Heat Capacities and Thermodynamic Functions of the Aqueous $Li_2B_4O_7$ Solution in the Temperature Range from 80 K to 355 K

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The molar heat capacities of the aqueous $Li_2B_4O_7$ solution at the concentration of 0.0187 mol·kg^{-1} have been measured using a precision automated adiabatic calorimeter in the temperature range from 80 K to 355 K. The dependence of the molar heat capacity on temperature was given as a function of the reduced temperature X by polynomial equations $C_{p,\mathrm{m}}$ (J·K^{-1}·mol^{-1}) $= 25.44 + 11.99X + 0.454X^2 + 1.671X^3$ for the solid phase [80 K∼258 K, $X = (T - 169)/89$] and $C_{p,\mathrm{m}}$ (J·K^{-1}·mol^{-1}) $= 77.33$ for the liquid phase [274 K∼355 K], respectively. The phase transition of the solution was determined on the basis of the curve of the heat capacity with temperature. The temperature of the phase transition was observed at 273.04 K, and the enthalpy and entropy of the phase transition were calculated to be $\Delta H_\mathrm{m} = 4.650$ kJ·mol^{-1} and $\Delta S_\mathrm{m} = 17.03$ J·K^{-1}·mol^{-1}, respectively. According to the polynomial equations and thermodynamic relationship, the values of the thermodynamic function of the aqueous $Li_2B_4O_7$ solution relative to 298.15 K were calculated in the temperature range from 80 K to 355 K with an interval of 5 K. The relative apparent molar heat capacities of the aqueous $Li_2B_4O_7$ solution, $C_{p,\phi}$, were calculated every 5 K in the temperature range from 80 K to 355 K from the experimental heat capacities of the aqueous $Li_2B_4O_7$ solution and the heat capacities of pure water.

Introduction

Boron and lithium play important roles in many industries. Boron compounds are used extensively in the pigment, papermaking, medicine, and textile industries, etc. Advanced rechargeable lithium batteries with high voltage and energy density as power sources of many portable instruments and electric vehicles are currently attracting great interest because of the environmental and resource benefits.

In China, there are hundreds of salt lakes which contain abundant mineral resources, such as boron, lithium, magnesium, and many others. Thermodynamic data for salt lake systems are required for the exploitation of the salt lake resource. The standard molar enthalpies of formation of hydrated magnesium, lithium, calcium, potassium, and sodium borates have been reported.[1−4] The enthalpies of dilution of the $Li_2B_4O_7-Li_2SO_4-LiCl-H_2O$ system in the range from a ternary point to very low concentration at 298.15 K have been studied. 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 EMF methods.[5−8] However, little information is available regarding the heat capacities of their aqueous solutions as a function of temperature. As a continuation of our previous investigations of aqueous solutions,[9] in the present study the molar heat capacities of an aqueous $Li_2B_4O_7$ solution were measured by an adiabatic calorimeter in the temperature range from 80 K to 355 K. The thermodynamic functions of the system relative to the standard temperature 298.15 K were derived on the basis of the relationship of the thermodynamic functions and the functions of the measured heat capacities with respect to temperature. In the present study, the concentration of the aqueous $Li_2B_4O_7$ solution was selected as 0.0187 mol·kg^{-1}, which is near the real contents of $Li_2B_4O_7$ in hundreds of salt lakes.

Experimental

Experimental Materials. The water used was distilled, deionized, and degassed, and the conductance was 1·10^{-4} S·m^{-1}. $Li_2B_4O_7$ commercial reagent (made in the Beijing Xinhua Reagent Factory, A.R. grade) was recrystallized twice from water. The molality of the solution was analyzed by mass titration in the presence of mannitol using a NaOH standard solution as the titrant and phenolphthalein as the indicator, and triplicate samples agreed to 0.07 %. The standardization method of the NaOH solution is similar to that in ref 5.

