Journal of Thermal Analysis and Calorimetry, Vol. 95 (2009) 2, 377–380

ENTHALPIES OF DILUTION OF AQUEOUS MIXED SOLUTIONS OF LiCl AND $Li_2B_4O_7$ AT 298.15 K

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The enthalpies of dilution, $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$, have been measured for $LiCl+Li_2B_4O_7+H_2O$ system at T=298.15 K by using a RD496-III microcalorimeter. A suitable measurement method was used to obtain the better data of the enthalpies of dilution for the ternary mixing solutions to low concentrations. The relative apparent molar enthalpies, L_ϕ, have been determined and the relationships between L_ϕ and ionic strength I at different molal fractions of $Li_2B_4O_7$ were obtained. The effect of the borate $Li_2B_4O_7$ on the heat properties for the studied system was discussed.

Keywords: *aqueous mixed solution, calorimetric method, enthalpy of dilution, $LiCl+Li_2B_4O_7+H_2O$, relative apparent molar enthalpy*

Introduction

Many of the natural salt-lake brines in the northwest regions of China contain abundant boron and lithium, in which solute–solvent and solute–solute interactions are complex. Studies on thermodynamic properties by calorimetric method for the ternary systems containing boron and lithium are essential for understanding the effects of temperature on excess free energies and for creating a comprehensive thermodynamic model to be applied to the predictions of thermodynamic properties and solubilities and to the development of the separation process of salts from the brines.

Literature data on thermodynamic properties of molar excess enthalpies, activity coefficients and partial molar enthalpies at infinite dilution for the binary mixtures containing perfluoroalkanes and dimethylsulfoxide have been described well using the models based on an extended quasi-chemical group contribution theory [1, 2]. The heats of dilution and heat capacities of the $Li_2B_4O_7+Li_2SO_4+LiCl+H_2O$ and its subsystems $Li_2B_4O_7+Li_2SO_4+H_2O$ and $Li_2B_4O_7+LiCl+H_2O$ have been measured from the initial ionic strengths of the eutonic point solutions to the low concentrations at 298.15 K respectively using an LKB-87001 calorimeter. However the molal fraction of $Li_2B_4O_7$ of 0.0009698 for the eutonic point solution of the $Li_2B_4O_7+LiCl+H_2O$ system was fixed for the measurements of the heats of dilution of the ternary system [3]. In our previous work, water activities, osmotic coefficients, and activity coefficients have been measured for aqueous $Li_2B_4O_7$ and $Li_2B_4O_7+LiCl+H_2O$ at 298.15 K by isopiestic and e.m.f. (electromotive force) methods [4, 5]. The enthalpies of dilution and the relative apparent molar enthalpies of $Li_2B_4O_7+H_2O$ system at 298.15 K and the representation with Pitzer ion-interaction model have been reported [6]. However the temperature dependence of the thermodynamic properties and the concentration dependence of the enthalpies of dilution for the mixed aqueous solutions containing borate have rarely been reported due to lack of the data of enthalpy of dilution and heat capacity for these ternary systems.

The purposes of the present studies were to determine the enthalpies of dilution and the relative apparent molar enthalpies for $LiCl+Li_2B_4O_7+H_2O$ system at three different molal fractions of $Li_2B_4O_7$ at 298.15 K by using a microcalorimeter, to derive the relationships between L_ϕ and ionic strength I at different molal fractions of $Li_2B_4O_7$, and to discuss the effect of the molal fractions on the relative apparent molar enthalpies L_ϕ.

Experimental

Preparations of stock and test solutions

The water used in the preparation and standardization of the solutions in this experiment was deionized and distilled, and the conductance was $1\cdot10^{-4}$ S m^{-1}. $Li_2B_4O_7$ commercial reagent (made in Beijing Xinhua Reagent Factory, A. R. grade) was recrystallized

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1388–6150/$20.00

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twice from the water free of CO_2. The near saturated stock solution of $Li_2B_4O_7$ was prepared from purified $Li_2B_4O_7$ using water in which CO_2 was removed. $LiCl\cdot H_2O$ commercial reagent (made in Beijing Chemical Reagent Factory, A.R. grade) was recrystallized twice. The purified LiCl was used to prepare a stock solution.

