

# Enthalpies of dilution of aqueous $\text{Li}_2\text{B}_4\text{O}_7$ solutions at 298.15 K and application of ion-interaction model

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## Abstract

The enthalpies of dilution have been measured for aqueous  $\text{Li}_2\text{B}_4\text{O}_7$  solutions from 0.0212 to 2.1530 mol kg<sup>-1</sup> at 298.15 K. The relative apparent molar enthalpies,  $L_\phi$ , and relative partial molar enthalpies of the solvent and solute,  $\bar{L}_1$  and  $\bar{L}_2$  were calculated. The thermodynamic properties of the complex aqueous solutions were represented with a modified Pitzer ion-interaction model.

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**Keywords:** Aqueous  $\text{Li}_2\text{B}_4\text{O}_7$ ; Enthalpy of dilution; Relative apparent molar enthalpy; Relative partial molar enthalpy; Ion-interaction model

## 1. Introduction

In the west of China, some salt lake brines contain abundant boron and lithium, in which solute–solvent and solute–solute interactions are complex. The studies on thermochemical properties for the systems related with the brines are essential to understand the effects of temperature on excess free energies and solubility, and to build a thermodynamic model that can be applied for prediction of the properties.

The standard molar enthalpies of formation of hydrated magnesium, lithium, calcium, potassium and sodium borates have been reported [1–4]. The heats of dilution of  $\text{Li}_2\text{B}_4\text{O}_7$ – $\text{Li}_2\text{SO}_4$ – $\text{LiCl}$ – $\text{H}_2\text{O}$  system in the range from a ternary point to the very low concentration at 298.15 K have been studied [5]. In our previous work, water activities, osmotic coefficients, and activity coefficients have been measured for aqueous  $\text{Li}_2\text{B}_4\text{O}_7$  and  $\text{Li}_2\text{B}_4\text{O}_7$ – $\text{LiCl}$ – $\text{H}_2\text{O}$  at 298.15 K by isopiestic and EMF methods [6–9]. However the temperature dependence of the thermodynamic properties for

the aqueous system containing borate has not been reported due to lack of the enthalpy of dilution and heat capacity data.

The purpose of the present study was to determine the enthalpies of dilution and the relative apparent molar enthalpies of  $\text{Li}_2\text{B}_4\text{O}_7$ – $\text{H}_2\text{O}$  system at 298.15 K, from low concentration to supersaturation; to derive the relationship between relative apparent molar enthalpies and the concentrations, and to represent the experimental results for the aqueous  $\text{Li}_2\text{B}_4\text{O}_7$  solution with an ion-interaction model.

## 2. Experimental

### 2.1. Preparations of stock and test solutions

The water used in the preparations and standardization of the solutions in this experiment was deionized and distilled, and the conductance was  $1 \times 10^{-4} \text{ S m}^{-1}$ .  $\text{Li}_2\text{B}_4\text{O}_7$  commercial reagent (made in Beijing Xinhua Reagent Factory, A.R. grade) was recrystallized twice from the water free of  $\text{CO}_2$ . The near saturated stock solution of  $\text{Li}_2\text{B}_4\text{O}_7$  was prepared from purified  $\text{Li}_2\text{B}_4\text{O}_7$  using water in which  $\text{CO}_2$  was removed. The molality of the stock solution was analyzed by mass titration in the presence of mannitol using NaOH

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Table 1  
The enthalpies of dilution of NaCl at 298.15 K

$m_i$ (mol kg <sup>-1</sup> )	$m_f$ (mol kg <sup>-1</sup> )	$\Delta H_{\text{dil}}^a$ (J mol <sup>-1</sup> )	$\Delta H_{\text{dil}}^b$ (J mol <sup>-1</sup> )
0.5039	0.1434	111.062	112.968
0.5039	0.3493	80.579	79.968

<sup>a</sup> Our results.

<sup>b</sup> Millero's results [13].

standard solution as titrant and phenolphthalein as indicator, triplicate samples agreed to 0.07%. The standardization method of the NaOH solution is similar with the reference [6]. All the initial test solutions of concentration lower than that of stock solution were made by diluting a known weight of stock solution with the deionized water. The more concentrated and supersaturated solutions were prepared by concentrating the stock solution in a desiccator containing a strong hygroscopic agent.

## 2.2. Equipment and experimental method

An RD496-III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) was used in this experiment, and has been described in detail before [10,11]. The accuracy and precision of the calorimeter were tested by chemical calibration. The enthalpy of solution of KCl (spectral purity) in purified water at 298.15 K was measured and the average experimental value of  $17.239 \pm 0.052$  kJ mol<sup>-1</sup> for six samples was obtained, in agreement with  $17.241 \pm 0.018$  kJ mol<sup>-1</sup> reported in the literature [10,12].