Equipment and Experimental Method. The principle of the high-precision automatic adiabatic calorimeter used for this study is based on the Nernst stepwise heating method. The calorimeter mainly consists of a sample cell, an adiabatic (or inner) shield, a guard shield, a platinum resistance thermometer, an electric heater, two sets of chromel−constantan thermocouples, and a high-vacuum can. The sample cell was made of gold-plated copper with an inner volume of 48 cm^3. Eight gold-plated copper vanes with a thickness of 0.2 mm were placed inside the cell to promote heat distribution between the sample and the cell. The platinum resistance thermometer was inserted into the copper sheath, which was fixed inside of the reentrant well of the sample cell. The heater wire was wound on the surface of the copper sheath. The vacuum can of the calorimeter was kept within a pressure of ca. 1·10^{-3} Pa during the heat capacity measurements, to eliminate the heat loss due to gas convection. Liquid nitrogen was used as the cooling medium.

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Table 1. Values of the Molar Heat Capacity of the Aqueous $Li_2B_4O_7$ Solution (m = 0.0187 mol·kg^{-1})

T/K	$C_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	T/K	$C_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	T/K	$C_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	T/K	$C_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	T/K	$C_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	T/K	$C_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$
79.85	13.20	232.51	34.30	283.13	77.43	157.14	23.94	272.73	1485.55	319.24	77.38
81.58	13.55	235.12	34.63	284.76	77.48	159.49	24.24	272.75	1560.79	320.54	77.21
84.21	14.00	237.75	35.08	286.28	77.44	161.82	24.54	272.77	1706.29	321.84	77.36
86.77	14.39	240.35	35.34	287.69	77.32	164.13	24.83	272.79	1971.88	323.17	77.27
89.27	14.78	242.91	35.69	289.02	77.29	166.42	25.23	272.81	2012.39	324.48	77.45
91.73	15.14	245.55	36.18	290.32	77.31	168.69	25.51	272.83	2248.11	325.74	77.48
94.13	15.51	248.33	36.58	291.62	77.37	170.93	25.73	272.85	2277.50	327.04	77.38
96.97	15.97	251.06	37.29	292.93	77.31	173.16	26.00	272.87	2470.60	328.36	77.21
100.24	16.45	253.74	37.88	294.23	77.21	175.36	26.27	272.89	2556.86	329.65	77.36
103.43	16.89	256.39	38.56	295.54	77.32	177.55	26.55	272.91	2694.20	330.97	77.43
106.55	17.32	258.98	39.49	296.63	77.23	179.72	26.83	272.92	2872.81	332.21	77.49
109.62	17.72	261.51	40.92	297.76	77.15	182.42	27.21	272.93	2947.11	333.55	77.22
112.63	18.10	263.95	43.39	298.91	77.18	185.66	27.66	272.95	3234.13	334.87	77.32
115.58	18.56	266.21	48.99	300.07	77.31	188.87	28.02	272.96	3505.85	336.18	77.36
118.45	19.01	268.17	62.22	301.19	77.44	192.03	28.38	272.97	4330.40	337.45	77.42
121.27	19.41	269.68	91.94	302.33	77.20	195.15	28.80	272.99	4511.24	338.72	77.16
124.05	19.79	270.71	148.98	303.43	77.24	198.24	29.17	272.99	5845.90	340.04	77.37
126.79	20.17	271.35	238.14	304.55	77.42	201.29	29.58	273.01	6203.92	341.31	77.21
129.49	20.54	271.75	351.30	305.88	77.24	204.32	29.97	273.02	6519.89	342.64	77.31
132.16	20.95	272.01	470.35	306.64	77.28	207.27	30.37	273.04	7155.88	343.93	77.25
134.79	21.26	272.19	620.27	307.73	77.50	210.21	30.82	273.06	5345.71	345.27	77.44
137.39	21.52	272.32	775.09	308.96	77.42	213.11	31.14	273.09	2628.02	346.59	77.28
139.96	21.83	272.43	865.67	310.23	77.46	215.99	31.55	273.15	1403.08	347.81	77.18
142.55	22.08	272.49	982.27	311.41	77.26	218.84	31.94	273.18	84.06	349.14	77.21
145.12	22.39	272.55	1141.76	312.72	77.28	221.65	32.31	274.73	77.52	350.48	77.44
147.48	22.78	272.59	1230.29	314.02	77.40	224.43	32.76	277.21	77.24	351.76	77.25
149.93	23.02	272.63	1335.94	315.35	77.19	227.19	33.21	279.41	77.34	353.04	77.44
152.36	23.38	272.67	1384.49	316.64	77.35	229.89	33.71	281.36	77.30	354.31	77.37
154.76	23.68	272.71	1414.42	317.98	77.44						

