0, and c_0 are the adjustable temperature dependent parameters. The

least-squares fitted parameters in Eq. (6) are summarized in Table 5.

The viscosity data of concentration less than 0.1 mol·L^{-1} were analyzed in terms of the extended Jones-Dole viscosity equation:

$$\eta_r = 1 + A_\eta c^{1/2} + B_\eta c + D c^2 \tag{7}$$

where $\eta_r = \eta / \eta_0 \cdot \eta_r$, η and η_0 are the relative viscosity, viscosity of the solution and viscosity of the solvent,

(a)
—— calculated data from nonlinear fitting
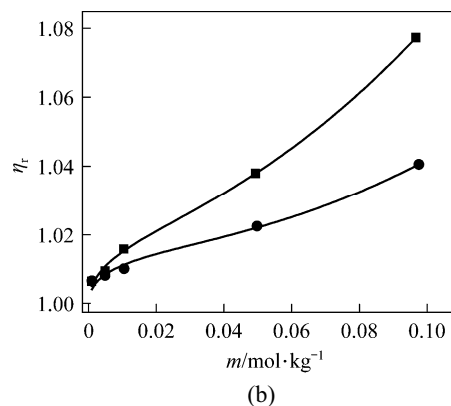
(b)
—— calculated data from the extended Jones-Dole equation

Figure 6   (a) Viscosity *vs.* concentration plots for solutions at 298.15 K and 333.15K and (b) relative viscosity *vs.* concentration (<0.01 mol·L^{-1})
● experimental values at 298.15 K; ■ experimental values at 333.15 K

Table 5   Coefficients for Eqs. (6) and (7) and the hydration number

T/K	a_0	b_0	c_0	R^2	A_η	B_η	D	R^2	H_n
298.15	0.8937	0.3569	0.0034	0.9999	0.1440	−0.3660	3.2923	0.98137	20.9
323.15	0.5895	0.4211	−0.0115	0.9987	0.1704	−0.2579	5.2630	0.99768	13.5

respectively, and c is the molar concentration. Coefficient (A_η) is a measure of ion-ion interactions and may be calculated from equilibrium theory, as summed by Jenkins and Marcus [31]. Coefficient (B_η), also called the Jones-Dole coefficient, is an empirical constant, qualitatively correlating on the size of solute particle and on ion-solvent interaction characteristic for electrolyte and solvent [31]. B_η of $B(OH)_4^-$ were calculated by subtracting the B_η of Na^+ ion [25] from the values of $NaB(OH)_4$ at 298.15 and 323.15 K, respectively, that is $B_{\eta,B(OH)_4^-,298.15} = -0.452$ L·mol^{-1} and $B_{\eta,B(OH)_4^-,323.15} = -0.339$ L·mol^{-1}, which are well consistent with the literature values of dilute aqueous $NaB(OH)_4$ solutions at 298.15 K [32]. The calculated B_η of $B(OH)_4^-$ ($B_\eta<0$) indicated it behaves as a structure disordering ion between 298.15 to 323.15 K, which is consistent with our study on volumetric properties of aqueous $NaB(OH)_4$ solution.

For a dilute solution of spherical colloidal suspensions, Einstein derived the relation

$$\eta_r = 1 + 2.5\varphi \tag{8}$$

where φ is the volume fraction of the solute. For 1 : 1 type electrolyte, Eq. (9) becomes

$$\eta_r = 1 + 2.5V_h c \tag{9}$$

where V_h is the hydrodynamic volume. Where V_h is the partial molar volume ($\overline{v}_2^\infty$) of the unsolvated solute particle in a continuum solvent. Thus, the value of the hydration number (H_n) can be calculated as

$$H_n = |B|/V_m^0 \tag{10}$$

H_n lies between 0 and 2.5 for unsolvated species and has higher values for solvated species. The calculated H_n of $B(OH)_4^-$ are 20.9 and 13.5 at 298.15 and 323.15 K indicated the $B(OH)_4^-$ are solvated in aqueous solution [33]. It's maybe another evidence for a tight hydration sphere is formed around $B(OH)_4^-$ in aqueous solutions.

3.3.2 *Electrical conductivity*

The experimental electrical conductivities of aqueous $NaB(OH)_4$ solutions are listed in Table 6.

Figure 7 (a) shows that a break can be found, the conductivity increases as concentration and temperature. The conductivity data over the whole concentration range studied were fitted to the Casteel-Amis

Table 6   Electrical conductivity of aqueous NaB(OH)₄ solutions at as functions of concentration at 298.15 and 323.15 K

