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Development of a thermodynamic model for the Li_2CO_3-NaCl-Na_2SO_4-H_2O system and its application

Junfeng Wang [a], Xiaowang Wu [b], Suojiang Zhang [a,*]

[a] State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Qinghai CITIC Guoan Science and Technology Development Co. Ltd, Qinghai Province 816000, PR China

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ABSTRACT

The study of the solid-liquid phase equilibrium for the Li_2CO_3-NaCl-Na_2SO_4-H_2O system is of significance to separate lithium from the mother liquor obtained by the reaction of lithium chloride/lithium sulfate and sodium carbonate. The phase equilibrium data for the binary system of Li_2CO_3-H_2O, the ternary systems of Li_2CO_3-NaCl-H_2O and Li_2CO_3-Na_2SO_4-H_2O, and the quaternary system of Li_2CO_3-NaCl-Na_2SO_4-H_2O over the temperature range from 283.15 K to 363.15 K were measured. Based on the Pitzer's model embedded in the Aspen Plus™, the phase equilibrium data for the systems of NaCl-H_2O, Na_2SO_4-H_2O and NaCl-Na_2SO_4-H_2O taken from literatures were firstly predicted to verify the applicability of parameters from the default database and literatures. Subsequently, besides the solubility of Li_2CO_3 in water at different temperatures, the values for the systems of Li_2CO_3-NaCl-H_2O and Li_2CO_3-Na_2SO_4-H_2O at 298.15 K and 343.15 K were correlated, and then the obtained parameters can well predict the phase equilibrium data for the systems of Li_2CO_3-NaCl-H_2O, Li_2CO_3-Na_2SO_4-H_2O Li_2CO_3-NaCl-Na_2SO_4-H_2O at T = (313.15, 323.15 or 363.15) K. Through the rigorous thermodynamic model representing the Li_2CO_3-NaCl-Na_2SO_4-H_2O system developed, the phase diagram of the ternary Li_2CO_3-NaCl-H_2O system at T = (298.15, 343.15 or 363.15) K visualized with lucidity, and the course of crystallization to produce Li_2CO_3 from the mother liquor was illustrated. All of these will provide a thermodynamic basis for the separation of lithium from mother liquor and optimization of Li_2CO_3 production process.

1. Introduction

In recent years, with the development of battery and single crystal industries in the world, the demand for lithium and its compounds are dramatically growing. Particularly, lithium carbonate (Li_2CO_3) which is one of the most important compounds, can be extensively applied in many industrial branches, such as battery [1], ceramics [2,3], metallurgical [4], pharmaceutical [5,6], and nuclear energy industries [7,8]. In addition, Li_2CO_3 is the starting material for the industrial production of both inorganic (such as high purity Li_2CO_3, lithium niobate, lithium tantalite, lithium fluoride, and lithium metal) and organic lithium compounds (such as butyllithium, phenyllithium, and lithium bis(trifluoromethanesul fonyl)imide) [9–13], due to its stability and simple form. For example, high purity Li_2CO_3 which is required for the fabrication of several materials in lithium ion batteries (such as the cathode materials and electrolyte salts) and in lithium ion secondary batteries, can be produced by the re-precipitation of Li_2CO_3 from the $LiHCO_3$ aqueous solution obtained by the reaction of a technical grade Li_2CO_3 and CO_2 [14–16].

Li_2CO_3 can be typically produced from the mineral sources containing lithium (such as spodumene and lepidolite) and lithium-containing brines (such as the Salar de Uyuni in Bolivia, the Salar de Atacama in Chile, the Salar de Hombre Muerte in Argentina, the Silver Peak in America, or the Zabuye and Qinghai Salt Lake in China) [17,18]. Li_2CO_3 production from brines can be performed by precipitation method from the purified brine (such as LiCl or Li_2SO_4 aqueous solution) on the addition of sodium carbonate solution, simultaneously generating a large amount of mother liquor [19]. It is estimated that, for each ton of Li_2CO_3 manufactured by using the purified LiCl aqueous solution as raw material, about 25 m^3 mother liquor containing (1.4–2.0) $g\cdot L^{-1}$ lithium is generated. The compositions of mother liquor from Qinghai CITIC Guoan Science and Technology Development Co. Ltd in China are listed in Table 1. As of now, mother liquor cannot be used effectively and directly discarded back into the saline lakes, thus causing a resource waste problem. Therefore, from an economic point of view, the problem for effective utilization of the mother liquor obtained from Li_2CO_3 process is necessary to be solved.

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* Corresponding author.
E-mail address: sjzhang@ipe.ac.cn (S. Zhang).

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Table 1
Compositions of Mother Liquor.

