Determination of the sodium-borate association constant $NaB(OH)_4^0$ between 75 and 200°C using new sodium selective glass electrodes

G. Pokrovski
J. Schott
A. Sergeyev

Laboratoire de Géochimie, UPS, Toulouse, France

St-Petersburg State University, Russia.

Introduction

Sodium is the major cation present in almost all types of natural waters. Despite its relatively weak capacity of complexing with different anions at low temperatures, this association may play an important role in Na-rich hydrothermal solutions. This process may strongly affect the speciation and transport of minor elements present in anionic forms. Among these elements, boron is particularly important because, through its isotopic fractionation, it has been shown to be a powerful tracer of geochemical processes, including seawater-basalt reactions at oceanic ridges and subduction zones (Spivack and Edmond, 1987). In aqueous solutions the isotopic fractionation of boron is due to the differences in the inter-atomic vibrational energy and symmetry between $B(OH)_3$ and $B(OH)_4^-$. As a result, knowledge of the thermodynamic properties of $B(OH)_3$, $B(OH)_4^-$ and $NaB(OH)_4$ is essential for the interpretation of $^{11}B:^{10}B$ fractionation in hydrothermal systems. Although the thermodynamic properties of $B(OH)_3$ and $B(OH)_4^-$ are well known to 300°C (Mesmer et al., 1972), this is not the case for $NaB(OH)_4$, the stability constant of which has been only determined at 25°C. The purpose of this study is to measure the stability constant of $NaB(OH)_4$ up to 200°C using new sodium selective glass electrodes. These data will enable accurate evaluation of boron speciation in Na-rich hydrothermal fluids.

Electrode technique

The electrodes used in this study were recently developed by the company 'Potential' (Beliustin et al., 1992). A detailed description of the potentiometric apparatus is given elsewhere (Pokrovski et al., 1993). The following cell with a liquid junction was used: Sn-Cu, Li-Sn alloy|| glass || test solution with Na | 3.2M KCl, Ag/AgCl. The e.m.f. of the cell is described by the equation: $E = E_0 + 2.3026RT/F \log a(Na^+) + E_j$, where E_0 is the sum of the standard potential of the glass electrode and 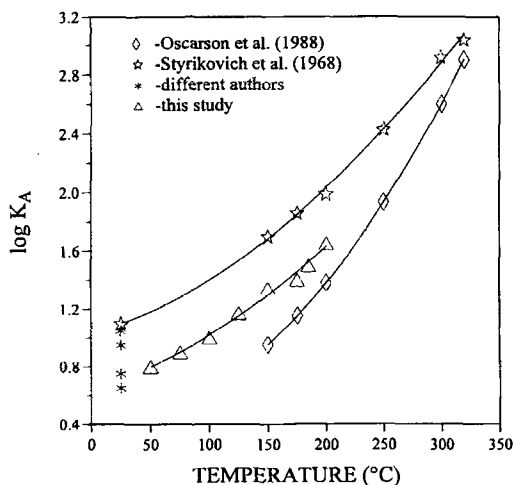the reference electrode potential, and E_j is the liquid junction potential. The latter was estimated by the Henderson equation (Bates, 1973) using limiting equivalent conductances of ions from Oelkers and Helgeson, 1989. For the same ionic strength the potential varied in the limit of ±0.5 mV. For $0.025 < I < 0.75$ M, the potential variations were less than 5 mV. The electrode calibration was performed in several NaCl solutions (0.025–0.75 M) from 50 to 200°C. The activity of Na^+ was calculated either assuming: $a(Na^+) = a(Cl^-) = a(NaCl)$ or using the Debye-Hückel equation with NaCl dissociation constant given in Shock et al., 1992. In both cases the e.m.f. showed a good linearity as a function of $\log a(Na^+)$ (correlation coefficient 0.999). Experiments performed in solutions having the same Na concentration but at various pH from 7 to 12 in the presence of different noncomplexing anions (NO_3^-, ClO_4^-) demonstrated that there is no influence of pH and anion composition on the electrode response.

