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Phase Equilibria and Phase Separation of the Aqueous Solution System Containing Lithium Ions

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Abstract

Brines including seawater, concentrated seawater after desalinization, salt lake, oil/gas water, and well bitter are widely distributed around the world. In order to promote the comprehensive utilization and effective protection of the valuable chemical resources existing in brines such as freshwater, lithium, sodium, potassium, and magnesium salts, the systematic foundation and application foundation research including phase equilibria and thermodynamic properties for the salt-water electrolyte solution are essential, especially for solid lithium salts and their aqueous solution systems.

Keywords: thermodynamics, phase equilibria, aqueous solution, lithium salts

1. Introduction

1.1. Lithium resources situation

Lithium is the lightest alkali metal, which plays a growing role in numerous processes such as rechargeable batteries, thermonuclear fusion, medical drugs, lubricant greases, ceramic, glasses, dyes, adhesives, and electrode welding [1–19]. Lithium is a critical energy material and a strategic resource for the twenty-first century. Consequently, the market demands for lithium resources are increasing around the world [20, 21].

Lithium naturally occurs in compound forms because of its high reactivity. Economic concentrations of lithium are found in brines, minerals, and clays in various parts of the world. Brines and high-grade lithium ores are the present sources for all commercial lithium production. The global lithium reserve is estimated at 14.0 megatons [22], which is 74.5 megatons of lithium carbonate equivalent. Lithium reserves are mainly distributed in South America, China, and Australia [23].

Generally, lithium is obtained from two major resources: the lithium mineral ores including spodumene and petalite ores and the containing-lithium brine resources including seawater, underground water and salt lake brine [24–27]. Currently, the former is well exploited while the latter is being developed by industries with relatively low efficiency. Nonetheless, more than 60% of the total lithium amount exists in sea water and brines [24]. Therefore, a great potential exists for obtaining lithium from aqueous sources, if an efficient lithium recovery technology can be developed. Separation and extraction of lithium from either sea water or brine is carried out on a semi-industrial scale and industrial scale in the USA from salt lakes [28], in Japan from thermal water [29, 30], in Israel from the Dead Sea [31], and in China from underground brines and salt lakes [22].

In addition, the most important physical and chemical processes occurring in brines are evaporation, concentration, crystallization, precipitation, dissolution, and phase transformation. It is obvious that phase equilibria and thermodynamics can explain above phenomenon and even guide those processes effectively. Therefore, it is particularly meaningful to engage the research on phase equilibria and thermodynamics properties of lithium-containing aqueous solution systems for describing the geochemical evolution of containing lithium brines and exploiting valuable lithium resources.

2. Phase equilibria of lithium-containing salt-water systems

Brines, including seawater, concentrated seawater after desalinization, salt lake, oil/gas water, and well bitter are all complex multi-component salt-water systems, whose study and application is mainly in reference to the solubility of salts in the water and the solid-liquid equilibrium rule. Hence, solid-liquid phase equilibria form the basis for salt-water systems, which in turn are used in the chemical industry for the separation of lithium [32].

2.1. Stable phase equilibria of lithium-containing salt-water systems

Early in the 1960s, Soviet scholars had conducted research on stable phase equilibria of lithium-containing salt-water systems [33–35]. The solubilities of the systems $(\text{Li}^+, \text{Na}^+, \text{Mg}^{2+} // \text{Cl}^- - \text{H}_2\text{O})$, $(\text{Li}^+, \text{Na}^+, \text{Mg}^{2+} // \text{SO}_4^{2-} - \text{H}_2\text{O})$, $(\text{Li}^+, \text{Na}^+, \text{K}^+ // \text{SO}_4^{2-} - \text{H}_2\text{O})$ in the temperature range from 288.15 to 373.15 K were determined. Three types of double salts containing lithium, $2\text{Li}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$, $\text{Li}_2\text{SO}_4 \cdot 3\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$, and $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ were found for the first time and the physico-chemical properties of these were measured. All these studies could provide the solubility data to extract lithium resources in sea water and other brines.