One set of six junctions of chromel−constantan thermocouples was used to detect the temperature difference between the sample cell and the inner shield. Similarly, the other set of thermocouples was installed between the inner and outer shields. The temperature difference between them was maintained at 0.5 mK during the entire experimental process. The sample cell was heated by the standard discrete heating method. The platinum resistance thermometer measured the temperature of the cell. The temperature increment in a heating period was 2 K∼4 K, and the temperature drift was maintained at about 10^{-3} K min^{-1} in an equilibrium period. All the calorimetric data were automatically recorded through a Data Acquisition/Switch Unit (model 34970A, Agligent, USA) and processed online by a computer.

The concentration of the aqueous $Li_2B_4O_7$ solution was 0.0187 mol·kg^{-1}. The sample mass used for the heat capacity measurement was 43.5638 g. The performance of this calorimetric apparatus was evaluated by heat capacity measurements of water. The deviations of experimental heat capacities from the corresponding smoothed values lie within ± 0.3 %, and the inaccuracy is within ± 0.4 %.[10] The apparatus and the experimental procedure are similar to those described by Tan et al.[11−14]

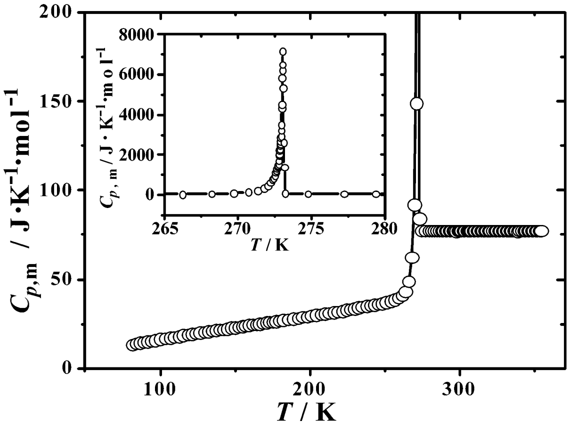

Figure 1. Molar heat capacity of the aqueous $Li_2B_4O_7$ solution.

Results and Discussions

Molar Heat Capacity of the Aqueous $Li_2B_4O_7$ Solution. The molar heat capacities of the aqueous $Li_2B_4O_7$ solution were determined by the adiabatic calorimeter in the temperature range from 80 K to 355 K at constant pressure (P/kPa = 101.325). The results of the molar heat capacities are listed in Table 1 and shown in Figure 1. No phase transition was observed, and no other thermal anomaly took place in the temperature range from 80 K to 258 K for the solid phase and from 274 K to 355 K for the liquid phase, respectively.

To fit the experimental heat capacity data, the temperature T was replaced by the reduced temperature X which is defined

$$X = [T - 0.5(T_{\max} + T_{\min})]/[0.5(T_{\max} - T_{\min})] \qquad (1)$$

where T is thermodynamic temperature and $T_{\max}$ and $T_{\min}$ are the maximum and the minimum of the temperature in the experimental temperature range of each phase (solid or liquid). Then, $-1 \leq X \leq 1$.

