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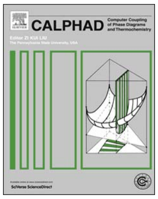

Phase diagram of the quaternary system LiCl+MgCl$_2$+KCl+H$_2$O at 323.15 K

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ABSTRACT

Solubility isotherms as well as the corresponding solid phases of the quaternary system LiCl+MgCl$_2$+KCl+H$_2$O and the eutectic points for the ternary systems LiCl+MgCl$_2$+H$_2$O, LiCl+KCl+H$_2$O and MgCl$_2$+KCl+H$_2$O at 323.15 K have been elaborately determined by an isothermal equilibrium method. Five crystallization fields including two double salts (LiCl·MgCl$_2$·7H$_2$O(s) and KCl·MgCl$_2$·6H$_2$O(s)), two hydrate salts (MgCl$_2$·6H$_2$O(s) and LiCl·H$_2$O(s)) and one single salt (KCl(s)) were detected in the quaternary system. The reliability of the experimental results were verified both by testing the phase diagram rule and comparing with the literature data. It was found that all of the results were accordance with the phase diagram rule, and moreover, the excellent agreement between the experimental data and the literature data was also obtained, which indicate that the solubility data obtained in this work are reliable. Based on the quaternary phase diagram, the example was provided for industrial application. The measured phase diagram reported in this work are the essential tool to guide industrial process of extracting Li from the salt lake brine containing MgCl$_2$ and LiCl using KCl reagent.

1. Introduction

After multi-step evaporation of the Qaidam salt-lake brine (mainly containing the ions K^+, Na^+, Li^+, Mg^{2+}, Cl^-, $SO_4{}^{2-}$, $CO_3{}^{2-}$, $B_4O_7{}^{2-}$, and H_2O) by solar ponds technology, the brine can be roughly treated as the system LiCl + MgCl$_2$ + H$_2$O [1]. For this system, the mass ratio of Mg:Li is approximately 20–60. Nevertheless, the method for economically separating the Mg and Li with such a high Mg:Li ratio is a challenge for all chemical engineers [2]. Among all the separating methods, Voigt [3] suggested an economical and practical method, by which the reagent KCl was proposed to add into the salt brine to crystallize out MgCl$_2$ as double salt MgCl$_2$·KCl·6H$_2$O (s). The obvious solubility difference between MgCl$_2$·KCl·6H$_2$O(s) and LiCl·H$_2$O(s) ensures the practicability of this method. Meanwhile, the abundant KCl(s) product in the process of evaporating the salt lake brine guarantees the economy of this method. However, to apply this method to guide the practical production, information on the phase diagram of the quaternary system LiCl+MgCl$_2$+KCl+H$_2$O and its sub-ternary systems from 273.15 to 323.15 K are urgent required.

To date, the phase diagrams of the ternary systems MgCl$_2$+LiCl+H$_2$O [4–6], LiCl+KCl+H$_2$O [7,8] and KCl+MgCl$_2$+H$_2$O [9–13] have been widely reported from 298.15 to 373.15 K. The stable phase diagram for the quaternary system at 298.15 K has been reported by Zhang [14]. Meanwhile, the metastable phase diagram for this quaternary system at 323.15 K has also been determined by Yu [15], but the crystallization zones are quite different with the results reported by Zhang [14]. For a solar pond technique in summer, however, the stable solubility isotherms of this quaternary system at 323.15 K are even more important but have been unknown so far.

In order to obtain the accurate phase diagram of the quaternary system LiCl+MgCl$_2$+KCl+H$_2$O at T=323.15 K, we elaborately determined the stable phase diagram by the isothermal equilibrium method in this work. To verify the reliability of the experimental data in this work, we also determined the eutectic points of the ternary systems MgCl$_2$+LiCl+H$_2$O, LiCl+KCl+H$_2$O and KCl+MgCl$_2$+H$_2$O at 323.15 K and compared with the literature data.

2. Experimental section

2.1. Materials

LiCl was prepared by neutralizing Li$_2$CO$_3$ with HCl and then purified by twice crystallization. MgCl$_2$ and KCl were directly recrystallized four times from water. Doubly distilled water ($S \leq 1.2\times10^{-4}$ S/m), silver nitrate (wt% > 0.999), EDTA (wt% > 0.999) and KB(C$_6$H$_5$)$_4$ (wt% > 0.999) were also used in the experiment. The main impurity

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Table 1
Specifications of chemicals used in this work.