Researchers in China also studied stable phase equilibria of complex system $(\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{borate} - \text{H}_2\text{O})$ and its subsystems. Some research results are shown in **Table 1**. In addition, depending on the aquatic chemical types, the lithium-containing salt-water systems can be divided into lithium-containing chloride system, sulfate system, carbonate system, and borate system.

In order to apply the hydride salting-out effect to the separation of lithium and magnesium, phase equilibria of the quaternary system $\text{H}^+, \text{Li}^+, \text{Mg}^{2+} // \text{Cl}^- - \text{H}_2\text{O}$ and its subsystems at

Category	Lithium-containing systems	Temperature (K)	Reference
LiCl	$H^+, Li^+, Mg^{2+}/Cl^- - H_2O$	273.15	[36]
	$Li^+, Na^+, K^+, Mg^{2+}/Cl^- - H_2O$	298.15	[37]
	$Li^+, Mg^{2+}/Cl^- - H_2O$	298.15	[38]
	$Li^+, NH_4^+/Cl^- - H_2O$	273.15, 298.15, 323.15	[39]
	$Li^+, Rb^+, Mg^{2+}/Cl^- - H_2O$	323.15	[40]
	$Li^+, Na^+, K^+, Sr^{2+}/Cl^- - H_2O$	298.15	[41]
	$Li^+, Mg^{2+}/Cl^- - H_2O$	288.15	[42]
Li ₂ SO ₄	$Li^+, K^+/SO_4^{2-} - H_2O$	298.15	[43]
	$Li^+, Mg^{2+}/SO_4^{2-} - H_2O$		
	$Li^+, K^+, Mg^{2+}/SO_4^{2-} - H_2O$	298.15	[44]
	$Li^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-} - H_2O$	298.15	[45]
	$Li^+, Na^+, K^+, Mg^{2+}/SO_4^{2-} - H_2O$	298.15	[46]
	$Li^+, K^+/SO_4^{2-} - H_2O$	288.15	[47]
	$Li^+/Cl^-, SO_4^{2-} - H_2O$	308.15	[48]
	$Li^+, Mg^{2+}/SO_4^{2-} - H_2O$	288.15	[42]
Li ₂ CO ₃	$Li^+, Na^+, K^+/CO_3^{2-} - H_2O$	298.15	[49]
	$Li^+, K^+/Cl^-, CO_3^{2-} - H_2O$	298.15	[50]
	$Li^+, Na^+/Cl^-, CO_3^{2-} - H_2O$	298.15	[51]
	$Li^+, K^+/Cl^-, CO_3^{2-} - H_2O$	298.15	[52]
	$Li^+, Na^+, K^+/CO_3^{2-} - H_2O$	288.15	[53]
Li ₂ B ₄ O ₇	$Li^+/Cl^-, SO_4^{2-}, B_4O_7^{2-} - H_2O$	298.15	[54]
	$Li^+, Mg^{2+}/SO_4^{2-}, B_4O_7^{2-} - H_2O$	298.15	[55]
	$Li^+/CO_3^{2-}, B_4O_7^{2-} - H_2O$	298.15	[56]
	$Li^+, K^+/CO_3^{2-}, B_4O_7^{2-} - H_2O$	298.15	[56]
	$Li^+, Na^+/CO_3^{2-}, B_4O_7^{2-} - H_2O$	298.15	[57]
	$Li^+, K^+/CO_3^{2-}, B_4O_7^{2-} - H_2O$	298.15	[57]
	$Li^+, Na^+, K^+/Cl^-, B_4O_7^{2-} - H_2O$	298.15	[58]
		288.15	[59]
	298.15	[60]	
	288.15	[61]	
LiBO ₂	$Li^+/SO_4^{2-}, BO_2^- - H_2O$	288.15, 298.15	[62]
	$Li^+/Cl^-, BO_2^- - H_2O$	288.15, 298.15	[63]
	$Li^+/Cl^-, BO_2^- - H_2O$	308.15	[64]
	$Li^+/Cl^-, SO_4^{2-}, BO_2^- - H_2O$	298.15	[65]
	$Li^+/SO_4^{2-}, CO_3^{2-}, BO_2^- - H_2O$	288.15, 298.15, 308.15	[66]
	$Li^+/Cl^-, BO_2^- - H_2O$	323.15	[67]
	$Li^+/SO_4^{2-}, BO_2^- - H_2O$		

