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HEATS OF DILUTION, HEAT CAPACITIES AND APPARENT MOLAL ENTHALPIES OF $Li_2B_4O_7$–Li_2SO_4–LiCl–H_2O SYSTEMS AT 298.15 K

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Abstract

The heats of dilution and heat capacities of the $Li_2B_4O_7$–Li_2SO_4–LiCl–H_2O quaternary system and the $Li_2B_4O_7$–Li_2SO_4–H_2O and $Li_2B_4O_7$–LiCl–H_2O ternary systems were measured in the range of ionic strengths from 19 to 0.1 at 298.15 K. The data of the heat of dilution were extrapolated to infinite dilution by use of Debye-Hückel limiting law to obtain relative apparent molal enthalpies over the range of ionic strengths I from 19 to 0.0001.

Keywords: heat capacities, heats of diluton, $Li_2B_4O_7$–Li_2SO_4–LiCl–H_2O systems

Introduction

Some of the salt lake brine on the Qinhai-Xizang plateau in China contain sodium, potassium and magnesium chlorides and sulfates with aboundant boron and lithium. In the late period of evaporation, because of deposition of most salts of sodium and potassium, the brine becomes actually the Li^+, Mg^{2+}/Cl^-, SO_4^{2-}, $B_4O_7^{2-}$–H_2O system. The phase equilibrium and properties of saturated solution in $Li^+/B_4O_7^{2-}$, SO_4^{2-}, Cl^-–H_2O systems have been studied [1, 2]. The enthalpies of dilution of $Mg^{2+}/B_{2n}O_{3n+1}^{2-}$, Cl^-–H_2O (n = 1, 2, 3) systems [3] and Li^+, Na^+, K^+, Mg^{2+}/Cl^- systems [4] have been studied in previous work.

This paper reports the heats of dilution, heat capacities and apparent molal enthalpies of the $Li_2B_4O_7$–Li_2SO_4–LiCl–H_2O quaternary system and $Li_2B_4O_7$–Li_2SO_4–H_2O and $Li_2B_4O_7$–LiCl–H_2O ternary systems at 298.15 K. The Debye-Hückel limiting law was used to extrapolate the heats of dilution in multi- component system. This study may be valuable for understanding the thermochemical properties of brine in the late period of evaporation after deposition of salts of sodium and potassium, for extraction and separation of boron and lithium from salt lake brine, and for the utilization of brine.

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Experimental

Lithium sulfate and lithium chloride used in the experiments were recrystallized from A.R. $Li_2SO_4{\cdot}H_2O$ and $LiCl{\cdot}H_2O$. Lithium tetraborate, $Li_2B_4O_7{\cdot}3H_2O$ was synthesized from analytical reagents (LiOH and H_3BO_3). Its composition is (wt%) Li_2O 13.39, B_2O_3 62.39, H_2O 24.53, B_2O_3/Li_2O (mole ratio) 1.991 (theoretical values are: 13.39, 62.39, 24.32, 2.000). It has been identified as the compound $Li_2B_4O_7{\cdot}3H_2O$ by X-ray diffraction analysis. The eutonic point solution of $Li_2B_4O_7$–Li_2SO_4–LiCl–H_2O (LB1) quaternary system and $Li_2B_4O_7$–Li_2SO_4–H_2O (LB2) and $Li_2B_4O_7$–LiCl–H_2O (LB3) subsystems were prepared by isothermal (25.00±0.03°C) method, their compositions are given in Table 1. Redistilled water was used in the recrystallization of the reagents, synthesis of the borate and preparation of equilibrium mixtures.

Table 1 Components of boron–lithium systems

Systems	$Li_2B_4O_7$/mol kg^{-1}	Li_2SO_4/mol kg^{-1}	LiCl/mol kg^{-1}	I
LB1	0.01127	0.00315	17.2097	17.2530
LB2	0.03201	3.0228	–	9.1644
LB3	0.01843	–	18.9863	19.0416

