Progresses on Thermodynamic Properties of the Systems Containing Lithium and Borate Ions by Isopiestic Method

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Abstract. Isopiestic method is a common experimental method used in the field of the thermodynamic property of electrolyte solutions. The principle of isopiestic method, the development of isopiestic equipment and the application of isopiestic method in the field of thermodynamic properties of aqueous solutions containing lithium and borate ions have been summarized. The Pitzer single salt parameters and mixing ion interaction parameters containing lithium, chloride, sulfate, borate ions at different temperatures and systems were introduced in details. The latest developments on thermodynamic properties of borate solution by isopiestic method were analyzed, and the new trends in the future on the thermodynamics of borate electrolyte solutions by isopiestic method were also pointed out.

Introduction

Thermodynamic properties of the electrolyte solution, significant for the exploitation of salt brine, marine resource and the research on life and environment involved electrolyte solution, is an important part of the chemical solution theory [1]. Therefore, study on the thermodynamic properties of electrolyte solutions has been taken seriously by chemistry and chemical engineering industry. Currently, the domestic and foreign methods used in the research of thermodynamic properties of electrolyte solution, are mainly isopiestic, chemical potential and calorimetry method, and so on. Compared with calorimetry and chemical potential method, isopiestic method has been widely applied to the study on thermodynamic properties of salt-water system, owing to its high accuracy, few restrictions, and it is easy to operate with simple experimental setup at room temperature [2]. As a result, the study on the thermodynamic properties of lithium and borate salt system, with isopiestic method, is an essential mean to construct thermodynamic models to predict the salt lake brine system in China as well as develop and improve the modern theory of electrolytes.

The Principle of the Isopiestic Method

Isopiestic method is generally used to the determination of water activity and osmotic coefficients of the solution, whose concentration varies from higher than 0.1 $mol \cdot kg^{-1}$ to the saturation concentration, the principle is with different chemical potentials of electrolyte solution was placed in a closed system, through the transfer of the solvent and eventually has the same chemical potential [3]. In the isopiestic experiments we need at least accurately know the functional relationship between concentration and water activity of a solution which works as a reference standard solution, so the water activity of the other solution can be obtained by calculation and balance of the reference standard solution of water activity. The common reference standard materials (RSM) used for isopiestic method are NaCl, KCl, H_2SO_4 and $CaCl_2$. The RSM of NaCl and KCl are relatively cheap, easy purification and acquire more accurate data easily, but good

applicability is presented only in the low concentration range, while H_2SO_4 and $CaCl_2$ solution is widely used in the high concentration range [1].

Thermodynamic Properties of Aqueous Solutions Containing Lithium Ions

The research of thermodynamic properties of lithium system using isopiestic equipment is very active. Yao et al [4] used isopiestic equipment were measured water activity, osmotic coefficients of the $LiCl-H_2O$ system (concentration from 0.5 to 19.8 mol·kg^{-1}) $MgCl_2-H_2O$ system (concentration from 0.3 to 6.0 mol·kg^{-1}) and mixed aqueous solution (the ionic strength from 0.6 to 19.4 mol·kg^{-1}) at 298.15 K and determined the solubility of LiCl. When ionic strength is higher than 5.7 mol·kg^{-1}, there are three different calculation methods to calculate the Pitzer mixing parameters. (I) introduced of the higher-order electrostatic item, (II) introduced the higher-order electrostatic item and the relations between θ-I, then got the $\theta^{(0)}$, $\theta^{(1)}$, (III) neither of them are introduced. The results show that the method I with increasing ionic strength, *SD* increased. (I) have little relationship between the higher-order electrostatic term and the relations of θ-I, while in method III *SD* bigger than method I, II [4]. Zhang et al [5] were determined osmotic coefficients of the $Li_2SO_4-H_2O$ (concentration from 0.2 to 8.7 mol·kg^{-1}), $MgSO_4-H_2O$ (concentration from 0.6 to 12.7 mol·kg^{-1}) and $Li_2SO_4-MgSO_4-H_2O$ mixing system (ionic strength from 1.4 to 13.5 mol·kg^{-1}) and have verified the applicability of Pitzer equation and Scatchard equation for this system. Guo [6] et al used isopiestic equipment were measured water activity of the $LiCl-SrCl_2-H_2O$ system. Li [7] by using improved isopiestic apparatus were determined water activity and osmotic coefficients of $LiCl-H_2O$ (concentration from 0.5 to 9.2 mol·kg^{-1}), $Li_2SO_4-H_2O$ (concentration from 0.3 to 2.5 mol·kg^{-1}) and $LiCl-Li_2SO_4-H_2O$ (ionic strength from 0.5 to 9.5 mol·kg^{-1}) at 273.15 K, based on Pitzer ion interaction model and analyzed the experimental data, fitting Pitzer parameters under this temperature and modified and extended the rules of Zdanovskii, so that it can better describe the mixed system. Then Li et al [8] measured the water activity and osmotic coefficients for the same system of different concentrations at 373.15 K and compare to 273.15 K reveals the rules between osmotic coefficient and temperature, ionic strength and ion concentration fraction of Li_2SO_4. Yao et al [9] tested isopiestic equilibrium concentration and osmotic coefficient of $Li_2SO_4-K_2SO_4-H_2O$, $LiCl-MgSO_4-H_2O$ system at 348.15 K, 373.15 K from 0.1 mol kg^{-1} to near the saturation concentration range with isopiestic devices and explains the variation between the osmotic coefficient, activity coefficient, and vapor pressure, components and ionic strength. Based on the original room isopiestic apparatus, Zhang [10] formatted a device can be used in high temperature and a low temperature, then measured osmotic coefficient of $LiCl-H_2O$, $MgSO_4-H_2O$ binary system and $LiCl-MgSO_4-H_2O$ ternary system at 273.15 K, 298.15 K, 323.15 K, 348.15 K , 373.15 K. The mass of balanced solution has been corrected and the impact of air has been considered, so that the accuracy of the experimental data improved significantly. These works provide the basis data for establishing thermodynamic and dynamic model the data are listed in Table 1, 2.