Table 1. Stable phase equilibria of lithium-containing salt-water systems.

273.15, 293.15, and 313.15 K had been researched [36, 68]. Phase distribution of the quaternary system was confirmed and the salting-out effect was investigated preliminarily, which provides the physical chemistry foundation for lithium-preparation technique in brines.

Furthermore, the phase equilibria and phase diagram of various salt-water systems containing lithium had been reported heavily. However, the experimental temperature was almost focused on 298.15 K. With the maturity of research techniques and the development of instruments, phase equilibria of multi-component systems at multiple temperatures should be the research focus point in the future. It is worth mentioning that the structures of borate are complicated and have diversified aggregation forms because of the changes of pH, boron contents, types of coexisting ions, and the concentration conditions in the brines. Most studies on the borate-type salt lake brine are mainly for lithium tetraborate. Our group has made excellent progress on phase equilibria of salt-water system containing different species of lithium borates [62–67].

2.2. Metastable phase equilibria of lithium-containing salt-water systems

In the process of seawater and salt lake brine evaporation, the metastable phenomenon is ubiquitous. Because of the conditions of temperature, wind speed, and humidity in the natural environment, brine systems are in a metastable state. Early in the eighteenth century, Van't Hoff had already found that some phase regions disappeared and some enlarged in the stable phase diagram when the salt-water system was in the process of simulating evaporation [32]. So it is useful for the metastable phase diagram to extract the products which cannot be obtained in the stable phase diagram [69].

Some of metastable phase equilibria of lithium-containing salt-water systems are shown in **Table 2**. A lot of lithium-containing systems of chloride, sulfate, carbonate, and borate were researched. The concentration of lithium salt becomes higher in the sulfate-type salt lake brine in the final evaporation period. In our group, metastable phase equilibria of the

Category	Lithium-containing systems	Temperature (K)	Reference
LiCl	$\text{Li}^+, \text{Na}^+, \text{Mg}^{2+} // \text{Cl}^- - \text{H}_2\text{O}$	308.15	[70]
	$\text{Li}^+, \text{Na}^+, \text{Ca}^{2+} // \text{Cl}^- - \text{H}_2\text{O}$	288.15	[71]
	$\text{Li}^+, \text{K}^+ // \text{Cl}^- - \text{H}_2\text{O}$	298.15	[72]
	$\text{Li}^+, \text{K}^+ // \text{Cl}^- - \text{H}_2\text{O}$	323.15	[73]
	$\text{Li}^+, \text{K}^+, \text{Rb}^+ // \text{Cl}^- - \text{H}_2\text{O}$	298.15	[74]
	$\text{Li}^+, \text{K}^+, \text{Rb}^+ // \text{Cl}^- - \text{H}_2\text{O}$	323.15	[75]
Li_2SO_4	$\text{Li}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$	298.15	[76]
	$\text{Li}^+, \text{Na}^+ // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$	273.15	[77]
	$\text{Li}^+, \text{Na}^+, \text{Mg}^{2+} // \text{SO}_4^{2-} - \text{H}_2\text{O}$	263.15	[78]
	$\text{Li}^+, \text{Mg}^{2+} // \text{SO}_4^{2-} - \text{H}_2\text{O}$	323.15	[79]
	$\text{Li}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$	323.15	[80]