The molality of the stock solution of $Li_2B_4O_7$ was analyzed by mass titration in the presence of mannitol using NaOH standard solution as titrant and phenolphthalein as indicator, triplicate samples agreed to 0.07%. The molality of the stock solution of LiCl was analyzed by gravimetric chloride analysis with five replicate samples in agreement to less than 0.05%. The $LiCl+Li_2B_4O_7$ (B) mixed stock solutions were prepared by combining appropriate masses of the stock solutions of LiCl, $Li_2B_4O_7$, and purified H_2O. The molal fractions of $Li_2B_4O_7$, Y_B, for three mixed stock solutions were 0.6885, 0.3795 and 0.1938, respectively.

$$Y_B = m_{Li_2B_4O_7}/(m_{LiCl} + m_{Li_2B_4O_7}) \quad (1)$$

The experiments were performed from diluting the mixed stock solutions with different values of Y_B and the molalities of the experimental points were distributed uniformly under the saturated molality line, Fig. 1.

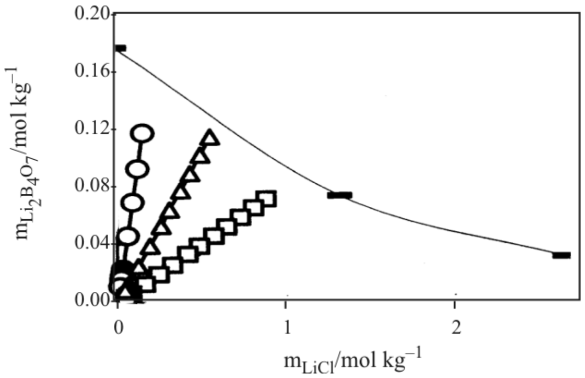

Fig. 1 The distribution of experimental points for LiCl–$Li_2B_4O_7$–H_2O system

Equipment and experimental method

An RD496-III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) was used in these measurements, and has been described in detail before [7, 8]. The test for accuracy and precision of the calorimeter by chemical calibration and the measurement procedure for the heats of dilution were similar with the literatures [6, 7]. The mixed stock solutions with the three different values of Y_B were taken as initial experimental solutions and different amounts of water in appropriate proportion added to the initial solutions for all the measurements of the heats of dilution. The heats of dilution in the ionic strength range lower than 0.1 mol kg^{-1} were obtained by subtraction using the experimental data in order to use a Debye–Hückel extended limiting law.

The amounts of sample solution and water were weighed with accuracy of ±0.00001 g into the inner and the outer tubes in the calorimeter cell. 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 enthalpies 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 Millero [9], the results have been listed in Table 1.

Table 1 The enthalpies of dilution of NaCl at 298.15 K

m_i/ mol kg^{-1}	m_f/ mol kg^{-1}	$\Delta H_{dil}{}^{*}$/ J mol^{-1}	$\Delta H_{dil}{}^{\#}$/ J mol^{-1}
0.5039	0.1434	111.062	112.968
0.5039	0.3493	80.579	79.968

*Our results, $^{\#}$Millero's results [9]

Results and discussion

Enthalpies of dilution and relative apparent molar enthalpies

The enthalpies of dilution ($I_i \rightarrow I_f$) were given by $\Delta H_{dil}=Q/n$, where Q was the measured heat, n was the number of mole of solute, I_i and I_f were the ionic strength of the electrolyte in the initial and final solutions, respectively. The measured enthalpies of dilution for the mixed system are given in Tables 2–4. In the ionic strength range lower than 0.1 mol kg^{-1}, the relative apparent molar enthalpy, L_ϕ, can be determined with the Debye–Hückel extended limiting law [6, 9], and the equations are:

$$\Delta H_{dil}(I_i \rightarrow I_f) = L_{\phi,f} - L_{\phi,i} \quad (2)$$

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

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

$$\sigma = (3/I^{3/2})\{(1 + I^{1/2}) - (1 + I^{1/2})^{-1} - 2\ln(1 + I^{1/2})\} \quad (5)$$

where S_H is the Debye–Hückel limiting-law slope (S_H=ωA_H; ω=(1/2)$\Sigma v_i z_i^2$; A_H=2.8786 kJ kg$^{1/2}$ mol$^{-3/2}$), S_H=3.303 kJ kg$^{1/2}$ mol$^{-3/2}$ for the mixed system, I is the ionic strength (I=1/2$\Sigma m_i z_i^2$) and B and C are adjustable parameters, which can be obtained by using the ΔH_{dil} in the low initial ionic strength range from 0.1 to 0.02 mol kg^{-1}, and plotting the left side of Eq. (4) *vs.* $\Delta I^{3/2}/\Delta I$ for the three series at the different Y_B , Figs 2–4. The values of B and C and the mean relative deviations of the fits were listed in Table 5.

