

Thermodynamics of ionic association 1

The standard association constant of the ion pair $\text{Li}^+\text{B}(\text{OH})_4^-$

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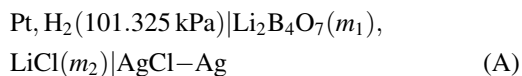
Abstract

Values of emf for the cell without liquid junction $\text{Pt}, \text{H}_2 (101.325 \text{ kPa}) | \text{Li}_2\text{B}_4\text{O}_7 (m_1), \text{LiCl} (m_2) | \text{AgCl}-\text{Ag}$ are reported at five temperatures from 278.15 to 318.15 K. The standard association constant of ionic pair $\text{Li}^+\text{B}(\text{OH})_4^-$, K_a , is determined by a fitting with the cell results. The dependence of $\text{p}K_a$ on temperature T is expressed in empirical equation: $\text{p}K_a = -131.6K/T - 0.08996 - 1.856 \times 10^{-3}T/K$. The other thermodynamic quantities of the association process are calculated and show that there truly exists ion pair $\text{Li}^+\text{B}(\text{OH})_4^-$ and the driving force for the ion association reaction is association entropy. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Thermodynamics; Ionic association; Pitzer's equation; Borate; Activity coefficient

1. Introduction

There are many salt lakes on Qinghai–Xizang Plateau. They are renowned for containing boron and lithium with high concentration in the world. The study on thermodynamics of boron containing aqueous solution with lithium is of interest in predicting the behavior of the high ionic strength brine of these salt lakes. Peng-Sheng Song [1–7] and his colleagues have made a lot of investigation in the research field. In this paper, we measured the emfs of cell (A) without liquid junction potential:



and determined the values of K_a of ionic pair $\text{Li}^+\text{B}(\text{OH})_4^-$ over temperature range 278.15–318.15 K from these precise emf measurements of cell (A) by extrapolation on the basis of Pitzer's theory [8]. Other thermodynamic quantities of the ion association process were calculated and discussed.

2. Experimental

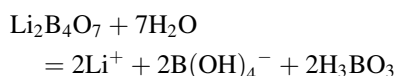
Water deionized was distilled in a quartz-still and its conductivity was $(0.9-1.3) \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$. Lithium chloride of AR grade was recrystallized twice from water and then its stock solution was standardized by gravimetric determination of chloride as AgCl. The relative standard deviation among five replicate determinations was less than $\pm 0.05\%$. Hydrochloride acid was prepared from the constant boiling acid mixture of

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Table 1
Standard emfs of cell (A), E^0/V

| T/K | 278.15 | 288.15 | 298.15 | 308.15 | 318.15 |
|---------------------------|---------|---------|---------|---------|---------|
| E^0 (this work) | 0.23418 | 0.22867 | 0.22248 | 0.21568 | 0.20833 |
| E^0 (White et al. [13]) | 0.23410 | 0.22857 | 0.22238 | 0.21566 | 0.20825 |

the aqueous using two distillations of the AR grade acid. $\text{Li}_2\text{B}_4\text{O}_7$ was the AR grade agent which was not purified any further. When $\text{Li}_2\text{B}_4\text{O}_7$ is dissolved in water, it yields an equimolal mixture comprised of boric acid and lithium orthoborate



However, formation of aqueous polyborates has been studied extensively by Ingri [9]. The formation of these polynuclear species at modest total boron concentrations and the resulting difficulty in describing the thermodynamics of these solutions have limited the studies of the excess thermodynamic properties of the aqueous boron solutions. To minimize polyborate formation, the total boron molality ($4m_1$ of the solution) in each run in this work has been held <0.08 mol/kg.

The details of electrode preparation and the cell design were given elsewhere together with a descrip-

tion of relevant experiment procedures [10,11]. The values of emfs measured at 298.15 K at the beginning, in the middle and at the end of each run are in agreement within ± 0.10 mV. Also, the deviations of the readings from four cells for the same solution were less than ± 0.10 mV. All emfs reported here have been corrected to a hydrogen fugacity of 101.325 kPa. The standard emfs of cell (A), E^0 , were determined by Bates's method [12] and their values are listed in Table 1.

The data given in Table 1 agrees with White's [13] within experimental uncertainty limit.

3. Results and discussion

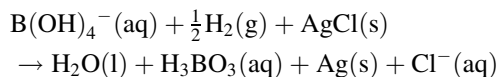
Table 2 contains the values for the corrected emfs of cell (A) over the temperature range 278.15–318.15 K at various molalities of $\text{Li}_2\text{B}_4\text{O}_7$ and LiCl , where each emf value is the average of four cells.

