

Volumetric Properties of Aqueous Solutions of $\text{Li}_2\text{B}_4\text{O}_7$ at Temperatures from 288.15 to 323.15 K

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Abstract: Densities of aqueous solutions of $\text{Li}_2\text{B}_4\text{O}_7$ have been measured by using vibrating-tube densimeter over the temperature ranges $288.15 \leq T/\text{K} \leq 323.15$ at 0.1 MPa pressure. The apparent molar volumes of $\text{Li}_2\text{B}_4\text{O}_7$ solution derived from these data were fitted using Pitzer ion interaction model. The volumetric ion interaction parameters of $\text{Li}_2\text{B}_4\text{O}_7$ at different temperatures were determined.

Key words: Lithium tetraborate; Density; Apparent molar volume; Pitzer ion interaction model

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1 Introduction

The composition of Salt Lake brine can be represented as $\text{Li}^+ - \text{Na}^+ - \text{K}^+ - \text{Mg}^{2+} - \text{Cl}^- - \text{SO}_4^{2-} - \text{CO}_3^{2-} - \text{B}_2\text{O}_3 - \text{H}_2\text{O}$ system. Knowledge of the volumetric characteristics (such as the solution mass density (ρ), the apparent molar volumes (V_ϕ), and the apparent ionic volumes (V_{ion}), etc.) of salts such as $\text{Li}_2\text{B}_4\text{O}_7$, and how they vary with temperature and concentration, are useful for both scientific and technological purposes. Such data can provide valuable insights into the influence of ion size on chemical and electrochemical behavior, and are required for engineering calculations involving mass transfer and for the inter-conversion of concentration units. As such, they play an important role in developing more efficient methods of extraction of lithium compounds on an industrial scale.

The physical-chemical theories and approaches can be very effectively used for the prediction of various properties of aqueous solutions. One of such useful approaches is the ion interaction model developed by Pitzer^[1,2] which allows the prediction of thermodynamic properties of concentrated brine^[3-6]. The ion interaction model allows the prediction of various thermodynamic properties of multiple solute electrolyte solutions by using ion interaction parameters, calculated from appropriate experimental data for single-solute electrolyte solutions and for ternary solutions. Among such properties are solution density and apparent molal volumes of solutes. Krumgalz^[7] developed databases for the densities and the apparent molar volumes versus concentrations using all available literature sources for 102 electrolytes. Volumetric properties of aqueous $\text{Li}_2\text{B}_4\text{O}_7$ solution are very limited. Recently, Guo *et al.*^[8] reported density values for aqueous lithium tetraborate solu-

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tion. Unfortunately, the apparent volumes (V_ϕ) in this publication are incorrect^[9,10]. The Pitzer single electrolyte parameters derived from the incorrect apparent volume of Guo *et al.* cannot be used in volumetric properties calculations.

In this paper, we report new experimental data on the volumetric properties of aqueous $\text{Li}_2\text{B}_4\text{O}_7$ solution at temperatures from (288.1 to 323.15) K and 0.1 MPa. The data were obtained using high precision vibrating-tube densimeter. Pitzer volumetric ion interaction parameters were calculated by using the experimental densities of aqueous $\text{Li}_2\text{B}_4\text{O}_7$ solution.

2 Experimental Section

$\text{Li}_2\text{B}_4\text{O}_7$ (Sinopharm Chemical Reagent Co., Ltd, AR, $\geq 99.5\%$) was directly used without further purification. Distilled, deionized water was used in all procedures. The solutions were prepared on the basis of mass, using an analytical balance with a precision of $\pm 1 \times 10^{-4}$ g (Sartorius Scientific Instrument Co. Ltd., SQP). The stock solution was prepared by dissolving $\text{Li}_2\text{B}_4\text{O}_7$ in distilled deionized water. The molality of the stock solution was analyzed by mass titration in the presence of mannitol using a NaOH standard solution as titrant and phenolphthalein as the indicator; triplicate samples agreed to 0.1% or better.