The values of molar heat capacities of the aqueous $Li_2B_4O_7$ solution were fitted in the following polynomial expressions using the least-squares method.

For the solid phase (80 K∼258 K)

$$C_{p,\mathrm{m}}\,(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 25.444 + 10.997X + 0.4540X^2 + 1.6707X^3 \qquad (2)$$

where $C_{p,\mathrm{m}}$ is the molar heat capacity of the aqueous $Li_2B_4O_7$ solution, X is the reduced temperature equal to $(T - 169)/89$, and T is the absolute temperature. The above equation is valid from 80 K to 258 K, with an uncertainty of ± 0.2 % and a fitting coefficient $R^2 = 0.9999$.

Table 2. Data of the Thermodynamic Functions of the Aqueous $Li_2B_4O_7$ Solution

T	$C_{p,\mathrm{m}}$	$H_T - H_{298.15}$	$C_{p,\mathrm{m}}/T$	$S_T - S_{298.15}$	T	$C_{p,\mathrm{m}}$	$H_T - H_{298.15}$	$C_{p,\mathrm{m}}/T$	$S_T - S_{298.15}$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-2} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-2} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
80	13.23	−21.99	0.1653	−64.10	175	26.19	−18.47	0.1496	−51.14
85	14.06	−21.86	0.1654	−63.26	180	26.81	−18.22	0.1489	−50.51
90	14.87	−21.71	0.1652	−62.45	185	27.45	−17.97	0.1483	−49.88
95	15.65	−21.56	0.1647	−61.67	190	28.09	−17.72	0.1478	−49.24
100	16.41	−21.46	0.1641	−60.91	195	28.74	−17.45	0.1473	−48.59
105	17.15	−21.25	0.1633	−60.18	200	29.40	−17.17	0.1478	−47.93
110	17.87	−21.09	0.1624	−59.46	205	30.08	−16.89	0.1467	−47.24
115	18.57	−20.92	0.1614	−58.76	210	30.77	−16.59	0.1465	−46.56
120	19.25	−20.74	0.1603	−58.08	215	31.48	−16.28	0.1464	−45.85
125	19.92	−20.56	0.1593	−57.41	220	32.21	−15.97	0.1464	−45.12
130	20.57	−20.38	0.1582	−56.75	225	32.96	−15.64	0.1464	−44.37
135	21.22	−20.19	0.1571	−56.11	230	33.73	−15.29	0.1466	−43.59
140	21.85	−19.99	0.1560	−55.48	235	34.53	−14.94	0.1469	−42.80
145	22.48	−19.79	0.1550	−54.85	240	35.35	−14.57	0.1473	−41.97
150	23.10	−19.59	0.1540	−54.23	245	36.21	−14.18	0.1477	−41.12
155	23.72	−19.37	0.1530	−53.61	250	37.09	−13.78	0.1483	−40.24
160	24.33	−19.16	0.1520	−52.99	255	38.00	−13.36	0.1490	−39.32
165	24.95	−18.93	0.1512	−52.38	260	38.95	−12.92	0.1498	−38.38
170	25.57	−18.70	0.1503	−51.76					
Phase Transition									
275	77.34	−1.795	0.2812	0.009	315	77.34	1.295	0.2454	−0.000
280	77.34	−1.409	0.2762	0.008	320	77.33	1.681	0.2416	−0.001
285	77.34	−1.022	0.2713	0.007	325	77.33	2.067	0.2379	−0.002
290	77.34	−0.636	0.2666	0.006	330	77.33	2.457	0.2343	−0.003
295	77.34	−0.250	0.2621	0.004	335	77.33	2.840	0.2308	−0.004
298.15	77.33	0.000	0.2593	0.000	340	77.33	3.226	0.2274	−0.005
300	77.33	0.136	0.2577	0.003	345	77.32	3.612	0.2241	−0.008
305	77.33	0.523	0.2535	0.002	350	77.32	3.998	0.2209	−0.008
310	77.33	0.909	0.2494	0.001	355	77.32	4.385	0.2178	−0.010