Table 2
Emf values in volts for cell (A) corrected to a hydrogen fugacity of 101.325 kPa at 278.15–318.15 K

| $10^2 m_1$ (mol/kg) | $10^2 m_2$ (mol/kg) | T/K | | | | |
|---|---------------------|---------|---------|---------|---------|---------|
| | | 278.15 | 288.15 | 298.15 | 308.15 | 318.15 |
| Pt, $\text{H}_2(101.325 \text{ kPa}) \text{Li}_2\text{B}_4\text{O}_7 (m_1), \text{LiCl} (m_2) \text{AgCl}-\text{Ag}$ | | | | | | |
| 0.1353 | 0.7148 | 0.87102 | 0.88227 | 0.89341 | 0.90442 | 0.91530 |
| 0.2657 | 1.881 | 0.83251 | 0.84140 | 0.85036 | 0.85982 | 0.86944 |
| 0.5127 | 4.671 | 0.82663 | 0.83624 | 0.84601 | 0.85564 | 0.86517 |
| 0.6632 | 6.593 | 0.81827 | 0.82740 | 0.83661 | 0.84593 | 0.85513 |
| 0.9179 | 9.106 | 0.80999 | 0.81883 | 0.82782 | 0.83685 | 0.84582 |
| 1.105 | 10.13 | 0.80736 | 0.81595 | 0.82490 | 0.83380 | 0.84263 |
| 0.2155 | 3.433 | 0.83343 | 0.84315 | 0.85296 | 0.86270 | 0.87217 |
| 0.4061 | 7.459 | 0.81422 | 0.82325 | 0.83223 | 0.84152 | 0.85051 |
| 0.5917 | 12.72 | 0.80042 | 0.80893 | 0.81782 | 0.82647 | 0.83512 |
| 0.8040 | 15.61 | 0.79536 | 0.80380 | 0.81233 | 0.82078 | 0.82906 |
| 0.9864 | 19.34 | 0.78964 | 0.79776 | 0.80614 | 0.81444 | 0.82263 |
| 1.225 | 23.09 | 0.78473 | 0.79262 | 0.80077 | 0.80890 | 0.81689 |
| 0.3140 | 3.416 | 0.83255 | 0.84205 | 0.85186 | 0.86165 | 0.87130 |
| $\text{p}K_a$ | | -1.079 | -1.082 | -1.085 | -1.089 | -1.094 |
| $s_K \times 10^3$ | | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 |
| $s_f \times 10^3$ | | 0.7 | 0.7 | 0.7 | 0.8 | 0.8 |

3.1. Extrapolation to determine the standard association constant of the ion pair

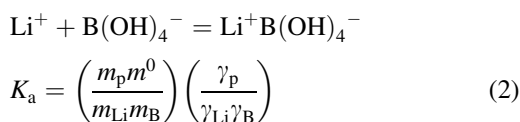
By considering the dissociation reaction of boric acid, the reaction in cell (A) is:



The cell emf is given by the following Nernst equation:

$$\frac{(E - E^0)}{k} = \text{p}K_1 - \log a_w - \log \left(\frac{m_{\text{HB}}}{m_{\text{B}}} \right) - \log \left(\frac{m_{\text{Cl}}}{m^0} \right) - \log \left(\frac{\gamma_{\text{HB}}\gamma_{\text{Cl}}}{\gamma_{\text{B}}} \right) \quad (1)$$

where $m^0=1$ mol/kg, m_i and γ_i are the molality and activity coefficient of species i , respectively. Subscripts B and HB mean B(OH)_4^- and H_3BO_3 , respectively. K_1 is the first standard dissociation constant of boric acid, $\text{p}K_1 = -\log K_1$. The values of $\text{p}K_1$ measured by Owen and King [14] were applied to this work. In the Eq. (1) $k=(RT \ln 10)/F$, where R is the gas constant, T the thermodynamic temperature and F the Faraday constant. LiCl in the run solution is the supporting electrolyte which is used to control the total ionic strength. The association constant of the ion pair between Li^+ and OH^- is less and may be neglected [15], so that only the ion pair between Li^+ and B(OH)_4^- can be considered in this work. Its association reaction is:



where subscript p means the ion pair, K_a the standard association constant. Substitution of Eq. (2) into Eq. (1) yields:

$$\frac{(E - E^0)}{k} - \text{p}K_1 + \log a_w = \text{p}K_a - \log \left[\frac{m_{\text{Li}}m_{\text{HB}}m_{\text{Cl}}}{m_{\text{p}}(m^0)^2} \right] - \log \left(\frac{\gamma_{\text{Li}}\gamma_{\text{Cl}}\gamma_{\text{HB}}}{\gamma_{\text{p}}} \right) \quad (3)$$