For multivariate system, Yao et al [11] also reported the research of Li^+, Na^+, K^+, $Mg^{2+}//Cl^-$, $SO_4^{2-}-H_2O$ at 298.15 K, determined their water activity and the osmotic coefficient and compared the two kinds of thermodynamic properties. Zhou [12] the first time to forecast solubility of Li^+, K^+, $Mg^{2+}//SO_4^{2-}-H_2O$ system with the Pitzer model.

The osmotic coefficient of hybrid system has calculated by used the Pitzer model, the standard deviation of osmotic coefficient between experiment and model computation shows that isopiestic method can be well applied to study the thermodynamic properties of lithium system and provides the basis for the establishment of the model of lithium salt-water solution system.

Tab. 1 The single salt parameters of lithium chloride and lithium sulfate at different temperatures

T (K)	$\beta^{(0)}$	$\beta^{(1)}$	C^{Φ}	m_{max} (mol·kg^{-1})	SD	Ref
			LiCl			
273.15	0.1269	1.0517	-0.00072	8.0	0.0045	[7]
298.15	0.14503	0.31578	0.00417	5.704	0.00089	[4]
298.15	0.15952	0.21017	0.00130	9.842	0.00828	[4]
298.15	0.22073	-0.52331	-0.00817	19.848	0.04971	[4]
298.15	0.1378	0.4876	0.00504	9.0	0.006	[13]
298.15	0.20972	-0.34380	-0.00433	19.219	0.05339	[14]
298.15	0.14667	0.33703	0.00393	6.0	0.0020	[14]
323.15	0.1509	0.2709	0.00116	8.2	0.0028	[8]
			Li$_2$SO$_4$			
273.15	0.1561	0.2458	0.00415	8.0	0.0082	[7]
298.15	0.14473	1.29952	0.00616	3.0000	0.00448	[11]
298.15	0.136912	1.011003	0.00425	1.8972	0.00729	[15]
323.15	0.1331	1.4904	-0.0056	3.1	0.0015	[8]

Tab. 2 The mixing ion interaction parameters for the aqueous solutions containing lithium ion systems

T (K)	System	θ	φ	I (mol·kg^{-1})	SD $\theta \neq \varphi \neq 0$	SD $\theta = \varphi = 0$	Ref
273.15	LiCl–Li$_2$SO$_4$–H$_2$O	0.0144	-0.003703	8.0	0.1490	0.0212	[7]
273.15	LiCl–Li$_2$SO$_4$–H$_2$O	0.0169	-0.003627	8.0	0.01508	0.0203	[7]
298.15	LiCl–MgCl$_2$–H$_2$O	0.04601	-0.00557	5.694	0.00311	0.0090	[4]
298.15	LiCl–MgCl$_2$–H$_2$O	0.03829	-0.00340	5.694	0.00301	0.00864	[4]
298.15	LiCl–MgCl$_2$–H$_2$O	0.06977	-0.00826	5.694	0.00211	0.01301	[4]
298.15	Li$_2$SO$_4$–MgSO$_4$–H$_2$O	0.00039	0.1182		0.0052	0.017	[5]
323.15	LiCl–Li$_2$SO$_4$–H$_2$O	0.03236	-0.01824	8.6	0.0164	0.0212	[8]

SD is the standard deviation of the fitting results by model with the experimental osmotic coefficient values.

