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Studies on the Thermodynamics and Thermal Chemistry Properties for Lithium Salts and Their Aqueous Solution Systems

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1 Introduction

With the industrial development of lithium battery, nuclear and aerospace industry, the demands of metal lithium and its compounds are increasing significantly. Lithium is called as the energy of the metal in the new century (Zhang et al. 2001).

The total reserve of lithium resources around the world is about 1.466×10^7 t (Ji, 2005). Although lithium resources are mainly existed either in the liquid minerals (salt lake brines) or in solid ores (granite pegmatite deposit for example), 87% of the world's lithium reserve is existed in salt lake brines (Zheng, 2007). Sin China, salt lake lithium resources mainly exist in Qinghai-Tibet plateau (Wu et al.,). The hydrochemical types of the salt lake brines include carbonate-type, sulfate-type, chloride-type and the complex borate-type. Therefore, in order to effectively exploit the lithium salt resources, studies on the thermodynamic and thermal chemical properties of the lithium salts and their aqueous system are essential.

As to the classical electrolyte theory, although Debye-Hückel theory is only suitable for the dilution solution with 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 (Song et al., 2000), Pitzer theory, 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 computational expressions for the activity coefficient and osmotic coefficient of any electrolytes in multi-component systems were proposed by Pitzer (Pitzer, 1991).

After measuring the thermodynamic parameters, such as osmotic coefficient, activity coefficient, heat of

dissolution, heat of dilution, heat of mixing, specific heat, it is easy to theoretical calculate and fit the relative model-parameter and solubility on the basis of Pitzer and its extended in-interaction model to promote the development of theory and practice, such as the new field of calculating phase diagram and its application (Deng et al., 2013).

In this paper, progresses on thermodynamic and thermal chemical properties of several lithium salts and their aqueous solutions including lithium chloride, lithium sulfate, and lithium borate were summarized. Some

Table 1 Thermodynamic and thermal chemical parameters of lithium salts and their aqueous solution systems

Salts/Systems	Thermodynamic parameters	Refs
$\Delta_{\text{sol}}H_m^\infty$ (298.15K, J•mol ⁻¹)		
LiCl	-(36653 ± 90)	Apelblat et al., 1984
LiCl•H ₂ O	-(18562 ± 54)	Apelblat et al., 1984
Li ₂ SO ₄	-(30502 ± 170)	Apelblat et al., 1985
Li ₂ SO ₄	-(17899 ± 152)	Apelblat et al., 1985
$\Delta_f H_m^\circ$ (298.15K, kJ•mol ⁻¹)		
LiBO ₂ •2H ₂ O	-1627.46 ± 0.90	Zhu et al., 2004
LiBO ₂ •8H ₂ O	-3397.00 ± 0.94	Zhu et al., 2004
LiB ₃ O ₈ •5H ₂ O	-5130.25 ± 4.05	Li et al., 1998
Li ₂ B ₄ O ₇ •3H ₂ O	-4290.86 ± 3.31	Li et al., 1998
Li ₃ B ₅ O ₈ (OH) ₂ (I)	-4724.1 ± 4.2	Li et al., 2010
Li ₃ B ₅ O ₈ (OH) ₂ (II)	-4723.8 ± 4.2	Li et al., 2010
Li ₄ [B ₅ O ₁₃ (OH) ₂]•3H ₂ O	-7953.8 ± 6.6	Li et al., 2012
Φ		
LiCl-MgCl ₂ -H ₂ O	(I=0.5-19.42, 298.15K)	Yao et al., 1992
γ		
Li ₂ SO ₄ -MgSO ₄ -H ₂ O	(I=0.2-13.5, 298.15K)	Zhang et al., 1993
LiCl-KCl-H ₂ O	(I=0.1-4.0, 298.15K)	Li et al., 1992
LiCl-MgCl ₂ -H ₂ O	(I=0.05-6.0, 298.15K)	Wang et al., 1993
γ		
H ₃ BO ₃ -Li ₂ B ₄ O ₇ -LiCl-H ₂ O	(278.15K, 288.15K, 298.15K, 308.15K, 318.15K)	Wang et al., 1994

Note: $\Delta_{\text{sol}}H_m^\infty$, Standard molar enthalpy; $\Delta_f H_m^\circ$, standard molar enthalpies of formation; Φ , osmotic coefficient; γ , average activity coefficient.

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thermodynamic parameters were presented in Table 1. Some works done in our laboratory will be introduced in this presentation.

2 Conclusions

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

In this presentation, progresses on thermodynamic and thermal chemical properties of several lithium salts and their aqueous solutions systems around the world were summarized. Some works studied in our research group will be introduced. In addition, more works on thermodynamic and thermal chemistry of lithium and its compounds as well as the new trends in the future is also carried out.

Key words: thermodynamics, thermal chemistry, Pitzer model, lithium salts, lithium-containing aqueous system

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