Components	Content/(g·L^{-1})
Li	1.41
Ca	3.29×10^{-3}
Mg	1.94×10^{-7}
Na	63.23
Cl	73.79
SO_4	7.83
CO_3	16.76
B_2O_3	0.00

In order to implement the utilization of the mother liquor obtained by the reaction of $LiCl/Li_2SO_4$ and Na_2CO_3, the phase equilibrium behaviour of system containing Li_2CO_3, NaCl and Na_2SO_4 is of significant importance to provide reliable reference for the design of separating lithium and optimizing the process of Li_2CO_3 production. Solid-liquid phase equilibria (SLE) data for Li_2CO_3-H_2O system can be found in the literature [20–22]. The ternary system of Li_2CO_3-NaCl-H_2O at 298.15 K which has been studied by Cheng and Geffecken et al. [21,23], but showed a large deviation. Also, the SLE data for the ternary Li_2CO_3-Na_2SO_4-H_2O system is very important to separate Li_2CO_3 from the mother liquor obtained by the reaction of Li_2SO_4 and Na_2CO_3. However, only the solubility data of Li_2CO_3 in Na_2SO_4 aqueous solution at 298.15 K have been reported [23]. The objective of this study is to establish a thermodynamically consistent model representing the phase equilibrium behaviour of Li_2CO_3 in the quaternary system of Li_2CO_3-NaCl-Na_2SO_4-H_2O system over a wide temperature range.

In this work, the SLE for the one binary system of Li_2CO_3-H_2O, the two ternary systems of Li_2CO_3-NaCl-H_2O and Li_2CO_3-Na_2SO_4-H_2O, as well as the one quaternary system of Li_2CO_3-NaCl-Na_2SO_4-H_2O over the temperature range from 283.15 K to 363.15 K were measured. In addition, to estimate the solubility of Li_2CO_3 in NaCl-Na_2SO_4 solutions accurately, one of the key problems for estimating the SLE data of Li_2CO_3-NaCl-Na_2SO_4-H_2O system is to accurately calculate the mean activity coefficients of salts in aqueous electrolyte solutions using the electrolyte models. Among the models used, the Pitzer model is widely used for aqueous electrolyte system in process calculations [24–34]. Also, the model is embedded in the Aspen Plus™ software with a general process-modeling tool, and parameters added in the default database can be used directly [34,35]. Therefore, it is conveniently used to develop the thermodynamic model for the system of Li_2CO_3-NaCl-Na_2SO_4-H_2O and was chosen for this study.

2. Experimental

2.1. Experimental materials

Lithium carbonate (mass fraction purity 0999, Sinopharm Chemical Reagent, high purity), sodium sulfate anhydrous (mass fraction purity 0.995, Xilong Chemical Group, analytical grade) and sodium chloride (mass fraction purity 0.990, Sinopharm Chemical Reagent, analytical grade) were used in the experiments. Chemical name, source, initial mass fraction purity, purification method, final mass fraction purity and analysis method are listed in Table 2. High-purity Milli-Q water (resistivity > 18.2 MΩ·cm and conductivity < 0.1 μS·cm^{-1}) was used to prepare all aqueous solutions.

2.2. Apparatus and procedure

Solubility was determined via the isothermal solution saturation method [34,36]. The 200-mL solution of known composition was poured into a 250-mL polytetrafluoroethylene bottle, which were equipped with a magnetic stirrer and sealed with a polytetrafluoroethylene-lined cap. The bottles were firstly immersed in a temperature-controlled water bath. The solution was stirred for about 0.5 h to establish the temperature equilibrium. Then excess Li_2CO_3 solid was added to the solution and was continuously stirred for another 72 h which was the standard equilibrium time used in this work. After the equilibrium was attained, stirring was stopped to allow solids to settle. The supernatant solution was then withdrawn and immediately filtered by using 0.22 μm Whatman Puradisc syringe filters. The clear filtrate was added into a 25-mL volumetric flask which was kept in the water bath and then heated to bath temperature for measuring the density of saturated solution. The contents of Li^+ and Na^+ were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the contents of Cl^- and SO_4^{2-} were determined by ion chromatography (ICS-3000). The solid phase was filtered and washed three times with hot water. But for the double saturation point, the solid phase was washed three times with ethanol to avoid NaCl loss. The washed solids were dried at 323.15 K for 12 h and then analyzed by X-ray powder diffraction to determine whether the solid phase had been altered by phase transformation or a new double salt was generated. All experiments were made at least three times, and the results were averaged.

3. Thermodynamic basis

3.1. Speciation and solution chemistry

The non-ideal behaviours of Li_2CO_3-saturated aqueous electrolyte solutions is due partly to the activity coefficient of ions and partly to the ion-association phenomenon [37,38]. Therefore, for the Li_2CO_3-NaCl-Na_2SO_4-H_2O system, the possible solubility equilibria can be described by the following equations:

$$Li_2CO_3(s) \overset{K_{sp}}{\leftrightarrow} 2Li^+(aq) + CO_3^{2-}(aq) \quad (1)$$

$$Li^+(aq) + CO_3^{2-}(aq) \overset{K_a}{\leftrightarrow} LiCO_3^-(aq) \quad (2)$$

Table 2
Summary of Requirements for Specification of Chemical Samples.

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
Sodium chloride	Sinopharm Chemical Reagent	0.990	Dried	0.991	ICP-AES[a], ICS-3000[b]
Sodium sulfate	Xilong Chemical Group	0.995	Dried	0.994	ICP-AES[a], ICS-3000[b]
Lithium carbonate	Sinopharm Chemical Reagent	0.999	Dried	0.999	ICP[a], Chemical titration

[a] Inductively coupled plasma atomic emission spectroscopy.
[b] Ion chromatography.