Category	Lithium-containing systems	Temperature (K)	Reference
	$\text{Li}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$	308.15	[81]
	$\text{Li}^+, \text{K}^+ // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$	308.15	[82]
	$\text{Li}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$	273.15	[83]
	$\text{Li}^+, \text{Na}^+ // \text{SO}_4^{2-} - \text{H}_2\text{O}$	288.15, 308.15	[84]
	$\text{Li}^+, \text{Na}^+ // \text{SO}_4^{2-} - \text{H}_2\text{O}$	308.15, 348.15	[85]
	$\text{Li}^+, \text{Na}^+, \text{K}^+ // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$	308.15	[86]
	$\text{Li}^+ // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$	308.15	[48]
	$\text{Li}^+, \text{K}^+ // \text{SO}_4^{2-} - \text{H}_2\text{O}$	288.15, 323.15	[87]
	$\text{Li}^+, \text{K}^+ // \text{SO}_4^{2-} - \text{H}_2\text{O}$	308.15	[88]
Li_2CO_3	$\text{Li}^+, \text{Na}^+ // \text{SO}_4^{2-}, \text{CO}_3^{2-} - \text{H}_2\text{O}$	288.15	[89]
	$\text{Li}^+, \text{K}^+ // \text{Cl}^-, \text{CO}_3^{2-} - \text{H}_2\text{O}$	298.15	[90]
$\text{Li}_2\text{B}_4\text{O}_7$	$\text{Li}^+, \text{Na}^+, \text{K}^+ // \text{Cl}^-, \text{B}_4\text{O}_7^{2-} - \text{H}_2\text{O}$	298.15	[60]
	$\text{Li}^+, \text{Na}^+ // \text{SO}_4^{2-}, \text{B}_4\text{O}_7^{2-} - \text{H}_2\text{O}$	288.15	[91]
	$\text{Li}^+, \text{Na}^+, \text{K}^+ // \text{CO}_3^{2-}, \text{B}_4\text{O}_7^{2-} - \text{H}_2\text{O}$	288.15	[92]
	$\text{Li}^+, \text{K}^+ // \text{Cl}^-, \text{SO}_4^{2-}, \text{B}_4\text{O}_7^{2-} - \text{H}_2\text{O}$	288.15	[93]
	$\text{Li}^+, \text{K}^+ // \text{SO}_4^{2-}, \text{B}_4\text{O}_7^{2-} - \text{H}_2\text{O}$	288.15	[94]
	$\text{Li}^+ // \text{Cl}^-, \text{CO}_3^{2-}, \text{B}_4\text{O}_7^{2-} - \text{H}_2\text{O}$	298.15	[95]
	$\text{Li}^+, \text{K}^+ // \text{CO}_3^{2-}, \text{B}_4\text{O}_7^{2-} - \text{H}_2\text{O}$	273.15	[96]
	$\text{Li}^+, \text{K}^+ // \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{B}_4\text{O}_7^{2-} - \text{H}_2\text{O}$	273.15	[97]
	$\text{Li}^+, \text{K}^+ // \text{CO}_3^{2-}, \text{B}_4\text{O}_7^{2-} - \text{H}_2\text{O}$	288.15	[98]

Table 2. Metastable phase equilibria of lithium-containing salt-water systems.

lithium-containing sulfate system ($\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$) and its subsystems at different temperature were determined, which has great help for industrial production and the comprehensive utilization of lithium-containing sulfate system salt lakes.

3. Thermodynamics of lithium salts and their aqueous solution systems

In the long-term production activities and scientific practice, it is troublesome for some production process of the new technology, new processes, or new product development, because there is no data and phase diagram of the relevant salt-water system. In addition, experimental determination on solubilities of multi-component systems is a complex work and it is virtually impossible for researchers to investigate all the salt-water systems. However, it is well-known that phase diagram is a geometry description of phase relation in the system under the condition of thermodynamic equilibrium. In theory, the phase diagram should be able to be gained based on the principles of thermodynamics [99].