Table 2 The enthalpies of dilution (from I_i to I_f) and the values of L_ϕ for LiCl–$Li_2B_4O_7$–H_2O system at 298.15 K (Y_B=0.6885)

No.	I_i/mol kg^{-1}	I_f/mol kg^{-1}	ΔH_{dil}/kJ mol^{-1}
1	0.6644	0.6644	0
2		0.5006	–0.447
3		0.4116	–0.632
4		0.2763	–1.539
5		0.1989	–1.958
6		0.1041	–2.679
7		0.0942	–2.697
8		0.0796	–2.882
9		0.0574	–3.045
10		0.0472	–3.148
11		0.0392	–3.225
12		0.0343	–3.281
13		0.0245	–3.378
14		0.0174	–3.433

Table 3 The enthalpies of dilution (from I_i to I_f) and the values of L_ϕ for LiCl–$Li_2B_4O_7$–H_2O system at 298.15 K (Y_B=0.3795)

No.	I_i/mol kg^{-1}	I_f/mol kg^{-1}	ΔH_{dil}/kJ mol^{-1}
1	1.0212	1.0212	0
2		0.8669	–0.058
3		0.7043	–0.203
4		0.6327	–0.260
5		0.5164	–0.462
6		0.3898	–0.779
7		0.3056	–0.831
8		0.1691	–1.211
9		0.0945	–1.396
10		0.0760	–1.436
11		0.0595	–1.544
12		0.0559	–1.609
13		0.0465	–1.667
14		0.0290	–1.742
15		0.0153	–1.993

Table 4 The enthalpies of dilution (from I_i to I_f) and the values of L_ϕ for LiCl–$Li_2B_4O_7$–H_2O system at 298.15 K (Y_B=0.1938)

No.	I_i/mol kg^{-1}	I_f/mol kg^{-1}	ΔH_{dil}/kJ mol^{-1}
1	1.2751	1.2751	0
2		1.0599	–0.021
3		1.0457	–0.046
4		0.9369	–0.035
5		0.7306	–0.090
6		0.6973	–0.108
7		0.6259	–0.153
8		0.5167	–0.196
9		0.3924	–0.208
10		0.2911	–0.271
11		0.1673	–0.356
12		0.0287	–0.466

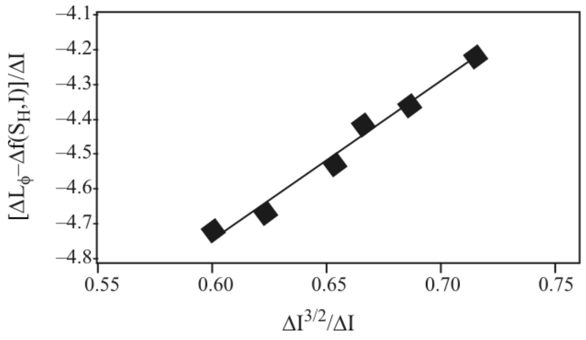

Fig. 2 Plot of {ΔL_ϕ–$\Delta f(S_H,I)$}/ΔI *vs.* $\Delta I^{3/2}/\Delta I$ for LiCl–$Li_2B_4O_7$–H_2O system at 298.15 K (Y_B=0.6885)

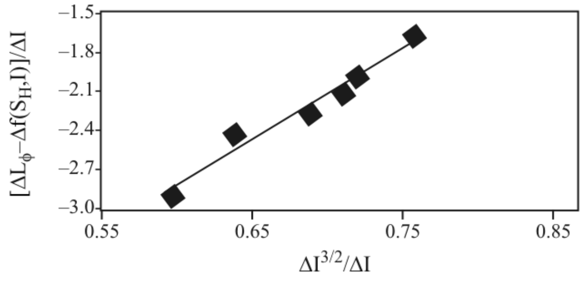

Fig. 3 Plot of {ΔL_ϕ–$\Delta f(S_H,I)$}/ΔI *vs.* $\Delta I^{3/2}/\Delta I$ for LiCl–$Li_2B_4O_7$–H_2O system at 298.15 K (Y_B=0.3795)