$m/\text{mol·kg}^{-1}$	$\kappa/\text{mS·cm}^{-1}$	
	298.15 K	323.15 K
0.0005	0.04254	0.06552
0.0010	0.08336	0.128
0.0040	0.3234	0.4909
0.0063	0.5058	0.7523
0.0101	0.7842	1.143
0.0725	5.267	7.713
0.1715	10.34	16.14
0.4003	19.16	31.57
0.6102	26.00	42.61
0.8159	31.58	51.7
1.0520	36.52	60.45
1.4565	43.34	73.01
1.9218	47.25	83.31
2.3792	49.55	90.31
2.8476	51.7	94.44
3.3676	52.31	97.54
3.8549	51.92	100.4
4.3318	50.99	99.92
4.9404	48.42	99.73
5.4909	44.57	98.52
6.0737	42.01	95.64

equation [30, 34]:

$$\kappa = \kappa_{\max}(m/\mu)^a \exp[b(m-\mu)^2 - a(m-\mu)/\mu] \tag{11}$$

where μ is the concentration corresponding to the maximum conductivity $\kappa_{\max}$ at a given temperature; a and b are empirical parameters; m is molality in units of mol·kg^{-1}. In all the concentration range a function between conductivity and concentration can be given though nonlinear fitting.

The decrease of molar conductivity with increasing concentration must be due to the increase of viscosity of the aqueous solution and polymerization. The polymerization makes charge carriers in unit volume decrease, and higher polyborate anions and their hydration also means the charge carriers are large in size, and the increasing viscosity make migration rate
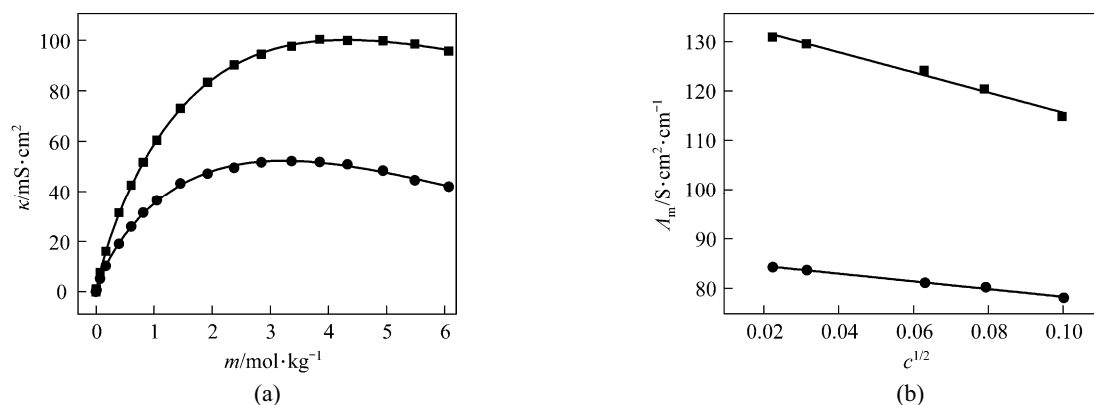
Figure 7 (a) Conductivity *vs.* concentration plots for solutions at 298.15 and 323.15 K and (b) molar conductivity *vs.* concentration (<0.01 mol·L^{-1}) to zero
● experimental values at 298.15 K; ■ experimental values at 323.15 K; —— calculated data from nonlinear fitting

Table 7 Values of k_{max}, *u*, *a* and *b* coefficients for Eq. (11) and the transport properties of aqueous NaB(OH)$_4$ solutions

T/K	κ_{max}	u	a	b	R^2	$\varLambda_m^\infty$	$\lambda_{B(OH)_4^-}^0$	$\mu_{B(OH)_4^-}^\infty$	$D_{B(OH)_4^-}^\infty \times 10^{-10}/m^2 \cdot s^{-1}$	r_s/nm	$t_{B(OH)_4^-}$
298.15	52.37	3.2297	−0.00208	0.80266	0.9995	86.02	35.92	3.72×10^{-4}	9.5646	0.2526	0.4175
323.15	100.11	4.3081	0.00475	0.84184	0.9999	134.97	56.15	5.82×10^{-4}	16.2050	0.1640	0.4160

slower. In extremely dilute solution (smaller than 0.01 mol·L^{-1}), it can be ensure that polyborates do not exist to any significant extent polymerization so the main species are B(OH)$_4^-$ and B(OH)$_3$ with an equilibrium as follows:

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^- \qquad (12)$$
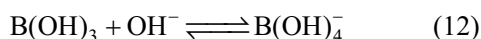
Limiting molar conductivity ($\varLambda_m^\infty$) of NaB(OH)$_4$ can be gotten by extrapolate to $c = 0$ mol·L^{-1} through the Kohlrausch correlations. As Fig. 7 (b) shown, the plot of $\varLambda_m$ against $c^{1/2}$ is a line with $\varLambda_m^\infty$ as intercept to slope A at concentration ($c<0.01$ mol·L^{-1}) where $\varLambda_{\infty,298.15} = 86.02$ and $\varLambda_{\infty,323.15} = 136.05$ S·cm^2·mol^{-1}. The limiting ionic conductivities for the B(OH)$_4^-$ ion were calculated by subtracting the limiting ionic conductivities of Na$^+$ ion [25] from the limiting molar conductivity of NaB(OH)$_4$, that is $\lambda_{B(OH)_4^-,298.15}^0 = 35.92$ and $\lambda_{B(OH)_4^-,323.15}^0 = 56.15$ S·cm^2·mol^{-1} which are well consistent with Corti's conclusion at 298.15 K [15].