As to the classical electrolyte theory, Debye-Hückel theory is only suitable for the dilution solution with a concentration below 0.1 m (molality) and it is unusable to solve the thermodynamic behaviors and to predictive the dissolution equilibria for the complex salt lake brine systems [100]. Pitzer theory [101], which was developed on the basis of Debye-Hückel ion-interaction theory, characterizing thermodynamics properties of electrolyte solution with brief and terse form is widely used either in geochemical behaviors of natural waters and mineral deposits or in the predictions of solubility of salt-water systems. A series of calculated expressions for the activity coefficient and osmotic coefficient of any electrolytes in multi-component systems were proposed by Pitzer [102]. After measuring the thermodynamic parameters, such as osmotic coefficient, activity coefficient, heat of dissolution, heat of dilution, heat of mixing, and specific heat, it is easy to calculate and fit the relative model-parameter theoretically and solubility on the basis of Pitzer and its extended ion-interaction model to promote the development of theory and practice, such as the new field of calculating phase diagram and its application [32].

At present, the domestic and foreign research methods of electrolyte solution of thermodynamic properties are mainly isopiestic method, electromotive force method, calorimetric method, conductivity method, hygrometry, density method, and so on. The isopiestic method and electromotive force method are the most common experimental method to be widely used in measuring the thermodynamic properties such as permeability and activity coefficient. They complement each other. The basic property of matter which is the change of energy can be measured directly by the calorimetric method. In recent years, the calorimetric method is widely implemented in the research of solution thermodynamic properties [103].

In 1992, Yao et al. [104] measured the osmotic and activity coefficients of aqueous mixtures of LiCl and MgCl₂ in the range of low concentration to near crystallization limits by the isopiestic method. The Pitzer single-salt parameters and the mixed parameters were calculated by the osmotic and activity coefficients, which were applicative for Pitzer's equation. The predicted solubilities for the system studied using Pitzer's approach were shown to be in reasonable agreement with experimental results from references. The osmotic coefficients of aqueous mixtures of Li₂SO₄ and MgSO₄ had been reported from 1.4 to 13.5 mol·kg⁻¹ at 298 K using the isopiestic method by Zhang et al [105]. In the ranges of 0.2–8.7 and 0.6–12.7 mol·kg⁻¹ the osmotic coefficients of Li₂SO₄ and MgSO₄ were also reported, respectively. The predicted solubilities for this system using Pitzer's approach showed good agreement with experimental results. Yang et al. [106] measured isopiestic molalities and water activities for the Li₂B₄O₇–LiCl–H₂O system at 298.15 K using an improved isopiestic apparatus, and the two types of osmotic coefficients were calculated and compared. Pitzer's primary model with minor modifications, in combination with the chemical equilibria, was used to represent the experimental data for the complex Li₂B₄O₇–LiCl–H₂O system.

Based on the principle of isopiestic method, the osmotic and activity coefficients can be obtained. However, it might be difficult to get these coefficients with the strict thermodynamics calculation in the mixed electrolyte solutions. The activity coefficients of KCl and LiCl in KCl–LiCl aqueous mixtures have been studied at 298.15 K in ionic strength range of 0.1–4.0 mol·kg⁻¹ by Li et al. [107]. The data were fitted to Pitzer's equation using the regression method, Pitzer parameters were obtained. The activity confidents of aqueous LiCl in the system LiCl–MgCl₂–H₂O were

determined at 298.15 K in the total ionic strength range from 0.05 to 6.0 mol·kg⁻¹ with the electromotive force method using a lithium-selective electrode and Ag/AgCl electrode by Wang et al. [108]. The activity coefficients of the experiment were compared with which calculated by the Pitzer equation with the known parameters of experimental osmotic coefficients.