Table 3. Relative Apparent Molar Heat Capacities of the Aqueous $Li_2B_4O_7$ Solution

T	C_p (solution)	C_p (pure water)	$C_{p,\phi}$	T	C_p (solution)	C_p (pure water)	$C_{p,\phi}$
K	$J \cdot K^{-1} \cdot g^{-1}$	$J \cdot K^{-1} \cdot g^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot g^{-1}$	$J \cdot K^{-1} \cdot g^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
80	0.7323	0.6918	2287	175	1.4495	1.4175	1958
85	0.7785	0.7395	2216	180	1.4842	1.4513	2011
90	0.8231	0.7856	2148	185	1.5192	1.4852	2070
95	0.8664	0.8302	2086	190	1.5546	1.5196	2135
100	0.9084	0.8733	2031	195	1.5906	1.5543	2210
105	0.9492	0.9152	1981	200	1.6273	1.5896	2293
110	0.9889	0.9558	1937	205	1.6648	1.6255	2384
115	1.0276	0.9954	1899	210	1.7031	1.6621	2484
120	1.0654	1.0339	1865	215	1.7424	1.6995	2592
125	1.1024	1.0714	1842	220	1.7828	1.7378	2707
130	1.1387	1.1082	1822	225	1.8244	1.7771	2834
135	1.1744	1.1442	1814	230	1.8672	1.8176	2967
140	1.2095	1.1796	1802	235	1.9113	1.8592	3107
145	1.2442	1.2144	1804	240	1.9569	1.9021	3258
150	1.2786	1.2488	1812	245	2.0040	1.9465	3418
155	1.3129	1.2828	1827	250	2.0529	1.9923	3588
160	1.3470	1.3166	1848	255	2.1035	2.0397	3768
165	1.3810	1.3503	1879	260	2.1559	2.0887	3955
170	1.4152	1.3839	1915				
Phase Transition							
275	4.2810	4.1762	6325	315	4.2809	4.1762	6322
280	4.2809	4.1762	6322	320	4.2804	4.1762	6292
285	4.2808	4.1762	6316	325	4.2803	4.1762	6289
290	4.2807	4.1762	6313	330	4.2803	4.1762	6286
295	4.2807	4.1762	6310	335	4.2802	4.1762	6283
298.15	4.2806	4.1762	6307	340	4.2801	4.1762	6280
300	4.2806	4.1762	6307	345	4.2801	4.1762	6277
305	4.2806	4.1762	6304	350	4.2800	4.1762	6271
310	4.2805	4.1762	6301	355	4.2799	4.1762	6268

For the liquid phase (274 K∼355 K)

$$C_{p,\mathrm{m}}\,(J \cdot K^{-1} \cdot mol^{-1}) = 77.33 \pm 0.19 \qquad (3)$$

where X is the reduced temperature equal to $(T - 314.5)/40.5$ and T is the absolute temperature. The above value is valid from 274 K to 355 K, and the uncertainty equates to ± 0.2 %.

Thermodynamic Data of the Phase Transition. It can be seen from Figure 1 that there is a heat capacity jump in the temperature range from 258 K to 275 K which corresponds to a phase transition. The temperature of the phase transition of the aqueous $Li_2B_4O_7$ solution was determined to be 273.04 K which is a little lower than the temperature of the phase transition of pure water, 273.15 K. The molar enthalpy, ΔH_m, and entropy, ΔS_m, of the phase transition were derived by the following equations:[15]

$$\Delta H_m = \frac{Q - \int_{T_i}^{T_f} \overline{H}_{cell} dT - n \int_{T_i}^{T_m} C_{p,m} dT - n \int_{T_m}^{T_f} C_{p,m} dT}{n} \tag{4}$$

$$\Delta S_m = \Delta H_m / T_m \tag{5}$$

where T_m is the phase transition temperature, T_i is a little lower than T_m, and T_f is a little higher than T_m; H_{cell} is the heat capacity of the empty calorimeter; Q is the total energy introduced into the calorimeter during the course of phase transition; and n is the mole number of the sample. The results of the calculation are $\Delta H_m = 4.650$ kJ·mol^{-1} and $\Delta S_m = 17.03$ J·K^{-1}·mol^{-1}.