The tested ternary aqueous solutions were prepared by using an analytical balance with a precision of ± 0.1 mg, the two stock solutions and the water were weighed in appropriate proportions according to the desired concentrations using mass burettes. Densities were measured using an Anton Paar model 5000 M vibrating-tube densimeter. Temperature was controlled to ± 0.005 K over the range $288.15 \leq T/\text{K} \leq 323.15$. An accuracy of less than $\pm 0.0005 \text{ g} \cdot \text{cm}^{-3}$ was always obtained. The densimeter was calibrated at 293.15 K with laboratory air and high purity degassed water, using the air and water densities provided within the software by the

manufacturer. Following calibration, the densimeter tube was filled with high purity de-gassed water at 288.15 K and, after appropriate stabilization and measurement periods, the temperature was increased automatically in 5 K steps to 323.15 K then decreased in the same manner. The length of time required for the overall temperature scan (up and back) was ~ 2 h and the reproducibility of ρ_w at each temperature (in the upwards and downward scans) was $\pm 10 \mu\text{g} \cdot \text{cm}^{-3}$ or better. The same procedure was then used for the target solution, immediately followed by a repeat water measurement. The agreement between the before-and-after water scan was typically better than $\pm 10 \mu\text{g} \cdot \text{cm}^{-3}$ at all temperatures and their average at each value of T was taken to be the value of $\rho_w(T)$ at the time of measurement of the solution density. The reproducibility of the densities of isoplethic solutions deteriorated slightly with increasing solute concentrations but was always within the range $\pm(2 \text{ to } 10) \mu\text{g} \cdot \text{cm}^{-3}$. Detailed operation of the vibrating-tube densimeter was stated in other place^[11].

3 Results and Discussion

Experimental densities data of the $\text{Li}_2\text{B}_4\text{O}_7$ solutions were summarized in Table 1. Solution densities, ρ , at the target temperatures, were based on the densities of water, ρ_w , at the same temperatures. The standard densities of water were calculated from the International Association of Properties of Water and Steam IAPWS-95 formulation^[12]. It should be noted that the measured quantity, $\Delta\rho = \rho - \rho_w$ is independent of the model used for representing ρ_w . The values of ρ can be trivially calculated from the data in Table 1. Apparent molar volumes (V_ϕ) were calculated from the experimental densities using the usual relationship:

$$V_{\phi, MX} = \frac{M_s}{\rho} - \frac{\rho - \rho_w}{m\rho\rho_w} \quad (1)$$

where ρ and ρ_w are respectively the densities of the solution and of pure water at the specified tempera-

ture and pressure, m is the molality of the solution (mol-solute/kg-water) and M_s is the molar mass of the solute. The calculated apparent molar volumes are also listed in Table 1.

Table 1 Experimental density differences, $\Delta\rho$, and apparent molar volumes, V_ϕ , of aqueous $\text{Li}_2\text{B}_4\text{O}_7$ solution as a function of molality, m , at $288.15 \leq T/\text{K} \leq 323.15$ and pressure $p = 0.1 \text{ MPa}$

m /mol·kg ⁻¹	$\Delta\rho$ /kg·m ⁻³	V_ϕ /cm ³ ·mol ⁻¹	m /mol·kg ⁻¹	$\Delta\rho$ /kg·m ⁻³	V_ϕ /cm ³ ·mol ⁻¹	m /mol·kg ⁻¹	$\Delta\rho$ /kg·m ⁻³	V_ϕ /cm ³ ·mol ⁻¹
$T = 288.15 \text{ K}, \rho_w = 999.100 \text{ kg} \cdot \text{m}^{-3}$			$T = 293.15 \text{ K}, \rho_w = 998.204 \text{ kg} \cdot \text{m}^{-3}$			$T = 298.15 \text{ K}, \rho_w = 997.045 \text{ kg} \cdot \text{m}^{-3}$		
0.019 98	3.330	2.30	0.019 98	3.292	4.08	0.019 98	3.249	6.03
0.040 01	6.550	5.28	0.040 01	6.470	7.16	0.040 01	6.398	8.76
0.060 00	9.660	7.97	0.060 00	9.548	9.68	0.060 00	9.451	11.12
0.079 98	12.713	9.97	0.079 98	12.571	11.60	0.079 98	12.449	12.94
0.099 99	15.735	11.49	0.099 99	15.564	13.05	0.099 99	15.419	14.33
0.120 00	18.719	12.78	0.120 00	18.524	14.26	0.120 00	18.357	15.47
0.140 0	21.682	13.89	0.140 0	21.462	15.31	0.140 0	21.273	16.49
0.160 0	24.644	14.67	0.160 0	24.392	16.09	0.160 0	24.178	17.25
$T = 303.15 \text{ K}, \rho_w = 995.647 \text{ kg} \cdot \text{m}^{-3}$			$T = 308.15 \text{ K}, \rho_w = 994.032 \text{ kg} \cdot \text{m}^{-3}$			$T = 313.15 \text{ K}, \rho_w = 992.216 \text{ kg} \cdot \text{m}^{-3}$		
0.019 98	3.215	7.53	0.019 98	3.184	8.83	0.019 98	3.158	9.88
0.040 01	6.337	10.07	0.040 01	6.284	11.16	0.040 01	6.238	12.06
0.060 00	9.368	12.31	0.060 00	9.296	13.27	0.060 00	9.235	14.03
0.079 98	12.345	14.04	0.079 98	12.258	14.91	0.079 98	12.180	15.63
0.099 99	15.295	15.37	0.099 99	15.188	16.21	0.099 99	15.097	16.88
0.120 00	18.213	16.47	0.120 00	18.092	17.26	0.120 00	17.989	17.87
0.140 0	21.111	17.45	0.140 0	20.974	18.20	0.140 0	20.858	18.79
0.160 0	23.997	18.18	0.160 0	23.841	18.94	0.160 0	23.709	19.52
$T = 318.15 \text{ K}, \rho_w = 990.213 \text{ kg} \cdot \text{m}^{-3}$			$T = 323.15 \text{ K}, \rho_w = 988.036 \text{ kg} \cdot \text{m}^{-3}$					
0.019 98	3.135	10.78	0.019 98	3.115	11.45			
0.040 01	6.200	12.74	0.040 01	6.166	13.27			
0.060 00	9.184	14.61	0.060 00	9.140	15.03			
0.079 98	12.115	16.17	0.079 98	12.060	16.56			
0.099 99	15.020	17.38	0.099 99	14.956	17.73			
0.120 00	17.901	18.34	0.120 00	17.824	18.70			
0.140 0	20.757	19.24	0.140 0	20.672	19.57			
0.160 0	23.596	19.97	0.160 0	23.500	20.29			

