

MgB₄O₇-MgSO₄-MgCl₂-H₂O 及次级体系 298.15K 时稀释热、热容和表观摩尔焓的研究

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本文研究了含硼四元水盐体系 MgB₄O₇-MgSO₄-MgCl₂-H₂O 及次级体系 MgB₄O₇-MgSO₄-H₂O 和 MgB₄O₇-MgCl₂-H₂O 在 298.15K 时不同离子强度下的稀释热和热容, 并将 Debye-Huckel 极限公式应用到多元电解质稀溶液中, 获得从高离子强度到低离子强度 I 为 19-0.0001 范围内的相对表观摩尔焓。

关键词: 含硼多元体系 稀释热 热容 相对表观摩尔焓

HEATS OF DILUTION, HEAT CAPACITIES AND APPARENT MOLAL ENTHALPIES OF MgB₄O₇-MgSO₄-MgCl₂-H₂O SYSTEMS AT 298.15K

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The heats of dilution and heat capacities of MgB₄O₇-MgSO₄-MgCl₂-H₂O quaternary system and MgB₄O₇-MgSO₄-H₂O and MgB₄O₇-MgCl₂-H₂O subsystems were measured in the ionic strength range from 19 to 0.1 at 298.15K. The data of the heat of dilution were extrapolated to infinite dilution by use of the Debye-Huckel limiting law to obtain relative apparent molal enthalpies over the ionic strength I range from 19 to 0.0001.

Keywords: multi-component system containing boron heat of dilution heat capacity
apparent molal enthalpy

INTRODUCTION

Most of the salt lakes on the Qinghai-Xizang plateau in China belong to the seawater system with abundant boron and magnesium. In the late period of evaporation, because of depo-

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sition of most salts of sodium and potassium and of high concentrating factors of boron and lithium, the brine becomes actually the Li^+ , $\text{Mg}^{2+} / \text{Cl}^-$, SO_4^{2-} , $\text{B}_4\text{O}_7^{2-} - \text{H}_2\text{O}$ system. The phase equilibria and properties of saturated solution in the Li^+ , $\text{Mg}^{2+} / \text{Cl}^-$, SO_4^{2-} , $\text{B}_4\text{O}_7^{2-} - \text{H}_2\text{O}$ systems have been studied^(1,2).

This paper reports the heats of dilution, heat capacities and apparent molal enthalpies of $\text{MgB}_4\text{O}_7 - \text{MgSO}_4 - \text{MgCl}_2 - \text{H}_2\text{O}$ quaternary system and $\text{MgB}_4\text{O}_7 - \text{MgSO}_4 - \text{H}_2\text{O}$ and $\text{MgB}_4\text{O}_7 - \text{MgCl}_2 - \text{H}_2\text{O}$ ternary systems at 298.15K. The Debye-Huckel limiting law was used for the heats of dilution extrapolations in multi-component systems. This study is very valuable for understanding the thermochemical characteristics of brine in the late period of evaporation after deposition of salts of sodium and potassium, for extracting process of boron and magnesium from salt lakes, and for comprehensive utilization of brine.

EXPERIMENTAL

Magnesium sulfate and magnesium chloride used in the experiment were recrystallized from A. R. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Magnesium tetraborate, $\text{MgB}_4\text{O}_7 \cdot 9\text{H}_2\text{O}$ was synthesized from analytical reagents. Its composition is (wt%) MgO 11.83, B_2O_3 40.76, H_2O 47.43; $\text{B}_2\text{O}_3 / \text{MgO}$ (mole ratio) 1.995 (theoretical values: 11.80, 40.75, 47.45, 2.000). X-ray diffraction analysis identifies it as the compound $\text{MgB}_4\text{O}_7 \cdot 9\text{H}_2\text{O}$. The co-saturated point solution of $\text{MgB}_4\text{O}_7 - \text{MgSO}_4 - \text{MgCl}_2 - \text{H}_2\text{O}(\text{MB}_1)$ quaternary system and $\text{MgB}_4\text{O}_7 - \text{MgCl}_2 - \text{H}_2\text{O}(\text{MB}_2)$ and $\text{MgB}_4\text{O}_7 - \text{MgSO}_4 - \text{H}_2\text{O}(\text{MB}_3)$ subsystems were prepared by isothermal ($25.00 \pm 0.03^\circ\text{C}$) method⁽³⁾. The components are given in Table 1. Redistilled water was used in the recrystallization of the reagents, the synthesis of the borate, and the preparation of equilibrium mixtures.