The process of chemical reaction, dissolution, dilution, and mixing are often accompanied with heat changes. Reaction heat data, such as dissolution heat, dilution heat, mixing heat, and special heat, were determined critically by the calorimetry technology, which can work out thermodynamic enthalpy, entropy, Gibbs free energy, and thermodynamic equilibrium constant. Hence, the calorimetric method became the research highlights to measure the thermodynamic properties (dissolution heat, dilution heat, mixing heat, and capacity heat).

There are some thermodynamic parameters measured by the calorimetric method. In 1965, Wu [109] and Wood [110] researched heats of mixing of a variety of aqueous containing lithium solutions of the same ionic strength at 298.15 K. Some of them were in the different concentration. The concentration dependence of the heats of mixing indicated that like-charged ion pairs were important contributors to the heat of mixing. The enthalpies of dilution of lithium in the range 0.1–1.0 m had been measured at 303.15 K with a microcalorimeter by Leung et al. [111]. The relative apparent enthalpies of these solutions had been determined with the aid of an extended form of Debye-Hückel limiting law. Enthalpies of solution of Li₂SO₄ and Li₂SO₄·H₂O in water at 298.15 K were investigated [112]. The molar enthalpies of solution extrapolated to infinite dilution at 298.15 K were $\Delta_{\text{sol}}H_{\text{m}}^{\infty}(\text{Li}_2\text{SO}_4) = -(30502 \pm 170) \text{ J}\cdot\text{mol}^{-1}$ and $\Delta_{\text{sol}}H_{\text{m}}^{\infty}(\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}) = -(17899 \pm 152) \text{ J}\cdot\text{mol}^{-1}$. The value for the monohydrate lithium sulfate had been calculated by assuming that the excess water in the sample was present as an aqueous saturated solution. There were presented preliminary specific heat capacities of lithium sulfate solution.

The standard molar enthalpy of the formation of some lithium borates were determined [113–116]. The results were $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{LiBO}_2\cdot 2\text{H}_2\text{O}) = -(1627.46 \pm 0.90) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{LiBO}_2\cdot 8\text{H}_2\text{O}) = -(3397.00 \pm 0.94) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{LiB}_5\text{O}_8\cdot 5\text{H}_2\text{O}) = -(5130.25 \pm 4.05) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Li}_2\text{B}_4\text{O}_7\cdot 3\text{H}_2\text{O}) = -(4290.86 \pm 3.31) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Li}_3\text{B}_5\text{O}_8(\text{OH})_2 \text{ (I)}) = -(4724.1 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Li}_3\text{B}_5\text{O}_8(\text{OH})_2 \text{ (II)}) = -(4723.8 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Li}_4[\text{B}_5\text{O}_{13}(\text{OH})_2]\cdot 3\text{H}_2\text{O}) = -(7953.8 \pm 6.6) \text{ kJ}\cdot\text{mol}^{-1}$.

Meanwhile, the thermodynamic properties in solution system contained lithium borates had been widely researched. Zhang et al. [117] determined the molar heat capacities of the aqueous Li₂B₄O₇ solution at a concentration of 0.0187 mol·kg⁻¹ in the temperature range from 80 to 355 K by a precision automated adiabatic calorimetry. The enthalpies of dilution for the aqueous Li₂B₄O₇ solutions from 0.0212 to 2.1530 mol·kg⁻¹ at 298.15 K have been measured [118]. The relative apparent molar enthalpies and relative partial molar enthalpies of the solvent and solute for the aqueous Li₂B₄O₇ system were also calculated. The thermodynamic properties of the binary aqueous system Li₂B₄O₇–H₂O were represented with the extended Pitzer ion-interaction model. And the enthalpies of dilution, $\Delta_{\text{dil}}H_{\text{m}}$, have been also measured for the LiCl–Li₂B₄O₇–H₂O system at $T = 298.15 \text{ K}$ [119]. A suitable microcalorimetric method was used to obtain the better data of the enthalpies of dilution for the ternary system LiCl–Li₂B₄O₇–H₂O at a low concentration. The relative apparent molar enthalpies have been determined and the