Thermodynamic Properties of Aqueous Solutions Containing Borate Ions

When the total boron concentration is higher than 0.05 mol·kg^{-1}, the reactions of polymerization and depolymerization of borates would be existed. It is difficult to predict the thermodynamic property because the effect of the total boron concentration [1]. Nowadays, when calculate the osmotic coefficient of the borate systems, the following three methods were usually used [15].

Method-I, only the ion-interaction between two ion species of Li$^+$ and B$_4$O$_7^{2-}$ were considered. Yuan [15] was studied the osmotic coefficient of Li$_2$SO$_4$ (ion concentration from 0.3577 to 5.6378 mol·kg^{-1}) Li$_2$B$_4$O$_7$ (ion concentration from 0.1757 to 2 mol·kg^{-1}) and mixed salt aqueous solution (ionic strength from 0.3118 to 5.5248 mol·kg^{-1}) and osmotic coefficient of the system is changing with the ionic strength. In order to better describe the polymerization and depolymerization reaction to join the $\beta^{(2)}$ and change the a$_2$ of Pitzer equation. Yin [16] also adopted the method I when determination MgSO$_4$–MgB$_4$O$_7$. While method-I is possible to describe the borate salt system but ignored the balance of the polymerization and depolymerizationboron. Method-II based on chemical equilibrium and Pitzers equations of osmotic coefficient for mixed electrolytes. Zhang [17] has used three methods to research the Li$_2$B$_4$O$_7$–H$_2$O systems, the research shows that method-II can reflect the internal of Li$_2$B$_4$O$_7$ solution. Yang et al [18-20] LiCl–Li$_2$B$_4$O$_7$–H$_2$O system under the different temperature is studied, on the basis of the original model modified, at $m < 0.08$ mol·kg^{-1}, the species H$_3$BO$_3$, B(OH)$_4^-$, Li$^+$, Cl$^-$ were considered, but at $m \geq 0.08$ mol·kg^{-1}, the species H$_3$BO$_3$, B$_3$O$_3$(OH)$_4^-$, B(OH)$_4^-$, Li$^+$, Cl$^-$ were considered. In the estimations of the ion interaction parameters the H$_3$BO$_3$ was neglected. Table 3 lists the Pitzer single salt parameters of the system under different temperature.

For the convenience in applying, we simplify the method II, merge the similar coefficient. Zhang et al [21] at 298.15 K under research Li$_2$B$_4$O$_7$–MgCl$_2$(B)–H$_2$O system adopts the θ_{XT} express combined action of the three kinds of boric acid salt and some kind of positive ion. The $\theta_{BT,X}$ said any one of the three kinds of boric acid salt combination of interaction; $\varphi_{Mg,Cl,BT}$ express combined

action of the three kinds of boric acid salt and positive ion. $\varphi_{\text{Mg Li BT}}$ express combined action of the three kinds of Li^+, Mg^{2+}.

Tab. 4 Relative deviations of the calculated and experimental osmotic coefficients of borate systems

T (K)	System	RSM	*RD*	*Ref*
298.15	$LiSO_4–Li_2B_4O_7–H_2O$	NaCl(aq)	0.02	[15]
298.15	$Li_2B_4O_7–H_2O$	NaCl(aq)	0.01	[17]
273.15	$LiCl–Li_2B_4O_7–H_2O$	NaCl(aq)	<0.04	[18]
298.15	$LiCl–Li_2B_4O_7–H_2O$	NaCl(aq)	<0.04	[19]
298.15	$LiCl–Li_2B_4O_7–H_2O$	NaCl(aq)	<0.01	[20]
298.15	$Li_2B_4O_7–MgCl_2(B)–H_2O$	NaCl(aq)	<0.05	[21]

RD is the relative deviation of fitting results with the experimental osmotic coefficient values.

It should be pointed out is that method-I has a less of parameters and easy to be used. Method-II and III considering the single boron, three boron and four boron species, has a lot of parameters but is more a reflection of internal reaction of the borate salt ions, we should to analysis when using the above three methods.

Conclusion

Based on a brief introduction to isopiestic technical analysis, the isopiestic researches of thermodynamic properties of the aqueous systems containing lithium and borate were introduced, the Pitzer single salt parameters and mixed ion interaction parameters of chloride and sulfate containing lithium at different temperatures and systems were summarized, and new progresses on the isopiestic on borates had been also raised, which is of great importance to promote the thermodynamic modulus of the complex lake brine systems containing lithium and boron ions. It is also worth noting that isopiestic study on thermodynamic properties of electrolyte solutions, which are mostly concentrated at normal temperature and pressure, with a narrow temperature range. As for the borate containing alkali metals and alkaline earth metal, the researches on thermodynamic properties are still very deficient, how to express the thermodynamic properties of the borate systems within a wide range of concentration and expand the thermodynamic model of borate electrolyte solutions is the main direction of future development.

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