Table 1 Components of $\text{MgB}_4\text{O}_7 - \text{MgSO}_4 - \text{MgCl}_2 - \text{H}_2\text{O}$ systems

systems	MgB_4O_7 $\text{mol} \cdot \text{kg}^{-1}$	Mg_2SO_4 $\text{mol} \cdot \text{kg}^{-1}$	MgCl_2 $\text{mol} \cdot \text{kg}^{-1}$	I^a
MB_1	0.5909	0.2247	5.4251	19.5373
MB_2	0.5420	—	5.4915	18.6425
MB_3	0.07843	3.0438	—	12.4891

^a I is the molal ionic strength ($I = (1/2)\sum M_i Z_i^2$, where M_i is the molality of ion i with charge Z_i).

A LKB-87001 precision calorimeter and a thermostatic bath ($25.00 \pm 0.01^\circ\text{C}$) were used to measure the heat of dilution and the heat capacity. The accuracy of the calorimeter has been tested previously by measuring the heat effect of the standard reaction of trishydroxymethylaminomethane (THAM) with HCl at 298.15K. A weighed amount of the solution (titrate) was loaded in the glass reaction vessel. The vessel with its contents were laid to the thermostat at $25.00 \pm 0.01^\circ\text{C}$ for 2h, then pre-fixed volumes of water (titrant) were titration-added by means of peristaltic pump. The titration rate was $3.1344 \pm 0.0016 \text{ cm}^3 \cdot \text{min}^{-1}$. The temperature changes in the reaction vessel were measured in terms of an electrical

potential output from the thermistor with 2000Ω resistance R . The output was amplified by a microvolt amplifier and recorded. Heat capacity and leakage constant were measured with twice heating electrically for 500s using 200mW and 500mW power range, and once lowering the temperature experiment before and after each titration^(4,5). The calorimetric measurements were processed by means of a computer program to obtain the heats of dilution and heat capacities according to the followign Eq. (1), (2):

$$C_i = W(t)^{-1}[C_i + (dC_B / dt)t] \quad (1)$$

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

where t [s] denotes time, C_i [kJ · K⁻¹ · kg⁻¹] is heat capacity of the solution of ionic strength I_i , ΔH_d [kJ · mol⁻¹] is heat of dilution, $W(t)$ [kg] is the weight of the solution in the reaction vessel at t , C_i [kJ · K⁻¹] is initial heat capacity of the solution before titration, dC_B / dt [kJ · K⁻¹ · s⁻¹] is the rise of heat capacity, M [mol] is the total molalities of all solutes in the titrate, $C(t)$ [kJ · K⁻¹] is the total heat capacity of the reaction vessel plus titrate and titrant at t , K [kJ · K⁻¹ · s⁻¹] is leakage constant, $T(t)$ [K] is the temperature of outer surface of the calorimeter at t , T_o [K] is the initial temperature of the titrate, T_a [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 MgB₄O₇-MgSO₄-MgCl₂-H₂O quaternary system and MgB₄O₇-MgSO₄-H₂O and MgB₄O₇-MgCl₂-H₂O subsystems were measured to cover a range from initial ionic strength I_o to I_i at 298.15K. The measured results are reported in Table 2, in which, M_i (mol · kg⁻¹) are the molalities of the total solutes of the systems.

The apparent molal enthalpies ${}^\phi L = -\Delta H_d(I_i \rightarrow 0)$ were determined with the extended limiting law equation⁽⁶⁻⁸⁾

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

where S_H is the Debye-Hückel limiting law slope ($S_H = w \cdot A_H$; $w = (1/2)\Sigma V_i Z_i^2$, V_i and Z_i are the numbers and charge of ion i ; and $A_H = 2.8786 \text{ kJ} \cdot \text{kg}^{1/2} \cdot \text{mol}^{-3/2}$ at 298.15K;

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

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

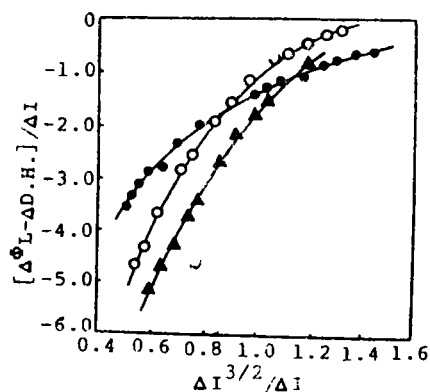
$$\Delta H_d = (I_i \rightarrow I_f) = -\Delta {}^\phi L(I_i \rightarrow I_f) \quad (3)$$