Thermodynamic Functions of the Aqueous $Li_2B_4O_7$ Solution. Thermodynamic functions of the aqueous $Li_2B_4O_7$ solution were calculated on the basis of the empirical eqs 2 and 3, which are a function of molar heat capacity with respect to thermodynamic temperature, and of the following thermodynamic functions:

$$H_T - H_{298.15} = \int_{298.15}^{T} C_{p,m} dT \tag{6}$$

$$S_T - S_{298.15} = \int_{298.15}^{T} \frac{C_{p,m}}{T} dT \tag{7}$$

The thermodynamic function data relative to the reference temperature (298.15 K) were calculated by eqs 6 and 7 in the temperature range from 80 K to 355 K with an interval of 5 K and are listed in Table 2.

Relative Apparent Molar Heat Capacities. According to the literature,[16] the relative apparent molar heat capacities, $C_{p,\phi}$, can be evaluated by the following equation:

$$C_{p,\phi} = \left(\frac{1000}{m} + M_2\right) C_p - \frac{1000}{m} C_p^{o} \tag{8}$$

where C_p is the experimental molar heat capacity of the aqueous $Li_2B_4O_7$ solution; m (mol·kg^{-1}) is the molality of $Li_2B_4O_7$ in the solution; M_2 is the molecular weight of the solute $Li_2B_4O_7$; and C_p^{o} is the specific heat capacity of pure water. The dependence of the molar heat capacity of pure water on temperature was calculated as a function of the reduced temperature X by the following polynomial equations from the literature.[11]

For the solid phase

$$C_p^{o}\,(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 24.80911 + 10.76836X + 0.05756X^2 + 1.63556X^3 \tag{9}$$

where reduced temperature $X = (T - 169)/89$ and T is the absolute temperature. The above equation is valid from 80 K to 258 K.

For the liquid phase

$$C_p^{o}\,(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 75.23 \pm 0.21 \tag{10}$$

The above equation is valid from 274 K to 355 K.

$C_{p,\phi}$ values were calculated every 5 K in the temperature range from 80 K to 355 K according to the experimental heat capacities of the aqueous $Li_2B_4O_7$ solution and the calculated heat capacities of pure water. The results are shown in Table 3. From Table 3, it can be seen that the relative apparent molar heat capacities of the aqueous $Li_2B_4O_7$ solution possess positive values in the whole measured temperature range from 80 K to 355 K; however, the relative apparent molar heat capacities of the aqueous LiCl solution are negative in the temperature range from 278.15 K to 393.15 K.[17] It can be concluded that the properties of the aqueous $Li_2B_4O_7$ solution and the aqueous LiCl solution are entirely different, though they possess a similar charge type.

Conclusion

In this work, the molar heat capacities of the aqueous $Li_2B_4O_7$ solution at the concentration of 0.0187 mol·kg^{-1} have been measured using a precision automated adiabatic calorimeter in the temperature range from 80 K to 355 K. The temperature, the molar enthalpy, and the entropy of fusion and decomposition were calculated using equations and diagrammatic area integration. The thermodynamic functions $[H_T - H_{298.15}]$ and $[S_T - S_{298.15}]$ were derived from 80 K to 355 K with a temperature interval of 5 K. The relative apparent molar heat capacities of the aqueous $Li_2B_4O_7$ solution, $C_{p,\phi}$, were calculated every 5 K in the temperature range from 80 K to 355 K from the experimental heat capacities of the aqueous $Li_2B_4O_7$ solution and the heat capacities of pure water.

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