relationships between apparent molar enthalpies and ionic strength at different molar fractions of $\text{Li}_2\text{B}_4\text{O}_7$ were obtained. Li [120] measured the heats of dilution and heat capacities of eutectic point solution system $\text{Li}_2\text{B}_4\text{O}_7\text{--Li}_2\text{SO}_4\text{--LiCl--H}_2\text{O}$ and subsystems $\text{Li}_2\text{B}_4\text{O}_7\text{--Li}_2\text{SO}_4\text{--H}_2\text{O}$ and $\text{Li}_2\text{B}_4\text{O}_7\text{--LiCl--H}_2\text{O}$ to cover the ionic strength range from 19 to 0.1 at 298.15 K. The data of the heat of dilution were extrapolated to infinite dilution by use of the Debye-Hückel limiting law to obtain relative apparent molar enthalpies.

In our group, the heat capacities of aqueous solution systems ($\text{Li}_2\text{B}_4\text{O}_7\text{--H}_2\text{O}$) $m = 0.00415\text{--}0.4208 \text{ mol}\cdot\text{kg}^{-1}$ at $T = 298.15, 308.15$ and 323.15 K were determined experimentally using the Setaram BT 2.15 microcalorimeter [121]. On the basis of experimental data, the apparent molar heat capacities at different concentrations and temperatures were calculated, and the relationship equations between apparent molar heat capacity and solution concentration of lithium tetraborate at 298.15, 308.15 and 323.15 K were obtained. On the other hand, the Pitzer single salt parameters of lithium tetraborate at different temperatures were fitted on the basis of the Pitzer ion-interaction theory of the electrolytes on the apparent molar heat capacity.

So far, the thermodynamic parameters of lithium salts are still scarce. The Pitzer single salt parameters and the mixing ion-interaction parameters at different temperatures have not been established yet. So, more works on the thermodynamics parameters of lithium salts and their aqueous solution systems at multi-temperatures are essential.

4. Conclusion

With the gradually increasing demands of lithium salt resources as the lithium energy battery, to exploit the lithium-containing brine resources including seawater, concentrated seawater after desalination, salted lake, oil/gas field water, and well bitter is essential. Therefore, studies on phase equilibria and phase separation of the lithium-containing brine systems are significant to guide the comprehensive utilization of those lithium-containing brine resources around the world. In this chapter, the following three main aspects were discussed: Firstly, the stable and metastable phase equilibria of lithium-containing salt-water multi-systems including the different types of chloride, sulfate, carbonate, and borate brines at different temperatures were summarized. Secondly, a series of valuable thermodynamic properties of standard molar enthalpy of formation for solid lithium salts such as $\text{LiCl}\cdot\text{H}_2\text{O}$, $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$, $\text{LiBO}_2\cdot 2\text{H}_2\text{O}$, $\text{LiBO}_2\cdot 8\text{H}_2\text{O}$, $\text{Li}_2\text{B}_4\text{O}_7\cdot 3\text{H}_2\text{O}$, $\text{Li}_3\text{B}_5\text{O}_8(\text{OH})_2$, and $\text{Li}_4[\text{B}_5\text{O}_{13}(\text{OH})_2]\cdot 3\text{H}_2\text{O}$, and the thermodynamic properties (dissolution heat, dilution heat, mixing heat, and capacity heat) for their relatively aqueous solutions were obtained combined by the isothermal dissolution equilibrium method, isopiestic method, and adiabatic calorimetry, and so on. Thirdly, on the basis of classical Debye-Hückel electrolyte theory, the extended modern electrolyte model, developed by Pitzer KS and his coworkers to express the activity coefficient and osmotic coefficient of any electrolytes in multi-component lithium-containing systems, was successfully used to obtain a series parameters such as the model parameter fitting, thermodynamic property calculation, and the solubility prediction.

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