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

plots of the left side of Eq.(4) versus $\Delta I^{3/2} / \Delta I$ for the MgB₄O₇-MgSO₄-MgCl₂-H₂O systems are given in Fig.1. Equation(4) was originally suggested to be useful in extrapolating heat-of-dilution data to infinite dilution and was used in the molality range from 0 to 0.1⁽⁶⁾. However, it was found later^(7,8) that this equation (4) would be valid for heat-of-dilution data of electrolytes as well as of seawater for the approximate molality and ionic strength range from 0.1 to 1.0. So that, Fig.1 was a plot from heat-of-dilution data of the MgB₄O₇-MgSO₄-MgCl₂-H₂O systems in molality and ionic strength less than 1.0.

Table 2 Heats of Dilution ΔH_d , Heat Capacities C and Apparent Molal Enthalpies $^{\circ}L$ of MgB_4O_7 - MgSO_4 - MgCl_2 - H_2O Systems at 298.15K

I_0	I_i	M_i $\text{mol} \cdot \text{kg}^{-1}$	C $\text{kJ} \cdot \text{kg}^{-1} \text{K}^{-1}$	ΔH_d $\text{kJ} \cdot \text{mol}^{-1}$	$^{\circ}L$ $\text{kJ} \cdot \text{mol}^{-1}$
19.5377	19.5377	6.2407	MB ₁ 2.524	0.000	16.875
	18.3221	5.8524	2.588	-0.826	16.049
	17.3640	5.5464	2.641	-2.108	14.767
	16.0168	5.1161	2.719	-3.707	13.168
	15.5014	4.9514	2.750	-4.288	12.587
	14.4201	4.6060	2.818	-5.447	11.428
	13.1393	4.1969	2.902	-6.727	10.148
	12.0722	3.8561	2.976	-7.729	9.146
	11.3853	3.6367	3.026	-8.341	8.534
	10.1836	3.2528	3.117	-9.276	7.599
	9.2555	2.9564	3.192	-10.174	6.701
	8.2528	2.6361	3.276	-11.055	5.820
	7.1101	2.2711	3.374	-11.927	4.948
	6.3319	2.0225	3.451	-12.440	4.435
	5.0429	1.6108	3.578	-13.231	3.644
	4.1465	1.3245	3.673	-13.741	3.134
	3.1159	0.9953	3.788	-14.188	2.686
	2.0101	0.6421	3.920	-14.632	2.243
	1.0041	0.3207	4.048	-14.962	1.913
	0.8163	0.2799	4.065	-15.020	1.855
	0.6194	0.1979	4.099	-15.142	1.733
	0.4034	0.1288	4.128	-15.268	1.607
	0.2042	0.0653	4.156	-15.495	1.380
	0.1024	0.0328	4.170	-15.157	1.124
	0.0894	0.0286	4.172	-15.811	1.064
18.6425	18.6425	6.0335	MB ₂ 2.538	0.000	15.945
	17.0231	5.5094	2.629	-1.465	14.480
	16.0918	5.2080	2.685	-2.618	13.327
	15.1869	4.9151	2.741	-3.659	12.286
	14.4196	4.6659	2.790	-4.494	11.451
	13.1429	4.2536	2.876	-5.827	10.118
	12.4171	4.0187	2.927	-6.553	9.392
	11.1819	3.6189	3.018	-7.702	8.242
	10.1753	3.2931	3.097	-8.564	7.381
	9.1484	2.9608	3.181	-9.509	6.436
	8.1024	2.6223	3.271	-10.492	5.453
	7.1186	2.3039	3.361	-11.291	4.654
	6.0122	1.9458	3.467	-12.044	3.901
	5.0203	1.6248	3.569	-12.684	3.260
	4.1968	1.3583	3.657	-13.178	2.767
	3.0836	0.9980	3.784	-13.688	2.256
	2.0056	0.6491	3.915	-14.060	1.884
	1.0506	0.3400	4.039	-14.243	1.702
	0.8026	0.2589	4.072	-14.316	1.629
	0.6061	0.1962	4.099	-14.507	1.437
	0.4022	0.1302	4.127	-14.729	1.216
	0.2133	0.0690	4.154	-14.901	1.044
	0.1036	0.0335	4.169	-14.979	0.966
	0.0921	0.0298	4.171	-15.012	0.933
12.4891	12.4891	3.1223	MB ₃ 3.064	0.000	4.532
	11.2655	2.8164	3.146	-0.422	4.111
	10.1658	2.5415	3.223	-0.808	3.724
	9.1325	2.2831	3.300	-1.109	3.423
	8.3062	2.0766	3.364	-1.313	3.219
	7.0465	1.7616	3.466	-1.570	2.962
	6.1998	1.5500	3.538	-1.733	2.799
	5.0163	1.2542	3.645	-1.940	2.593
	4.1652	1.0414	3.726	-2.064	2.468
	3.1742	0.7936	3.826	-2.268	2.264
	2.0621	0.5155	3.944	-2.420	2.112
	1.0055	0.2514	4.063	-2.768	1.765
	0.8519	0.2130	4.081	-2.847	1.686
	0.6420	0.1605	4.106	-2.980	1.552
	0.4152	0.1038	4.133	-3.158	1.375
	0.2044	0.0511	4.159	-3.270	1.263
	0.1023	0.0256	4.171	-3.355	1.177
	0.0759	0.0190	4.175	-3.371	1.161