Since HB and the ion pair, $\text{Li}^+\text{B(OH)}_4^-$, are neutral, it is supposed that $\log (\gamma_{\text{HB}}/\gamma_{\text{p}})=bI$, where I is the effec-

tive total ionic strength in the cell solution, and b an empirical parameter. Consequently, the extrapolation working equation to determine standard association constant of the ion pair $\text{Li}^+\text{B(OH)}_4^-$ was obtained from rearrangement of the above equation:

$$\text{p}K' = \frac{(E - E^0)}{k} - \text{p}K_1 + \log \left[\frac{m_{\text{Li}}m_{\text{HB}}m_{\text{Cl}}}{m_{\text{p}}(m^0)^2} \right] + \log a_w - \log (\gamma_{\text{Li}}\gamma_{\text{Cl}}) = \text{p}K_a - \frac{bI}{m^0} \quad (4)$$

where the empirical parameter b is the slope of the linear Eq. (4), and $\text{p}K'$ is an extrapolation function which may be obtained by using the following procedure. The equilibrium molalities of various species in $\text{p}K'$ can be calculated from the equilibrium reactions:

$$m_{\text{p}} = m_2 - m_{\text{Li}} \quad (5)$$

$$m_{\text{HB}} = 4m_1 - m_{\text{B}} - m_{\text{p}} \quad (6)$$

$$K_1 = \left(\frac{a_{\text{H}}}{a_w} \right) \left(\frac{m_{\text{B}}}{m_{\text{HB}}} \right) \left(\frac{\gamma_{\text{B}}}{\gamma_{\text{HB}}} \right) \quad (7)$$

where the hydrogen ion activity, a_{H} , can be estimated from the emf measurement of cell (A):

$$\log a_{\text{H}} = \frac{(E^0 - E)}{k} - \log \left(\frac{m_{\text{Cl}}}{m^0} \right) - \log (\gamma_{\text{Cl}}) \quad (8)$$

the water activity, a_w , can be calculated in terms of the following relationship:

$$\ln a_w = - \frac{M_w \sum m_i \varphi}{m^0} \quad (9)$$

where φ is the osmotic coefficient, and M_w the molar mass of water. According to Pitzer's theory [8], the equation to calculate osmotic coefficient φ in mixed electrolyte is:

$$\begin{aligned} \varphi - 1 = & \left(\frac{2m^0}{\sum m_i} \right) \left[-A_\varphi \left(\frac{(I/m^0)^{3/2}}{(1 + 1.2(I/m^0)^{1/2})} \right) \right. \\ & + \sum_c \sum_a \left(\frac{m_c}{m^0} \right) \left(\frac{m_a}{m^0} \right) (B_{ca}^\varphi + SC_{ca}) \\ & \times \sum_c \sum_{c'} \left(\frac{m_c}{m^0} \right) \left(\frac{m_{c'}}{m^0} \right) \left(\Phi_{cc'}^\varphi + \sum_a \left(\frac{m_a}{m^0} \right) \psi_{cc'a} \right) \\ & \left. + \sum_a \sum_{a'} \left(\frac{m_a}{m^0} \right) \left(\frac{m_{a'}}{m^0} \right) \left(\Phi_{aa'}^\varphi + \sum_c \left(\frac{m_c}{m^0} \right) \psi_{ca'a} \right) \right] \quad (10) \end{aligned}$$

where the sums are carried out over the cations c, c' and over the anions a, a' . The definition of S is

$$S = \left| \sum_a \left(\frac{m_a}{m^0} \right) z_a \right| = \sum_c \left(\frac{m_c}{m^0} \right) z_c \quad (11)$$

In Eq. (10), A_ϕ is the limiting slope for the osmotic coefficient. The values of A_ϕ were calculated from the dielectric constant expression of Bradley and Pitzer [16]. In operation of Pitzer's theory it was assumed that: (1) since total boron concentration is low, only the ionic interaction between i species and supporting electrolyte LiCl was considered; (2) the total ionic strength of each run solution equals to the molality of LiCl, and parameters of three-body interactions C and ψ may neglect; (3) the parameter of two-body interactions Φ is regarded as independent of total ionic strength so that Eq. (10) is reduced to

$$\begin{aligned} \phi - 1 = & \left(\frac{2m^0}{\sum m_i} \right) \left[-A_\phi \frac{(I/m^0)^{3/2}}{(1 + 1.2(I/m^0)^{1/2})} \right] \\ & + \left(\frac{m_{\text{Li}}}{m^0} \right) \left(\frac{m_{\text{Cl}}}{m^0} \right) B_{\text{LiCl}}^\phi \end{aligned} \quad (12)$$

where

$$B_{\text{LiCl}}^\phi = \beta_{\text{LiCl}}^{(0)} + \beta_{\text{LiCl}}^{(1)} \exp \left[-\alpha \left(\frac{I}{m^0} \right)^{1/2} \right] \quad (13)$$