The concentration dependence of apparent molar volumes V_ϕ was described using the volumetric ion interaction mode:^[7]

$$V_{\phi, MX} = \bar{V}_{MX}^0 + v |Z_M Z_X| \left(\frac{A_V}{2b} \right) \ln(1 + b\sqrt{I}) + 2RT v_M v_X [m B_{MX}^V + m^2 v_M v_X C_{MX}^V], \quad (2)$$

$$B_{MX}^V = \beta_{MX}^{(0)V} + \beta_{MX}^{(1)V} g(2\sqrt{I}), \quad (3)$$

$$g(2\sqrt{I}) = \frac{1}{2I} [1 - (1 + 2\sqrt{I}) e^{-2\sqrt{I}}], \quad (4)$$

Where \bar{V}_{MX}^0 is the partial molar volume of $\text{Li}_2\text{B}_4\text{O}_7$ at infinite dilution; ν_M, ν_X are the number of cations and

anions, z_{M} and z_{X} are the charges of cations and anions in a solute molecule, respectively. I is the ionic strength of solution and A_{V} is the theoretical Debye – Hückel constant; $\beta_{\text{MX}}^{(0)\text{V}}$, $\beta_{\text{MX}}^{(1)\text{V}}$ and C_{MX}^{V} are the Pitzer ion interaction parameters. Calculations of volumetric ion interaction parameters for each electrolyte were based on the experimental density at various temper-

atures in Table 1. The values of \bar{V}_{MX}^0 , $\beta_{\text{MX}}^{(0)\text{V}}$, $\beta_{\text{MX}}^{(1)\text{V}}$, C_{MX}^{V} at different temperatures were computed by the least square method and listed in Table 2. The SD in Table 2 is the standard deviation between experimental apparent molar volumes and calculated ones.

Table 2 Volumetric Pitzer parameters of $\text{Li}_2\text{B}_4\text{O}_7$ at different temperatures

T/K	\bar{V}^0 $/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\beta^{(0)\text{V}} \times 10^4$ $/(\text{kg} \cdot \text{mol}^{-1} \cdot \text{bar}^{-1})$	$\beta^{(1)\text{V}} \times 10^4$ $/(\text{kg} \cdot \text{mol}^{-1} \cdot \text{bar}^{-1})$	$C^{\text{V}} \times 10^4$ $/(\text{kg}^2 \cdot \text{mol}^{-2} \cdot \text{bar}^{-1})$	SD_1
288.15	-2.816 8	1.924 9	22.817	-7.979 3	0.07
293.15	-1.386 8	-5.260 9	33.949	-0.946 37	0.04
298.15	1.214 9	0.417 21	20.900	-5.226 2	0.06
303.15	2.936 2	1.755 7	16.487	-5.905 1	0.05
308.15	4.588 7	4.057 1	10.183	-7.274 0	0.05
313.15	5.878 4	5.480 5	5.842 1	-8.066 4	0.05
318.15	7.222 7	9.413 7	-3.021 2e	-11.068	0.07
323.15	8.154 9	11.184	-8.775 5e	-12.887	0.06

Apparent molar volumes of aqueous $\text{Li}_2\text{B}_4\text{O}_7$ solution at 298.15 K were calculated by using the parameters listed in Table 2.