Measurements of the association constants of $NaSO_4^-$ and $NaB(OH)_4$

To check the accuracy of the method we first measured the association constant of $NaSO_4^-$ using two series of solutions: (1) 0.1M NaCl-0.05M Na_2SO_4 and (2) 0.25M NaCl-0.125M Na_2SO_4. The difference in the e.m.f. between the NaCl and Na_2SO_4 solutions in each series can be attributed to the uptake of free Na^+ by sulphate anion. For boron two series of measurements were also performed: (1) 0.25M NaOH, 0.18M HCl-0.25M NaOH,0.18M $B(OH)_3$ and (2) 0.5M NaOH, 0.45M HCl-0.5M NaOH, 0.45M $B(OH)_3$. The concentration of free NaOH in each series of measurements was kept constant to minimize diffusion potentials and the effect of NaOH pairing. The calculations were carried out with the computer code 'BALANCE' (Akinfiev, 1986) using the Debye-Hückel equation with $a^0 = 4A$ for all species and the association constant of NaCl from Shock et al., 1992.

TABLE 1. Logarithm of $NaSO_4^-$ and $NaB(OH)_4^0$ association constants

T°C	$NaSO_4^-$		$NaB(OH)_4^0$	
	0.1 M	0.25 M	0.25 M	0.5M
75	1.00 ± 0.30	0.80 ± 0.20	0.24 ± 0.17	0.19 ± 0.20
90	1.05 ± 0.20	1.11 ± 0.15	0.30 ± 0.15	0.22 ± 0.20
100	1.10 ± 0.07	1.10 ± 0.15	0.33 ± 0.17	0.35 ± 0.20
125	1.13 ± 0.15	1.17 ± 0.15	0.37 ± 0.10	0.40 ± 0.15
150	1.40 ± 0.10	1.28 ± 0.20	0.43 ± 0.13	0.49 ± 0.15
175	1.35 ± 0.15	1.44 ± 0.10	0.57 ± 0.10	0.60 ± 0.20
200	1.63 ± 0.10	1.68 ± 0.10	0.70 ± 0.20	0.75 ± 0.25

FIG. 1. Association constant of $NaSO_4^-$.

FIG. 2. Boron coordination as a function of pH at 300°C and in 2M NaCl: dashed lines, without Na-B association; solid lines, with $NaB(OH)_4^0$ species.

Discussion

The association constants of $NaSO_4^-$ and $NaB(OH)_4$ generated in this study are given in the Table. It can be seen that they are independent of ionic strength which confirms the validity of the Debye-Huckel approach even up to 0.5 M. Fig.1 demonstrates good agreement between the $NaSO_4^-$ constants generated in this study and available literature values.

The association constant of $NaB(OH)_4$ determined in this study is in agreement with the data at 25°C (Reardon, 1976: logK = 0.22 ± 0.1; Corti *et al.*,1980: logK = −0.15 ± 0.07 and Rowe *et al.*,1988: logK = −0.19 ± 0.1). Note also that this constant is very close to that of $NaAl(OH)_4$ (Diakonov *et al.*, 1994).

Using our experimental data within the framework of the density (Anderson *et al.*, 1991) and electrostatic (Ryzhenko, 1981) models we calculated $NaB(OH)_4$ association constant to 350°C: logK = 1.6 ± 0.3 and 2.35 ± 0.5 at 300 and

350°C respectively. These values imply that Na-B complexation can dramatically modify boron speciation in Na-rich hydrothermal fluids. For example Fig.2 shows that at 300°C and in 2M NaCl Na-B complexing will shift the field of dominance of $B(OH)_3$ to acidic pH by nearly two pH units. Note that at pH 8 nearly 90% of B(IV) is in the form of $NaB(OH)_4$.

As a result Na-B complexing is likely to affect greatly the isotopic fractionation of boron in hydrothermal solutions. It should be taken into account when using the boron isotopes to model geochemical cycles and water–rock interaction.

References

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