The ion activity coefficients, γ_{Cl} , γ_{B} and γ_{Li} can also be estimated from the Pitzer's theory:

$$\begin{aligned} \ln \gamma_{\text{Cl}} = & F + 2 \left(\frac{I}{m^0} \right) B_{\text{LiCl}} \quad (14) \\ \ln \gamma_{\text{B}} = & F + 2 \left(\frac{I}{m^0} \right) B_{\text{LiB}} + \left(\frac{I}{m^0} \right)^2 C_{\text{LiB}} \\ & + 2 \left(\frac{I}{m^0} \right) \Phi_{\text{BCl}} \end{aligned}$$

where other quantities in eqs. (14) and (15) are defined by the following equations:

$$\begin{aligned} F = & -A_\phi \left\{ \left(\frac{(I/m^0)^{1/2}}{[1 + 1.2(I/m^0)^{1/2}]} \right) + \left(\frac{2}{1.2} \right) \right. \\ & \left. \times \ln \left[1 + 1.2 \left(\frac{I}{m^0} \right)^{1/2} \right] \right\} + \left(\frac{I}{m^0} \right)^2 B'_{\text{LiCl}} \end{aligned} \quad (16)$$

$$B_{\text{LiCl}} = \beta_{\text{LiCl}}^{(0)} + \beta_{\text{LiCl}}^{(1)} Y_1 \quad (17)$$

$$B'_{\text{LiCl}} = \beta_{\text{LiCl}}^{(1)} Y_2 \quad (18)$$

$$Y_1 = 2 \left[\frac{1 - \{1 + \alpha(I/m^0)^{1/2}\} \exp \{-\alpha(I/m^0)^{1/2}\}}{(\alpha^2 I/m^0)} \right] \quad (19)$$

$$\begin{aligned} & - 2[1 - \{1 + \alpha(I/m^0)^{1/2} + \alpha^2(I/m^0)/2\} \\ & \exp \{-\alpha(I/m^0)^{1/2}\}] \\ Y_2 = & \frac{\exp \{-\alpha(I/m^0)^{1/2}\}}{\{\alpha^2(I/m^0)^2\}} \end{aligned} \quad (20)$$

where α is a general parameter which is usually equal to 2.0, and $\beta_{\text{MX}}^{(0)}$ and $\beta_{\text{MX}}^{(1)}$ are empirically determined characteristic parameters of the electrolyte MX. The parameter Φ_{jk} represents two-body interactions where j and k are ions of the same sign.

The equation for the calculation of γ_{Li} is similar to Eq. (14). Making simultaneous equation of Eq. (2) and eqs. (5)–(20), the equilibrium molalities of various species in the extrapolation function $\text{p}K'$ can be obtained. Then the effective ionic strength, $I = (1/2)(m_{\text{Li}} + m_{\text{B}} + m_2)$, can be calculated. In the calculation, the equilibrium molality of the ionic pair $\text{Li}^+\text{B}(\text{OH})_4^-$ was obtained by iteration. The values of $\beta_{\text{LiB}}^{(0)}$ and $\beta_{\text{LiB}}^{(1)}$ used in the calculation were taken from Wang's paper [5], the values of Φ_{BCl} were taken from Simonson's paper [17], the values of the remaining Pitzer's parameters were taken from literature [8].

Then the least-squares estimate of the intercept of the linear regression of $\text{p}K'$ versus I from Eq. (4) is $\text{p}K_a$ and fitting standard deviation s_f are listed in Table 2. Very small values of the standard deviations for the linear regression shown in Table 2 mean that the calculation of ionic interactions has been done successfully by the Pitzer's treatment. These results show that the extrapolation on the basis of Pitzer's theory is a good method for obtaining the ionic association constant. The value of $\text{p}K_a = -1.085$ for $[\text{Li}^+\text{B}(\text{OH})_4^-]$ at 298.15 K in this work is in good agreement with $\text{p}K_a = -1.043$ in our former paper [7] at the same temperature.

