



Solubility of Li_2CO_3 in Na–K–Li–Cl brines from 20 to 90 °C



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ABSTRACT

The solubility of Li_2CO_3 in Na–K–Li–Cl brines was measured by isothermal dissolution method within the temperature range of 20 to 90 °C. It was found the solubility of Li_2CO_3 in all systems investigated decreased with increasing temperature. In NaCl and KCl solutions, the solubility of Li_2CO_3 initially increased to a maximum value and then decreased gradually with increasing solution concentration. However, the solubility of Li_2CO_3 in LiCl solutions decreased with increasing LiCl concentration due to the common ion effect of added Li^+ . New Pitzer activity coefficient model parameters for the Li^+ – CO_3^{2-} ion pair were obtained by using experimental solubility data of Li_2CO_3 in pure water, and a new chemical model was built with the aid of Aspen Plus platform. The new model was shown to successfully predict the solubility of Li_2CO_3 in NaCl, KCl, LiCl and mixed NaCl–KCl solutions. Moreover, the new model could aid in analyzing the separation of lithium and magnesium in brines.

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1. Introduction

Nowadays lithium and their compounds have mostly been extracted from salt lake brines [1–3] instead of producing from minerals due to the low expense, high purity and large-scale productions. The technique used in the separation of magnesium from concentrated lithium containing brines is described as follows. The brine is first contacted with a fatty alcohol dissolved in kerosene to extract boron. Then the nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) is precipitated by adding sodium carbonate to the brine at low temperature [4,5]. After that, residual magnesium and sulfate ion are removed by precipitation with calcium oxide and liquid–solid separation. The liquor is then treated with sodium carbonate to precipitate lithium carbonate (Li_2CO_3) at high temperature.

The solubility and phase equilibrium phenomena play an important role in the development, design, optimization, and operation of separation process [6–9]. The dissolution and precipitation of substances in solutions are all controlled by the principles of solubility [10]. Therefore, the solubility of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ at low temperature as well as that of Li_2CO_3 at high temperature are important in separation of magnesium from concentrated lithium containing brines. As early as in 1915 Wells [11] determined the solubility of magnesium carbonate in nature waters. Recently, the solubility and stability of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ in NaCl, KCl, LiCl and MgCl_2 have been determined systematically by authors [8,9]. Broul

et al. [12] reported the solubility of Li_2CO_3 in pure water over the temperature range of 0 to 100 °C. Smith *et al.* [13] measured the aqueous solubility of Li_2CO_3 between 100 and 300 °C and an equation was generated for calculating solubility. Deng *et al.* [14] determined the experimental solubility data and the relevant physicochemical property data of the Li^+ , Na^+/Cl^- , CO_3^{2-} – H_2O system at 298.15 K. Sang *et al.* [15] studied the metastable equilibria of the quinary system $\text{Li}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{Li}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{B}_4\text{O}_7 + \text{K}_2\text{B}_4\text{O}_7 + \text{H}_2\text{O}$ at 288 K by isothermal evaporation method. However, the systematic solubility data of Li_2CO_3 in geologically relevant brines containing NaCl, KCl and LiCl were lacked.

Moreover, modeling of relationships between chemical speciation and phase equilibrium in aqueous electrolyte systems is of great importance in fundamental research involved in salt lake development and for the design of new chemical processes [16,17]. Numerous electrolyte solution models including those for the mixed-solvent systems have been reported in the literatures. Bromley–Zemaitis activity coefficient model [18] was applied to predict the supersaturation of $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ in the MgCl_2 – Na_2CO_3 system in supersaturated solutions over the temperature range of 50 to 90 °C by authors [19]. Graber *et al.* [20] used NRTL model [21] to correlate the equilibrium data for Li_2SO_4 –PEG (polyethylene glycol) 4000– H_2O systems at 5, 25 and 45 °C. Taboada *et al.* [22] modeled the solubility of LiOH in ethanol– H_2O system at 25 °C with Chen's model [23,24], and the extended Pitzer–Debye–Huckel equation [25] was used to represent the long-range ion–ion interaction. Kwok *et al.* [26] predicted the thermodynamics of a simplified salt lake system Li^+ , Na^+ , K^+ , $\text{Mg}^{2+}/\text{Cl}^-$, SO_4^{2-} – H_2O at 25 °C and 1 atm by UNIQUAC model and

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used the resulting phase diagram for recovering $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. Recently, Ma *et al.* [27] developed a model for calculating the solubility of Friedel's Salt in the $\text{Na-OH-Cl-NO}_3\text{-H}_2\text{O}$ systems over the temperature range from 20 to 200 °C with the help of the OLI platform. However, the solubility modeling of Li_2CO_3 in salt lake system Na-K-Li-Cl has not been investigated previously.

In this work, the isothermal dissolution method was used to determine the solubility of Li_2CO_3 in Na-K-Li-Cl brines. On the other hand, a chemical equilibrium model was developed to estimate the solubility of Li_2CO_3 in Na-K-Li-Cl brines with the aid of Aspen Plus platform. Pitzer parameters of the $\text{Li}^+\text{-CO}_3^{2-}$ ion pair were obtained by correlating solubility data of Li_2CO_3 in pure water. These new parameters were incorporated in Aspen platform to construct a new speciation model capable of representing the Li_2CO_3 solubility in Na-K-Li-Cl brines. Finally, the separation of lithium and magnesium in brines was analyzed with the aid of the newly developed model.

2. Experimental methods

2.1. Materials

All chemical reagents used in the experiments were analytical grade without further purification (table 1). The water used in all experimental work for solution preparation, dilution, crystal washing *etc.* was double distilled water (conductivity $<0.1 \mu\text{S} \cdot \text{cm}^{-1}$) unless otherwise specified.