An LKB-87001 precision calorimeter and a thermostatic bath (25.00±0.01°C) were used to measure the heat of dilution and the heat capacity. The accuracy of the calorimeter has been tested previously [3] by measuring the heat effect of a standard reaction of trishydroxymethylaminomethane (THAM) with HCl at 298.15 K. A weighed amount of the solution (titrand) was loaded in a glass reaction vessel. The vessel with contents was immersed into a thermostat at 25.00±0.01°C for 2 h, then pre-fixed volumes of water (titrant) were added by means of a pump. The titration rate was 3.1344±0.0016 cm^3 min^{-1}. The heat of dilution caused temperature changes. The temperature changes in the reaction vessel were measured as an electrical potential output by a thermistor with a resistance $R = 2000\ \Omega$. The output was amplified by a microvolt amplifier and recorded. The heat capacity and leakage constant were measured by twice heating electrically for 500 s using 200 mW and 500 mW power range, and once lowering the temperature before and after each titration [5]. The results of calorimetric measurements were processed by means of a computer program to obtain the heats of dilution and heat capacities according to the following Eqs (1–2):

$$C_\mathrm{i} = W(t)^{-1}\left(C_\mathrm{l} + \frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}t}t\right) \quad (1)$$

$$\Delta H_d = -M^{-1}\{C(t)[T(t) - T_o] + Kt[T(t) - T_s] + t\frac{dC_B}{dt}(T_o - T_B)\} \tag{2}$$

where t/s denotes time, C_i/kJ K^{-1} kg^{-1} is the heat capacity of the solution of ionic strength I_i, ΔH_d/kJ mol^{-1} is the heat of dilution, $W(t)$/kg is the mass of the solution in the reaction vessel at t, C_1/kJ K^{-1} is the initial heat capacity of the solution before titration, dC_B/dt/kJ K^{-1} s^{-1} is the rate of change of the heat capacity with time, M/mol is the sum of the molalities of all solutes in the titrand, $C(t)$/kJ K^{-1} is the total heat capacity of the reaction vessel with titrand and titrant at t, K/kJ K^{-1} s^{-1} is the leakage constant, $T(t)$/K is the temperature of the outer surface of the calorimeter at t, T_o/K is initial temperature of the titrand, T_s/K is the final equilibrium temperature, T_B/K is the temperature of titrant.

Results and discussion

The heats of dilution and heat capacities of the $Li_2B_4O_7$–Li_2SO_4–LiCl–H_2O quaternary system and the $Li_2B_4O_7$–Li_2SO_4–H_2O and $Li_2B_4O_7$–LiCl–H_2O subsystems were measured a range from the initial ionic strength I_o to I_i at 298.15 K. The results are given in Table 2. In Table 2, M_i/mol kg^{-1} is the sum of molalities of all the solutes in the systems; C/kJ kg^{-1} K^{-1} is the specific heat capacity, ΔH_d/kJ mol^{-1} *is the heat of dilution*; $^{\Phi}L$/kJ mol^{-1} is the apparent molal enthalpy.

The apparent molal enthalpies $^{\Phi}L_i$ can be obtained from

$$^{\Phi}L_i = {}^{\Phi}L_f - \Delta H_d(I_i - I_f) \tag{3}$$

where $^{\Phi}L_f$ is the apparent molal enthalpy at the final ionic strength ($I < 0.1$). The $^{\Phi}L_f$ values were calculated using the extended limiting law equation [6–8]

$$^{\Phi}L = S_H I^{1/2}\left[(1 + I^{1/2})^{-1} - \frac{\sigma}{3}\right] + BI + CI^{3/2} \tag{4}$$

where S_H in the Debye-Hückel limiting law slope ($S_H = wA_H$; $w = 1/2\Sigma V_i Z_i^2$, V_i and Z_i are the number and valence of the ion i; and A_H=2.8786 kJ mol^{-1} $ion^{-1/2}$ at 298.15 K);

$$\sigma = \frac{3}{I^{3/2}}[(1 + I^{1/2}) - (1 + I^{1/2})^{-1} - 2\ln(1 + I^{1/2})] \tag{5}$$

and B, C are adjustable parameters. The values of B and C have been determined from the experimentally measured enthalpies of dilution

$$\Delta H_d(I_i \rightarrow I_f) = -\Delta^{\Phi}L(I_i \rightarrow I_f) \tag{6}$$

using

$$\frac{\Delta^{\Phi}L - S_{\mathrm{H}}\Delta\{I^{1/2}[(1+I^{1/2})^{-1} - \sigma/3]\}}{\Delta I} = B + C\frac{\Delta I^{3/2}}{\Delta I} \tag{7}$$

The plots of the left hand side of Eq. (7) *vs.* $\Delta I^{3/2}/\Delta I$ for the boron–lithium systems are given in Fig. 1. Equations (4) and (7) were originally suggested to be useful in extrapolating heat-of-dilution data to infinite dilution and to be used in the molality range 0 to 0.1 [6]. However, it was found later [7–10] that Eqs. (4) and (7) would represent heat-of-dilution data for electrolytes as well as seawater within experimental error for the approximate molality and ionic strength from 0.1 to 1.0. So that, Fig. 1 was plotted using heat-of-dilution data *vs.* ionic strength less than 1.0 for the boron–lithium systems.