3.2. Other thermodynamic quantities for the ionic association process

The values of $\text{p}K_a$ obtained at different temperatures were fitted by the method of least-squares to an

Table 3
Thermodynamic quantities for ion pair [LiB(OH)₄] at 278.15–318.15 K

| T/K | $\Delta G^0/(\text{kJ mol}^{-1})$ | $\Delta H^0/(\text{kJ mol}^{-1})$ | $\Delta S^0/\text{J (kJ mol}^{-1})$ | $\Delta C_p^0/\text{J (kJ mol}^{-1})$ |
|--------|-----------------------------------|-----------------------------------|-------------------------------------|---------------------------------------|
| 318.15 | -6.66 | 1.08 | 24.3 | 22.6 |
| 308.15 | -6.42 | 0.85 | 23.6 | 21.9 |
| 298.15 | -6.19 | 0.64 | 22.9 | 21.2 |
| 288.15 | -5.97 | 0.43 | 22.2 | 20.5 |
| 278.15 | -5.75 | 0.23 | 21.5 | 19.8 |

empirical equation:

$$pK_a = \frac{A_1 K}{T} + A_2 + \frac{A_3 T}{K} \quad (21)$$

The values of the parameters A_i could be obtained: $A_1 = -131.6$, $A_2 = -0.08996$, $A_3 = -1.856 \times 10^{-3}$, with a fitting standard deviation $s_f = 9.6 \times 10^{-4}$.

The standard molar thermodynamic quantities ΔG_m^0 , ΔH_m^0 , ΔS_m^0 and $\Delta C_{p,m}^0$ for the ionic association reaction are calculated by the thermodynamic relationship to the parameters of Eq. (21):

$$\Delta G^0 = (R \ln 10) \left[\frac{A_1 + A_2 T}{K} + A_3 \left(\frac{T}{K} \right)^2 \right] \quad (22)$$

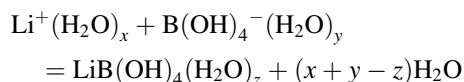
$$\Delta H^0 = (R \ln 10) \left[A_1 - A_3 \left(\frac{T}{K} \right)^2 \right] \quad (23)$$

$$\Delta S^0 = -(R \ln 10) \left[A_2 + 2A_3 \left(\frac{T}{K} \right) \right] \quad (24)$$

$$\Delta C_p^0 = -2(R \ln 10) A_3 \left(\frac{T}{K} \right) \quad (25)$$

And the results calculated from equations (22) to (25) are listed in Table 3.

The implication of the ionic association may be discussed in terms of bonding changes (or interaction changes), and changes in the ordering of the system as ion association occurs. The overall process is:



which takes account of hydration of the species in the ion association reaction. The process can be viewed as three hypothetically separable steps: (1) a new bond or interaction is formed between Li^+ and $\text{B}(\text{OH})_4^-$; (2) the $(x+y-z)$ water molecules are liberated from the hydration spheres; and (3) these liberated water mole-

cules become bound to bulk water. For step (1), ΔH_1^0 and ΔS_1^0 are all expected to be negative. For step (2), ΔH_2^0 and ΔS_2^0 are all expected to be positive as bond and structure are lost, and for step (3), ΔH_3^0 and ΔS_3^0 are expected to be negative. The experimental association entropy ΔS_m^0 must be the sum of the above three terms, that is, $\Delta S_m^0 = \Delta S_1^0 + \Delta S_2^0 + \Delta S_3^0$. From Table 3, $\Delta S_m^0 > 0$ and the values of ΔS_m^0 increase with increasing temperature. The magnitude of the positive changes of ΔS_m^0 would increase if the number of water molecules liberated increases with temperature, or conversely if the bulk water structure, or hydrogen bonding, decreases. The experimental total association enthalpy, ΔH_m^0 is positive and varies with temperature. These results mean that static–electric interaction is essential in the ionic association process. However, the small positive value of ΔH_m^0 in the low temperature may mean that less partial covalent bond was contained in the ionic pair $\text{Li}^+\text{B}(\text{OH})_4^-$. Reurdon [18] also obtained similar conclusions in the study of the ion pair $[\text{MgB}(\text{OH})_4]^+$.

The negative experimental association Gibbs free energy, $\Delta G_m^0 < 0$, means that the ionic association reaction can occur spontaneously under the conditions of constant temperature and pressure. As is well known, association Gibbs energy includes two factors, that is $\Delta G_m^0 = \Delta H_m^0 - T\Delta S_m^0$. In the association reaction of the ion pair $\text{Li}^+\text{B}(\text{OH})_4^-$, $\Delta H_m^0 < T\Delta S_m^0$ leads us to conclude that the association entropy is the driving force for the ionic association reaction. In our former paper the same conclusion was obtained.

Acknowledgements

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