The amounts of sample solution and water were weighted with accuracy of  $\pm 0.00001$  g into the inner and the outer tubes in the calorimeter cell. In the reference cell both the outer and inner tubes are empty. After thermal equilibration of the two cells for about 2 h, the thin glass bubble at the bottom of the inner tube was broken, and the reaction heat rate measured for about 0.5 h. The measured heats of dilution were reproducible to less than 0.2% for duplicate runs in this work. In order to confirm the measuring reliability the heats

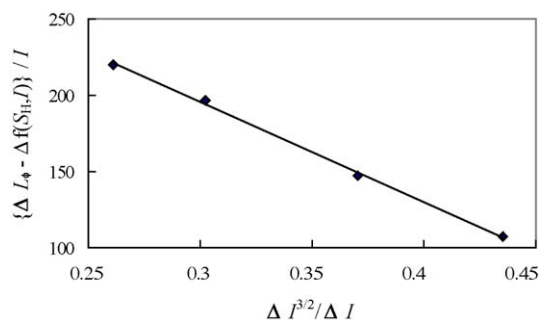


Fig. 1. Plot of  $\{\Delta L_\phi - \Delta f(S_H, I)\}/I$  versus  $\Delta I^{3/2}/\Delta I$  for  $\text{Li}_2\text{B}_4\text{O}_7$  solutions at 298.15 K.

of dilution of NaCl solutions at 298.15 K were measured and compared with the data obtained from a least square equation fitted with the experimental data given by Leung and Millero [13], the results have been listed in Table 1.

## 3. Results and discussion

### 3.1. Enthalpies of dilution and relative apparent molar enthalpies

The enthalpies of dilution (from  $m_i$  to  $m_f$ ) were given by  $\Delta H_{\text{dil}} = Q/n$ , where  $Q$  is the measured heat,  $n$  is the number of mole of solute,  $m_i$  and  $m_f$  are the molalities of the electrolyte in the initial and final solutions, respectively. The experimentally measured dilution enthalpies are given in Table 2.

In concentration range lower than  $0.1$  mol kg<sup>-1</sup>, the relative apparent molar enthalpy,  $L_\phi$ , can be determined with the Debye–Hückel extended limiting law [13,14]:

$$L_\phi = S_H I^{1/2} \left\{ (1 + I^{1/2})^{-1} - \frac{1}{3} \sigma \right\} + BI + CI^{3/2} \quad (1)$$

where  $S_H$  is the Debye–Hückel limiting-law slope  $S_H = \omega A_H$ ;  $\omega = (1/2) \sum v_i z_i^2$ ;  $A_H = 2.8786$  kJ kg<sup>1/2</sup> mol<sup>-3/2</sup>,  $I$  is

Table 2  
The enthalpies of dilution (from  $m_i$  to  $m_f$ ) and the values of  $L_{\phi,i}$  and  $L_{\phi,f}$  for aqueous  $\text{Li}_2\text{B}_4\text{O}_7$  at 298.15 K

No.	$m_i$ (mol kg <sup>-1</sup> )	$m_f$ (mol kg <sup>-1</sup> )	$\Delta H_{\text{dil}}$ (kJ mol <sup>-1</sup> )	$L_{\phi,i}$ (kJ mol <sup>-1</sup> )	$L_{\phi,f}$ (kJ mol <sup>-1</sup> )
1	2.1530	0.0089	-28.180	36.629	8.449
2	1.7096	0.0055	-28.635	34.384	5.749
3	1.2497	0.0047	-29.203	34.254	5.051
4	0.7906	0.0114	-23.541	33.765	10.224
5	0.5321	0.0097	-23.310	32.388	9.078
6	0.4168	0.0114	-21.083	31.307	10.224
7	0.3393	0.0100	-20.979	30.214	9.235
8	0.1445	0.0116	-16.680	27.058	10.378
9	0.1121	0.0033	-21.561	25.343	3.782
10	0.0760	0.0023	-21.231	24.051	2.820
11	0.0599	0.0019	-19.941	22.326	2.385
12	0.0410	0.0029	-17.791	21.217	3.426
13	0.0282	0.0014	-16.731	18.541	1.810
14	0.0212	0.0009	-14.291	15.538	1.247