Chemical Name	Source	Initial Mass Fraction Purity	Purification Method	Final Mass Fraction Purity	Analysis Method
Potassium chloride (KCl)	Sinopharm Chemical Reagent Co.	> 0.999	recrystallized four times	0.9999	ICP
Magnesium chloride hexahydrate ($MgCl_2·6H_2O$)	Sinopharm Chemical Reagent Co.	> 0.999	recrystallized four times	0.9999	ICP
Lithium chloride ($LiCl·H_2O$)	synthesized by ourselves		recrystallized two times	≥0.9999	ICP
Lithium chlorate (Li_2CO_3)	Shanghai China-Lithium Industry	0.9995	none		ICP
Hydrochloric acid (HCl)	Sinopharm Chemical Reagent Co.	0.9998	none		ICP
Silver nitrate ($AgNO_3$)	Sinopharm Chemical Reagent Co.	0.9998	none		ICP
Hydrogen nitrate (HNO_3)	Sinopharm Chemical Reagent Co.	0.9998	none		ICP
Zinc oxide (ZnO)	Sinopharm Chemical Reagent Co.	0.9999	none		ICP
Disodium EDTA	Sinapharm Chemical Reagent Co.	0.9998	none		ICP
Absolute ethylalcohol (C_2H_5OH)	Sinapharm Chemical Reagent Co.	0.9998	none		ICP
Normal butylalcohol (C_4H_9OH)	Sinapharm Chemical Reagent Co.	0.9998	none		ICP
Sodium tetraphenylboron ($NaB(C_6H_5)_4$)	Sinapharm Chemical Reagent Co.	0.9998	none		ICP
Potassium tetraphenylborate ($KB(C_6H_5)_4$)	Sinapharm Chemical Reagent Co.	0.9998	none		ICP
Acetic acid glacial (C_2H_5COOH)	Sinapharm Chemical Reagent Co.	0.9998	none		ICP
Water (H_2O)			distilled three times	$\sigma \leq 1.1\times10^{-4}$ S/m	TDS

elements Ca, Mg, Li, Na, K, Fe and Ba in the prepared reagents were analyzed by Inductively Coupled Plasma (ICP) emission spectrometry (US Perkin Elmer Corporation, Optima 5300DV), and the content of each element was determined to be less than 200 ppm. Table 1 gives the instructions of all the chemical reagents used in this work.

2.2. Experimental apparatus

A vertical section of the isotherm equilibrium apparatus used in this work is presented in Fig. 1a. The thermostat (Germany, LAUDA E219) consists of four parts, including a stainless steel tank (A), the digital heating controller (B), the heating coils (C) and a stirring pump (D), exhibiting the temperature stability ± 0.01 K. The temperature difference between the diagonal lying corners of the thermostat is less than 0.008 K. The temperature was determined using a calibrated glass thermometer with an accuracy of ± 0.005 K. A sealing plate (F) was used to separate the water vapor from the mixture of the bath (E). The plastic pads with holes (J) were used to make the temperature of the samples more uniform. A Sartorius (CPA225D) balance was used for weighing with an error of ± 0.1 mg.

2.3. Experimental procedures

As reported in the literature [1], solid-liquid equilibrium experiments were carried out in a ground 250 cm^3 glass equilibrium flask (G) which was immersed in the thermostat filled with a glycol-water mixture (E). The solution and solid in the flask were stirred with a magnetic stirrer (I) outside the thermostat. Each sample was placed and stirred in the thermostat for approximately 200 h, and then kept static for approximately 12 h. The sample of the saturated solution was then removed using a pipette, with the tip covered in glass cloth as a filter, and transferred to two weighed 30 cm^3 quartz bottles (a, b, c). The wet solid was transferred using a glass scoop into a 25 cm^3 sintered glass filtering crucible. The solid was analyzed by X-ray diffraction and the solution was analyzed according to the following procedures:

(1) The concentration of $MgCl_2$ in this system was determined by titrating the Mg^{2+} ions in bottle (a) with EDTA, as described in the literature [16,17].
(2) The concentration of KCl in this system was determined by precipitating K^+ ions in bottle (b) with $NaB(C_6H_5)_4$, as described in the literature [16,17] except for some slight differences: (i) the $NaB(C_6H_5)_4$ solution was prepared ahead of a night to analyze the solution; (ii) the mass of $KB(C_6H_5)_4$ precipitation was controlled between 0.2 g to 0.3 g; (iii) a drop of saturated HNO_3 solution and 2 mL 1% CH_3COOH solution were added before $NaB(C_6H_5)_4$ solution added into the system, which is benefit to get a coarse grained $KB(C_6H_5)_4$. Through the above improvements, the analysis error can be reduced from 0.5% to 0.2%.
(3) The total concentration of $MgCl_2$, LiCl and KCl in the quaternary system was determined by precipitating Cl^- ions in bottle (c) with $AgNO_3$, as described in the literature [16,17]. The difference