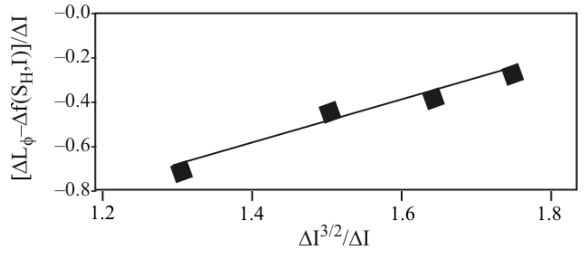

Fig. 4 Plot of {ΔL_ϕ–$\Delta f(S_H,I)$}/ΔI *vs.* $\Delta I^{3/2}/\Delta I$ for LiCl–$Li_2B_4O_7$–H_2O system at 298.15 K (Y_B=0.1938)

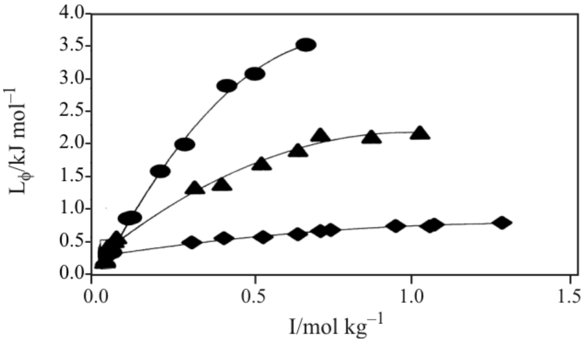

Fig. 5 The relative apparent molar enthalpies of $LiCl–Li_2B_4O_7–H_2O$ system plotted *vs.* I at 298.15 K: ● – Y_B=0.6885, ▲ – Y_B=0.3795, ◆ – Y_B=0.1938

Table 5 Values of B and C for the extended Debye–Hückel equation

Y_B	B	C	Rel. dev.
0.6885	–7.4607	4.5392	0.003
0.3795	–6.9844	6.9609	0.015
0.1938	–1.9159	0.9489	0.026

In this experiment, the relative apparent molar enthalpies, L_ϕ, can be calculated by using the Eq. (3) with the values of B and C above. The enthalpies, L_ϕ, at the different Y_B are presented in Fig. 5.

Relationships between relative apparent molar enthalpy and ionic strength

The relationships between L_ϕ and ionic strength I can be represented with the three experimental Eqs (6)–(8) for the different Y_B respectively and shown in Fig. 5.

$$L_{\phi 1} = -6.0056I^2 + 9.3804I - 0.0557,\quad \text{at } Y_B = 0.6885,\ R^2 = 0.9985 \tag{6}$$

$$L_{\phi 2} = -1.9212I^2 + 3.7467I + 0.3197,\quad \text{at } Y_B = 0.3795,\ R^2 = 0.9831 \tag{7}$$

$$L_{\phi 3} = -0.2733I^2 + 0.7115I + 0.2513,\quad \text{at } Y_B = 0.1938,\ R^2 = 0.9887 \tag{8}$$

It is found from Fig. 5 that the values of the relative apparent molar enthalpies increase with increasing the ionic strengths and increase obviously with increasing the values of Y_B at the same ionic strength, for example, the values of the relative apparent molar enthalpies are 0.539 kJ mol^{-1} for Y_B=0.1938, 1.713 kJ mol^{-1} for Y_B=0.3795 and 3.133 kJ mol^{-1} for Y_B=0.6885 at I=0.5 mol kg^{-1}, which indicates that the borate, $Li_2B_4O_7$, could effect greatly on the heat properties for the studied mixed system.

Acknowledgements

The authors thank Professor Rongzu Hu and Professor Shengli Gao for their helps with this work. This project was supported by the National Nature Science Foundation of China. (No. 20373084).

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DOI: 10.1007/s10973-008-9239-0