Fig.1 Plots of $[\Delta^{\circ}L - \Delta D.H.]/\Delta I$ versus $\Delta I^{3/2}/\Delta I$ forMgB₄O₇-MgSO₄-MgCl₂-H₂O systems at 298.15K●, MB₁; ○, MB₂; ▲, MB₃

The values of B and C determined by a least-square fit are given in Table 3, along with the sum of square errors R . The sum of square errors of the least-square fit for all the systems is less than $1.0 \text{ kJ} \cdot \text{mol}^{-1}$.

Table 3 Values of B and C for the Extended Debye-Huckel Equation at 298.15K

	B	C	R
MB ₁	-4.90955	3.48947	0.89
MB ₂	-7.12360	5.81439	0.68
MB ₃	-10.09040	8.17033	0.32

The apparent molal enthalpies $^{\circ}L_r$ over an ionic strength range I_f 0.1–0.0001 were calculated from Eq.(1) using the coefficients B , C in Table 3, the results are given in Table 4.

Table 4 Apparent Molal Enthalpies of MgB₄O₇-MgSO₄-MgCl₂-H₂O Systems over the Ionic Strength Range 0.1–0.0001 at 298.15K

I	$^{\circ}L(\text{kJ} \cdot \text{mol}^{-1})$		
	MB ₁	MB ₂	MB ₃
0.1	1.095	0.947	1.216
0.09	1.066	0.929	1.197
0.08	1.032	0.908	1.173
0.07	0.994	0.882	1.143
0.06	0.950	0.851	1.106
0.05	0.898	0.813	1.059
0.04	0.834	0.764	0.998
0.03	0.754	0.700	0.918
0.02	0.648	0.610	0.803
0.01	0.490	0.470	0.622
0.005	0.363	0.353	0.468
0.001	0.170	0.168	0.223
0.0001	0.037	0.037	0.050

The apparent molal enthalpies ${}^{\phi}L_i$ of $\text{MgB}_4\text{O}_7\text{--MgSO}_4\text{--MgCl}_2\text{--H}_2\text{O}$ systems of the ionic strength range from 19 to 0.1 can be calculated from

$${}^{\phi}L_i = {}^{\phi}L_f - \Delta H_d(I_i - I_f) \quad (5)$$

using the heats of dilution ΔH_d and the apparent molal enthalpies ${}^{\phi}L_f$ of the final ionic strength (MB_1 0.0894; MB_2 0.0921; MB_3 0.0759). The results are given in Table 2.

To summarize, the heats of dilution and the heat capacities of the $\text{MgB}_4\text{O}_7\text{--MgSO}_4\text{--MgCl}_2\text{--H}_2\text{O}$ quaternary system and $\text{MgB}_4\text{O}_7\text{--MgSO}_4\text{--H}_2\text{O}$ and $\text{MgB}_4\text{O}_7\text{--MgCl}_2\text{--H}_2\text{O}$ subsystems have been measured over the ionic strength I range from 0.1 to 19 at 298.15K. The apparent molal enthalpies have been calculated by means of Debye-Huckel limiting law for the ionic strength range from 19 to 0.0001. The results give that the heats of dilution are negative, indicating exothermic dilution processes of various systems. With stronger ionic strength I or higher molalities, the values of heat capacities are smaller and the values of apparent molal enthalpies are greater. All these systems have shown similar heat behavior to a single electrolyte solution of alkaline-earth metal⁽⁹⁾.

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