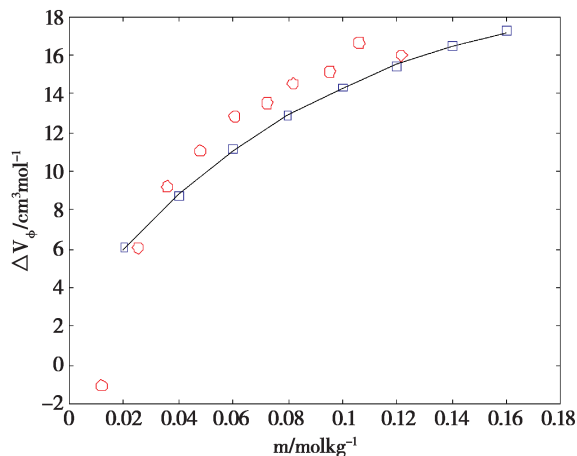


Fig. 1 Literature values for the apparent molar volume V_{ϕ} of aqueous solution of $\text{Li}_2\text{B}_4\text{O}_7$ as a function of concentration at 298.15 K. \square , present work; \circ , Guo *et al.*; [8] The line represents fits of the present data using eq. 2

As indicated in Fig 1, theoretical results are in good agreement with experimental results at almost all concentration range. The abilities of eq. 2 to fit

the data over the investigated ranges of molality and temperature are illustrated as deviation plots in Fig 2. Maximum deviations between the experimental V_{ϕ} values and those calculated from eq. 2 using the parameters in Tables 2 were always $\leq \pm 0.13 \text{ cm}^3 \cdot \text{mol}^{-1}$.

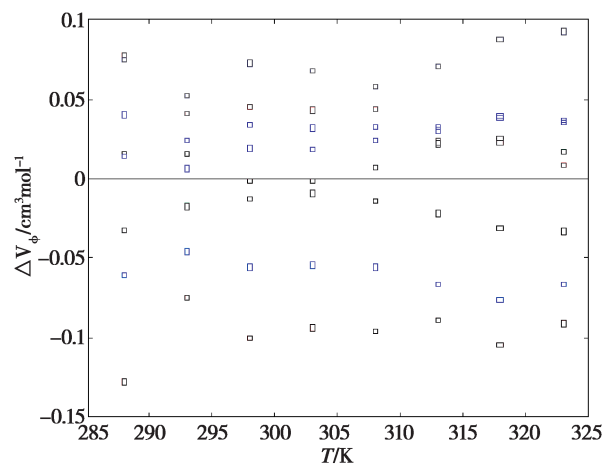


Fig. 2 Comparison of the present experimental apparent molar volumes V_{ϕ} ($\text{Li}_2\text{B}_4\text{O}_7$ (aq)) at $288.15 \leq T/\text{K} \leq 323.15$ with those calculated from eq 2 using the parameters from Table 2

4 Conclusions

This work provides reliable densities and volumetric Pitzer parameters of aqueous solutions of lithium tetraborate, and the apparent molar volumes derived from them show smooth dependencies on solute molality and temperature over wide ranges. The volumetric single electrolyte parameters for $\text{Li}_2\text{B}_4\text{O}_7$ can be used in calculation of densities, apparent molar volumes, etc. for Salt Lake brines.

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288. 15 K – 323. 15 K 下四硼酸锂溶液的体积性质

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摘要: 用振荡管密度计测定了常压下 288. 15 K ~ 323. 15 K 范围内不同浓度的 $\text{Li}_2\text{B}_4\text{O}_7$ 溶液的密度, 计算了其在不同温度下的表观摩尔体积。用 Pitzer 离子相互作用模型拟合了 $\text{Li}_2\text{B}_4\text{O}_7$ 在不同温度下的 Pitzer 单电解质体积参数, 模型的计算值与实验值相吻合良好。

关键词: 四硼酸锂; 密度; 表观摩尔体积; Pitzer 离子相互作用模型