Table 2 Heats of dilution, heat capacities and apparent molal enthalpies of boron–lithium systems at 298.15 K

I_0	I_i	M_i/mol kg^{-1}	C/kJ kg^{-1} K^{-1}	H_d/kJ mol^{-1}	L/kJ mol^{-1}
		LB1			
17.2530	17.2530	17.2227	2.6447	0.0000	17.5247
	16.0847	16.0646	2.7066	−1.0074	16.5173
	15.0077	14.9889	2.7669	−2.2139	15.3108
	14.3207	14.3028	2.8075	−2.9757	14.5490
	13.4781	13.4612	2.8589	−3.9080	13.6167
	12.3567	12.3412	2.9313	−5.1339	12.3908
	11.1084	11.0945	3.0171	−6.4182	11.1065
	10.0160	10.0034	3.0978	−7.4404	10.0843
	9.1955	9.1840	3.1618	−8.1567	9.3680
	8.1782	8.1683	3.2455	−9.0920	8.4327
	7.1659	7.1573	3.3346	−10.0213	7.5034
	6.2685	6.2609	3.4187	−10.7467	6.7780
	5.1058	5.0996	3.5355	−11.5406	5.9841
	4.1520	4.1470	3.6384	−12.2188	5.3059
	3.0789	3.0751	3.7631	−12.8927	4.6320
	2.0701	2.0674	3.8899	−13.4823	4.0424
	1.0068	1.0054	4.0346	−14.1256	3.3991
	0.8455	0.8443	4.0576	−14.2444	3.3234
	0.6001	0.5993	4.0936	−14.4485	3.0922
	0.4177	0.4171	4.1204	−14.6822	2.8945
	0.2011	0.2008	4.1530	−15.0870	2.4813
	0.1052	0.1050	4.1677	−15.4481	2.0766

Table 2 Continued

I_0	I_i	M_i/mol kg^{-1}	C/kJ kg^{-1} K^{-1}	H_d/kJ mol^{-1}	L/kJ mol^{-1}
			LB2		
9.1645	9.1645	3.0548	3.3372	0.0000	7.5496
	8.2249	2.7417	3.4037	0.4528	7.0968
	7.1947	2.3982	3.4794	–0.9852	6.5644
	6.0532	2.0177	3.5723	–1.4879	6.0617
	5.0586	1.6862	3.6568	–1.8526	5.6970
	4.0380	1.3460	3.7493	–2.2127	5.3369
	3.0258	1.0086	3.8476	–2.5560	4.9936
	2.0240	0.6747	3.9509	–2.9176	4.6320
	1.0380	0.3460	4.0606	–3.6778	3.8718
	0.8173	0.2724	4.0857	–3.8783	3.4597
	0.6047	0.2016	4.1108	–4.1450	3.2305
	0.4498	0.1499	4.1292	–4.4453	3.0388
	0.2113	0.0704	4.1581	–4.9814	2.5653
	0.1599	0.0533	4.1643	–5.1670	2.3826
			LB3		
19.0416	19.0416	19.0047	2.6020	0.0000	18.9821
	18.2552	18.2198	2.6388	–0.4636	18.5185
	17.0138	16.9808	2.6999	–1.7665	17.2156
	16.4071	16.3754	2.7309	–2.3988	16.5833
	15.3327	15.3030	2.7886	–3.5604	15.4217
	14.4088	14.3809	2.8326	–4.3936	14.5885
	13.1347	13.1092	2.9171	–5.9094	13.0727
	12.0646	12.0412	2.9853	–6.9397	12.0424
	11.2161	11.1944	3.0426	–7.7083	11.2738
	10.1863	10.1666	3.1158	–8.8288	10.1533
	9.1953	9.1775	3.1903	–9.8159	9.1662
	8.0750	8.0594	3.2807	–10.8192	8.1629
	7.4721	7.4576	3.3317	–11.3459	7.6362
	6.0898	6.0780	3.4572	–12.3094	6.6727
	5.1897	5.1796	3.5451	–13.0110	5.9711
	4.0210	4.0132	3.6681	–13.7755	5.2066