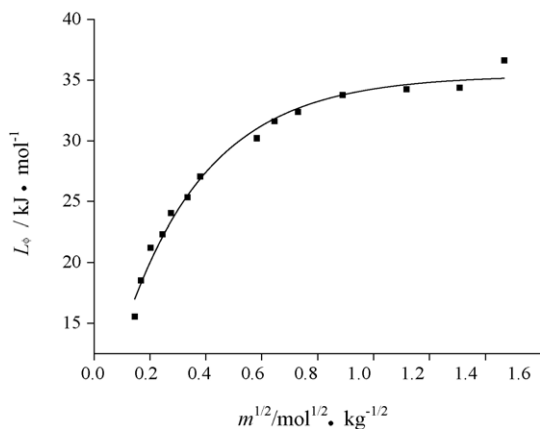


Fig. 2. The relative apparent molar enthalpies of  $\text{Li}_2\text{B}_4\text{O}_7$  solutions plotted versus  $m^{1/2}$  at 298.15 K.

the ionic strength ( $I = 1/2 \sum m_i z_i^2$ )

$$\sigma = (3/I^{3/2})\{(1 + I^{1/2}) - (1 + I^{1/2})^{-1} - 2 \ln(1 + I^{1/2})\} \quad (2)$$

and  $B$  and  $C$  are adjustable parameters, which can be obtained from the experimentally measured enthalpies

$$\Delta H_{\text{dil}}(m_i \rightarrow m_f) = L_{\phi,f} - L_{\phi,i} \quad (3)$$

$$\frac{\Delta L_{\phi} - S_H \Delta [I^{1/2} \{(1 + I^{1/2})^{-1} - \sigma/3\}]}{\Delta I} = B + \frac{C \Delta (I^{3/2})}{\Delta I} \quad (4)$$

$L_{\phi,i}$  and  $L_{\phi,f}$  were the relative apparent molar enthalpies at the initial and the final concentrations, respectively. Using the  $\Delta H_{\text{dil}}$  in the low initial concentration range from 0.1 to 0.02 mol  $\text{kg}^{-1}$ , a plot of the left side of Eq. (4) versus  $\Delta I^{3/2}/\Delta I$  is given in Fig. 1. The  $B$  and  $C$  constants determined by a least-squares fit were 393.0592 and  $-658.0429$ , respectively, with the mean relative deviation of 0.0096. In this experiment, all the final concentrations were lower than 0.1 mol  $\text{kg}^{-1}$ ,

so  $L_{\phi,f}$  can be calculated with Eq. (1), by using the values of  $B$  and  $C$  above. These  $L_{\phi,f}$  values when combined with the enthalpies of dilution yield values for  $L_{\phi,i}$  at the initial concentrations, according to Eq. (3). These data ( $L_{\phi,i}$  and  $L_{\phi,f}$ ) are also presented in Table 2. The relationship between  $L_{\phi}$  and  $m^{1/2}$  is shown in Fig. 2.

The values of  $L_{\phi}$  for  $\text{Li}_2\text{B}_4\text{O}_7$  can be represented by an analytical expression for concentrations greater than 0.02 mol  $\text{kg}^{-1}$ . The equation with a average relative deviation of 0.0207 is:

$$L_{\phi} = 5.524 + 94.31m^{1/2} - 124.09(m^{1/2})^2 + 73.07(m^{1/2})^3 - 15.37(m^{1/2})^4 \quad (5)$$

### 3.2. Relative partial molar enthalpies

Using Eqs. (6) and (7) [15], the relative partial molar enthalpies of the solvent and solute,  $\bar{L}_1$  and  $\bar{L}_2$ , were calculated from  $L_{\phi}$  as represented by Eq. (5), the results are shown in Table 3

$$\bar{L}_1 = -\frac{M_1 m^{3/2}}{2000} \left( \frac{\partial L_{\phi}}{\partial m^{1/2}} \right) \quad (6)$$

$$\bar{L}_2 = L_{\phi} + \frac{m^{1/2}}{2} \left( \frac{\partial L_{\phi}}{\partial m^{1/2}} \right) \quad (7)$$

### 3.3. Ion-interaction model representation for aqueous $\text{Li}_2\text{B}_4\text{O}_7$

The Pitzer ion-interaction model has been successfully used to describe the thermodynamic properties including osmotic and activity coefficient, relative apparent molar enthalpy, heat capacity and density, etc. over a wide ranges of molality and various types of aqueous electrolytes [16]. However, for the complex aqueous  $\text{Li}_2\text{B}_4\text{O}_7$  solutions, a large standard deviation raised when we employed the original ion-interaction (Pitzer) equations to fit the experimental data in

Table 3  
The partial molar enthalpies in the  $\text{Li}_2\text{B}_4\text{O}_7$ – $\text{H}_2\text{O}$  system at 298.15 K