2.2. Measurement of solubility

The dissolution method [28] is considered to be more reliable and feasible than other solubility determine approaches since it avoids the complication of formation of intermediate phases that is commonly encountered in precipitation. The solubility of Li_2CO_3 in Na-K-Li-Cl brines was determined by this method.

The experimental set-up employed in the determining of Li_2CO_3 solubility was shown in figure 1. The experiments were carried out in 250 ml iodine flasks, which were sealed with glass stoppers, containing 200 ml of known concentration of electrolyte solutions (NaCl , KCl , LiCl , *etc.*). The flasks were located in a water bath heated by a thermostatic heater/circulator. The solution temperature was monitored by a thermometer. The uncertainty in the measure of solution temperature was ± 0.01 °C. Once the desired temperature was reached, excess solids (8 g of Li_2CO_3) were introduced to the electrolyte solutions in flasks and magnetic stirring initiated. The standard equilibration time used was 6 h (the determination of equilibration time was explained in the next section). After the (solid + liquid) equilibrium was attained, the supernatant solution was then withdrawn and immediately filtered by using 0.22 μm Whatman Puradisc syringe filters. Density measurements of Li_2CO_3 -saturated solutions were performed with an Anton Paar DMA4500 (with an accuracy of $\pm 0.00005 \text{ g} \cdot \text{mL}^{-1}$). The content of C (carbon) was determined by TOC analyzer (TNM-1, Shimadzu Corporation) which was used to determine C of organic and inorganic substances in environmental applications. The uncertainty in the measure of the content of C is estimated to be less than

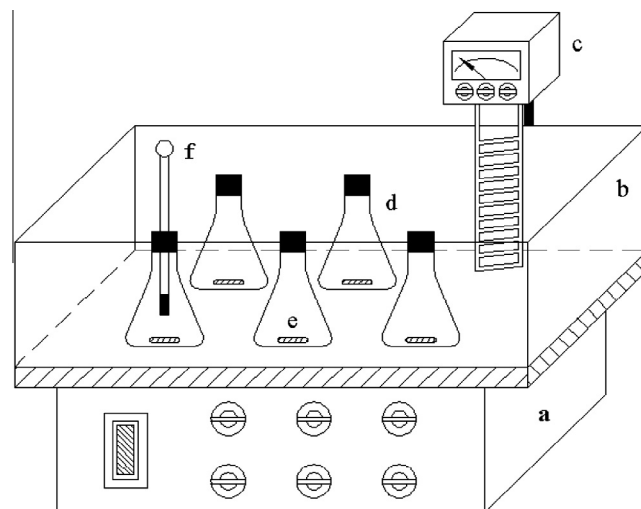


FIGURE 1. Experimental set-up used in the solubility measurement. (a) magnetic stirrer; (b) water bath; (c) thermostatic heater/circulator; (d) iodine flask; (e) magnetic rotor; (f) thermometer.

$0.0001 \text{ g} \cdot \text{L}^{-1}$. The solubility of Li_2CO_3 , expressed as molality ($\text{mol} \cdot \text{kg} \cdot \text{H}_2\text{O}^{-1}$), was obtained from the C analysis. The solid phase was filtered and washed three times with water. The washed solids were dried at 60 °C for 12 h and then analyzed by X-ray powder diffraction to determine whether the solid phase had been altered by phase transformation. X-ray powder diffraction (XRD, X'Pert PRO MPD, PANalytical, Netherlands) patterns were recorded on a diffractometer (using $\text{Cu K}\alpha$ radiation) operating at 40 kV/30 mA. A scanning rate of $0.02^\circ \cdot \text{s}^{-1}$ was applied to record the patterns in the 2θ angle range from 10° to 80° .

2.3. Determination of equilibration time

The equilibration time in solubility measurements normally varies from several hours to several days depending on the dissolution rate of the solid phase and the applied conditions. [29] Li and Demopoulos [18] reported that the equilibration time of calcium sulfate dihydrate in HCl solution is 0.5 h. Authors [8] reported that the equilibrium of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ in solution could be reached within 3 h. The experimental results (section 4.1.1.) showed that the solubility equilibrium between Li_2CO_3 and solution could be obtained within 1 h. However, a longer time of 6 h was selected to ensure solubility equilibrium.

2.4. Reproducibility

The solubility experiments were conducted three times to check the reproducibility and accuracy of the adopted procedure in this work. The comparison of solubility values of Li_2CO_3 in pure water from the literature [12] with the experimental data in this study was shown in figure 2(b). As it can be observed, the comparison was satisfactory and the average deviation of the determined solubility values was $\pm 0.00127 \text{ mol} \cdot \text{kgH}_2\text{O}^{-1}$ with a relative deviation of 0.818%.

3. Chemical modeling approach

3.1. Thermodynamic equilibria of $\text{Na-K-Li-Cl-CO}_3\text{-H}_2\text{O}$ system

In the $\text{Na-K-Li-Cl-CO}_3\text{-H}_2\text{O}$ system, the following main solubility equilibrium is considered.

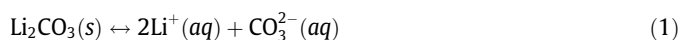


TABLE 1

Chemical reagents employed.

Compound name	Formula	Provider	Purity (%)
Lithium carbonate	Li_2CO_3	Strem Chemicals, Inc.	≥ 99.0
Sodium chloride	NaCl	Chemical Company of Beijing	≥ 99.5
Potassium chloride	KCl	Chemical Company of Beijing	≥ 99.5
Lithium chloride	LiCl	Strem Chemicals, Inc.	≥ 99.0

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