Table 2 Continued

I_o	I_i	M_i/mol kg^{-1}	C/kJ kg^{-1} K^{-1}	H_d/kJ mol^{-1}	L/kJ mol^{-1}
		LB3			
19.0416	3.1066	3.1005	3.7719	–14.3747	4.6074
	2.0811	2.0771	3.8970	–14.9705	4.0116
	1.0223	1.0204	4.0367	–15.6004	3.3817
	0.8235	0.8219	4.0643	–15.7334	3.1664
	0.6377	0.6365	4.0907	–15.8762	3.0333
	0.4084	0.4076	4.1238	–16.0721	2.8316
	0.2000	0.1996	4.1543	–16.4660	2.4589
	0.1108	0.1106	4.1677	–16.8814	2.1007

The values of B and C determined by a least-squares fit are given in Table 3. The sum of square errors of the least-squares fit for all the systems is less than 0.7 kJ mol^{-1}.

The apparent molal enthalpies $^{\Phi}L_f$ over an ionic strength range I_f from 1.0 to 0.0001 were calculated from Eq. (4) using the coefficients B, C given in Table 3; the results are given in Table 4.

The apparent molal enthalpies $^{\Phi}L$ of boron–lithium systems to cover the ionic strength range from 19 to 0.1 can be calculated by Eq. (3), using the heat of dilution ΔH_a and the apparent molal enthalpies $^{\Phi}L_f$ (LB1 2.0766; LB2 2.3826; LB3 2.1007) of the final ionic strength I (LB1 0.1052; LB2 0.1599; LB3 0.1108). The results are given in Table 2.

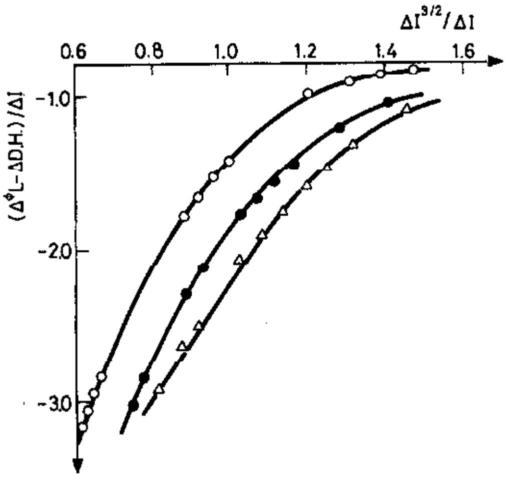

Fig 1 Plots of [$\Delta^{\Phi}L - \Delta D.H.$]/$\Delta I$ vs. $\Delta I^{3/2}/\Delta I$ for $Li_2B_4O_7$–Li_2SO_4–LiCl–H_2O systems at 298.15 K; • – LB1; o – LB2; Δ – LB3

Table 3 Values of B and C for the extended Debye-Hückel equation at 298.15 K

System	B	C	R
LB1	–5.09947	3.01925	0.27
LB2	–4.79223	2.90881	0.64
LB3	–5.12801	2.86884	0.07

Table 4 Apparent molal enthalpies of $Li_2B_4O_7$–Li_2SO_4–LiCl–H_2O systems over the ionic strength range 0.1–0.0001at 298.15 K

I	$^{\Phi}L$/kJ mol^{-1}		
	LB1	LB2	LB3
0.1	2.2711	2.3257	2.2802
0.09	2.1854	2.2348	2.1936
0.08	2.0918	2.1360	2.0992
0.07	1.9885	2.0274	1.9950
0.06	1.8734	1.9070	1.8791
0.05	1.7432	1.7714	1.7480
0.04	1.5925	1.6153	1.5964
0.03	1.4132	1.4304	1.4161
0.02	1.1877	1.1993	1.1897
0.01	0.8726	0.8785	0.8736
0.005	0.6338	0.6368	0.6343
0.001	0.2892	0.2898	0.2893
0.0001	0.06294	0.0630	0.06295

To summarize, the heats of dilution and the heat capacities of the $Li_2B_4O_7$–Li_2SO_4–LiCl–H_2O quaternary system and the $Li_2B_4O_7$–Li_2SO_4–H_2O and $Li_2B_4O_7$–LiCl–H_2O subsystems have been measured over the ionic strength I from 0.1 to 19 at 298.15 K.The apparent molal enthalpies have been calculated by means of Debye-Hückel limiting law covering the ionic strength range from 19 to 0.0001. The results make clear that the heats of dilution are negative which means that the dilution processes of various systems are exothermic. When the ionic strength I is higher or the molalities are greater, the heat capacities are smaller and the apparent molal enthalpies are greater. All these systems are similar to single electrolyte solutions of alkaline-earth metal in respect of heat effects.

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