No.	$m$ (mol $\text{kg}^{-1}$ )	$m^{1/2}$ (mol <sup>1/2</sup> $\text{kg}^{-1/2}$ )	$-\bar{L}_1$ (kJ $\text{mol}^{-1}$ )	$\bar{L}_2$ (kJ $\text{mol}^{-1}$ )
1	2.1530	1.4673	0.2245	42.416
2	1.7096	1.3075	0.1438	39.053
3	1.2497	1.1179	0.0620	37.007
4	0.7906	0.8892	0.0236	35.422
5	0.5321	0.7294	0.0211	34.595
6	0.4167	0.6460	0.0216	34.482
7	0.3393	0.5825	0.0213	33.701
8	0.1445	0.3801	0.0140	32.430
9	0.1121	0.3348	0.0113	30.948
10	0.0760	0.2758	0.0078	29.739
11	0.0599	0.2447	0.0060	27.930
12	0.0410	0.2024	0.0039	26.535
13	0.0282	0.1678	0.0025	23.453
14	0.0212	0.1457	0.0017	20.099

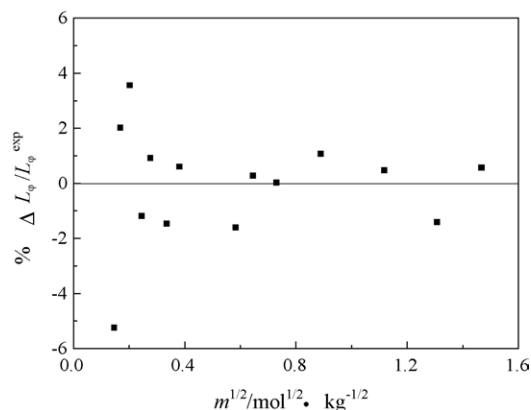


Fig. 3. Percentage deviations of the experimental relative apparent molar enthalpies from the corresponding values calculated by using the ion-interaction model.

this work. So we added a parameter of  $\beta_{MX}^{(2)L}$  into the equations for the relative apparent molar enthalpy, which can be written in the form as

$$L_\phi = \frac{\nu |Z_M Z_X| A_L}{2b} \ln(1 + bI^{1/2}) - 2\nu_M \nu_X RT^2 m B_{MX}^L - 2(\nu_M \nu_X)^2 RT^2 m^2 C_{MX}^L \quad (8)$$

$$B_{MX}^L = \beta_{MX}^{(0)L} + \beta_{MX}^{(1)L} g(x_1) + \beta_{MX}^{(2)L} g(x_2) \quad (9)$$

$(x_1 = \alpha_1 I^{1/2}; x_2 = \alpha_2 I^{1/2})$

$$g(x) = \frac{2[1 - (1 + x) \exp(-x)]}{x^2} \quad (10)$$

where  $\beta_{MX}^{(0)L}$ ,  $\beta_{MX}^{(1)L}$ ,  $\beta_{MX}^{(2)L}$  and  $C_{MX}^L$  are ion-interaction parameters that are dependent on temperature and pressure. The quantities  $\alpha_1$  and  $b$  were set to the standard values of 1.4 and  $1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ , respectively. The value of  $\alpha_2$  could be adjusted from 3 to  $50 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  [17], and the value of  $10 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  was taken at which the minimum standard deviation of least-square analysis was obtained.  $A_L$  is Pitzer–Debye–Hückel parameter for the apparent molar enthalpy,  $\nu = \nu_M + \nu_X$ , where  $\nu_M$  and  $\nu_X$  are the stoichiometric numbers of the cations and anions for one molecular,  $Z_M$  and  $Z_X$  are the charges of the cation and the anion, respectively in the salt  $M_{\nu_M} X_{\nu_X}$ ;  $m$  is the molality

of the electrolyte solution,  $I$  is the ionic strength. The ion-interaction parameters were estimated by fitting the equation to experimental  $L_\phi$  data in Table 2, based on stoichiometric molalities of  $\text{Li}_2\text{B}_4\text{O}_7$  (aq), and the parameter values of  $5.5252 \times 10^{-3}$ ,  $-3.0111 \times 10^{-2}$ ,  $-0.9818$ , and  $-6.9133 \times 10^{-4}$  for  $\beta_{MX}^{(0)L}$ ,  $\beta_{MX}^{(1)L}$ ,  $\beta_{MX}^{(2)L}$  and  $C_{MX}^L$  were obtained with the average relative deviation of 0.0157. The experimental relative apparent molar enthalpies were compared with the corresponding values calculated by using the ion-interaction model and shown in Fig. 3, which indicated that the experimental data can be represented with the modified ion-interaction model.

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