$$\lambda_{B(OH)_4^-}^0 = \varLambda_m^\infty - \varLambda_{m,+}^\infty \qquad (13)$$

$$\lambda_{B(OH)_4^-}^0 = F|Z_i|e/6\pi\eta_0 r_s \qquad (14)$$

$$\mu_{B(OH)_4^-}^\infty = \lambda_{B(OH)_4^-}^\infty \Big/ (z_i \times F) \qquad (15)$$

$$D_{B(OH)_4^-}^0 = \lambda_{B(OH)_4^-}^0 \left(RT \Big/ z_i F^2 \right) \qquad (16)$$

$$t_{B(OH)_4^-} = \varLambda_{m,B(OH)_4^-}^\infty \Big/ \varLambda_m^\infty \qquad (17)$$

where $\lambda_{B(OH)_4^-}^0$ is limiting conductivity (S·m^2·s^{-1}); F is the Faraday constant (9.64846×10^4 C·mol^{-1}); e the elementary charge (1.6022×10^{-19} C); z_i the charge number of the ion; η_0 the viscosity of water ($\eta_0 = 8.903$ and 5.494×104 Pa·s at 298.15 and 323.15 K, respective); R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}); T is the absolute temperature (K). The conductivity of an ion in pure water, which is the limiting ionic conductivity, is related to the water viscosity by the Stokes-Einstein equation [Eq. (14)], where r_s is the Stokes radius or hydrodynamic radius [35, 36]. The r_s, the ionic mobility ($\mu_{B(OH)_4^-}^\infty$), the diffusion coefficient ($D_{B(OH)_4^-}^0$) and the transference number ($t_{B(OH)_4^-}$) for B(OH)$_4^-$ anion can be calculated as Eqs. (14)−(17), respectively, and list in Table 7.

4 CONCLUSIONS

pH of aqueous NaB(OH)$_4$ solutions were precisely measured as functions of concentration from dilute to saturation at 298.15 and 323.15 K. Coupling with Raman spectra of some concentrated samples, polyborate distribution calculated using measured pH values and literature equilibrium constants of aqueous

$NaB(OH)_4$ solutions shows that covering all the concentration range, $B(OH)_4^-$ is the most dominant species, other polyborate anions are less than 5.0%. Densities of aqueous sodium borate solutions as functions of concentration (from diluted to saturate) and temperatures (293.15, 298.15, 303.15, 313.15 and 323.15 K) were summed, and semi-empirical equations for those properties *vs.* concentration were also suggested. Apparent molar volumes (φ_v), limit partial molar volumes ($\bar{v}_2^\infty$) and apparent molar expansibilities (ϕ_E^0) of sodium metaborate have been determined from those precision density. Conductivity data were analyzed with a semi-empirical equation over range concentration, and the limiting molar conductivity of $B(OH)_4^-$ at the infinite dilution were estimated to be of 35.92 and 56.15 $S \cdot cm^2 \cdot mol^{-1}$, respectively, at 298.15 and 323.15 K by the Kohlrausch correlations. From those values, the ionic mobility, diffusion coefficients and transference number for the $B(OH)_4^-$ anion were given. Viscosity data were analyzed with a semi-empirical equation over range concentration, and the ion-solvent and ion-ion interactions were analyzed with an extended Jones-Dole type correlation at the extremely dilute concentration. Values of -0.452 and -0.339 $L \cdot mol^{-1}$ were estimated for the $B(OH)_4^-$ B-coefficient at 298.15 and 323.15 K, respectively. Both of the volumetric and transport properties of aqueous $NaB(OH)_4$ solutions indicate that the $B(OH)_4^-$ behaves like "structure breakers" between 293.15 and 323.15 K.

NOMENCLATURE

$D_{B(OH)_4^-}^0$	diffusion coefficient for $B(OH)_4^-$, $m^2 \cdot s^{-1}$
m	molality, $mol \cdot kg^{-1}$
R	universal gas constant, 8.314 $J \cdot mol^{-1} \cdot K^{-1}$
r_s	stokes radius, m
T	absolute temperature, K
t	temperature, °C
$t_{B(OH)_4^-}$	transference number of $B(OH)_4^-$
$\bar{v}_2^\infty$	limit partial molar volumes, $cm^3 \cdot mol^{-1}$
δ	fraction of total boron
η_r	relative viscosity
$\lambda_{B(OH)_4^-}^0$	limiting molar conductivity, $S \cdot cm^2 \cdot mol^{-1}$
Λ_m^∞	limiting molar conductivity, $S \cdot cm^2 \cdot mol^{-1}$
$\mu_{B(OH)_4^-}^\infty$	ionic mobility $B(OH)_4^-$, $cm^2 \cdot s^{-1} \cdot V^{-1}$
ρ	density of solution, $g \cdot cm^{-3}$
ρ^0	density of pure water, $g \cdot cm^{-3}$
ϕ_E^0	apparent molar expansibilities
φ_v	apparent molar volumes, $cm^3 \cdot mol^{-1}$

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