

Thermodynamic study of the system (LiCl + CaCl₂ + H₂O)

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Abstract

Solubility isotherms of the ternary system (LiCl + CaCl₂ + H₂O) were elaborately determined at $T = (283.15 \text{ and } 323.15) \text{ K}$. Several thermodynamic models were applied to represent the thermodynamic properties of this system. By comparing the predicted and experimental water activities in the ternary system, an empirical modified BET model was selected to represent the thermodynamic properties of this system. The solubility data determined in this work at $T = (283.15 \text{ and } 323.15) \text{ K}$, as well as those from the literature at other temperatures, were used for the model parameterization. A complete phase diagram of the ternary system was predicted over the temperature range from (273.15 to 323.15) K. Subsequently, the Gibbs free energy of formation of the solid phases CaCl₂ · 4 H₂O_(s), CaCl₂ · 2 H₂O_(s), LiCl · 2H₂O_(s), and LiCl · CaCl₂ · 5H₂O_(s) was estimated and compared with the literature data.

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1. Introduction

Thermodynamic properties of the ternary system (LiCl + CaCl₂ + H₂O), including its solid–liquid phase diagram, are of essential importance in the extraction of lithium from natural salt brine containing magnesium and lithium chloride mainly. For example, a nano-filtration technology has been proved to be an effective method to separate Mg²⁺ and Li⁺ ions utilizing their difference in ionic radius, and substituting the Mg²⁺ ion with Ca²⁺ by adding Ca(OH)₂ into the (LiCl + MgCl₂ + H₂O) system will make the separation of Ca²⁺ and Li⁺ easier for the larger ionic radius of Ca²⁺ than Mg²⁺. In the exchange process of the cations, it is usually desirable to know the solubility phase diagram of the (LiCl + CaCl₂ + H₂O) system. Up to now, although some solubility isotherms of this system have been measured [1–4], large disagreement still exists among them. A complete solubility phase diagram of this system including the crystallization field of the dou-

ble salt LiCl · CaCl₂ · 5H₂O at temperatures other than 298.15 K is unavailable so far. Theoretically, Christov *et al.* [5,6] has simulated the solubility properties of the ternary system and its sub-binary systems in an original Pitzer model [7] and obtained the standard molar Gibbs free energy of formation of the double salt LiCl · CaCl₂ · 5H₂O at $T = 298.15 \text{ K}$. As Pitzer *et al.* discussed [8,9], with the original Pitzer model [7] as used by Christov [5,6] it is even difficult to describe the properties of water activity of the binary system (CaCl₂ + H₂O) near the solubility limit at $T = 298.15 \text{ K}$. Thus, the thermodynamic data for the double salt LiCl · CaCl₂ · 5H₂O_(s) given in [5,6] may be less accurate.

In this paper, the solubility isotherms of the system (LiCl + CaCl₂ + H₂O) have been elaborately determined at $T = (283.15 \text{ and } 323.15) \text{ K}$. These solubility results and data of water activity in the ternary system from the literature [3] were then used to parameterize an empirically modified BET model. In this way, a complete solubility diagram of this system between $T = (273 \text{ and } 323) \text{ K}$, as well as the Gibbs free energy of formation of the hydrates CaCl₂ · 4H₂O_(s), CaCl₂ · 2H₂O_(s), LiCl · 2H₂O_(s), and LiCl · CaCl₂ · 5H₂O_(s), were obtained.

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2. Experimental

2.1. Materials and apparatus

The lithium chloride and calcium chloride used in this work were prepared by neutralizing lithium carbonate (mass fraction purity >0.9999, Shanghai China-Lithium Industry Co. Ltd.) and calcium carbonate (mass fraction purity >0.999) with hydrochloric acid (AR), respectively. For each case, the chloride salts were purified by double crystallization to 50% salt recovery. Doubly distilled water was used in the experiment. Solubility measurements were carried out in a thermostat (TECHNE 18/TE-10D, England) with temperature stability of ± 0.01 K. The temperature was measured by means of a calibrated glass thermometer (MILLER & WEBER INC., USA) with accuracy of ± 0.01 K. A Sartorius BS224S balance was used for weighing with an error of ± 0.1 mg.

2.2. Experimental procedures

Various mixtures of salt and water were made by starting with a ground 250 cm³ Erlenmeyer flask containing only one salt and water and in each subsequent run more of the second salt was added to the solution and solid left from the previous run. The flask was immersed in the thermostat and the solution and solid in the flask were stirred with a magnetic stirrer. Each sample was stirred at a specific constant temperature for 72 h, and then kept static for about 8 h. A sample of the saturated solution was then taken with a pipette. The sample was transferred to a weighed 30 cm³ ground quartz beaker with cover. The salt concentration in pure LiCl- or CaCl₂-saturated salt aque-

ous solution and the total salt concentration in the three-component solutions were determined by evaporation to dryness, fusing, and weighing. The CaCl₂ content in the ternary system was determined by precipitating Ca²⁺ ion with ammonium oxalate, baking the residuals at about $T = 773$ K for 6 h, then cooling and weighing the CaCO₃, as described in [10]. The wet residuals were analyzed in the same way as for the solution. The composition of the solid phase in the wet residues was identified by the method of Schreinemaker.

2.3. Accuracy analysis

Several gravimetric methods were compared with each other to determine the salt content of the pure LiCl or CaCl₂ solution. Our experiments showed that the LiCl or CaCl₂ percentage content determined by precipitating Cl⁻ ions with AgNO₃, differs from that of direct drying of the solution by maximal 0.06% (mass percentage). When LiCl is present, the accuracy of the CaCl₂ concentration analyzed by precipitation with ammonium oxalate is relatively low, *ca.* 0.2% mass percentage. Duplicate analyses of the same sample (solution and wet residuals) gave maximum deviations of 0.08% mass percentage. Totally, the uncertainty of the experimental solubility results in this work can be reasonably evaluated to be less than 0.1% (mass percentage) for the binary systems and 0.3% (mass percentage) for the ternary system.

3. Experimental results

In tables 1 and 2 the experimental results are listed. The isotherms of the ternary system obtained from these at

TABLE 1
(Solid + liquid) phase equilibrium data for the system LiCl + CaCl₂ + H₂O at $T = 283.15$ K

Mass fraction solution/100 · w			Mass fraction wet-solid phase/100 · w			Solid phase
LiCl	CaCl ₂	H ₂ O	LiCl	CaCl ₂	H ₂ O	
0	39.28	60.72				CaCl ₂ · 6H ₂ O
3.83	35.59	60.58	1.95	42.54	55.51	CaCl ₂ · 6H ₂ O
7.80	31.82	60.38	4.21	40.49	55.30	CaCl ₂ · 6H ₂ O
13.08	27.12	59.80	6.80	38.41	54.79	CaCl ₂ · 6H ₂ O
17.12	24.21	58.67	12.11	31.92	55.97	CaCl ₂ · 6H ₂ O
21.25	23.63	55.12	16.27	29.88	53.85	CaCl ₂ · 6H ₂ O
21.28	24.37	54.35	17.86	28.63	53.51	CaCl ₂ · 6H ₂ O
21.33	24.85	53.82	14.78	32.84	52.38	(CaCl ₂ · 6H ₂ O + CaCl ₂ · 4H ₂ O)
21.35	24.85	53.8	10.96	39.56	49.48	(CaCl ₂ · 6H ₂ O + CaCl ₂ · 4H ₂ O)
23.15	23.50	53.35	13.40	39.20	47.40	CaCl ₂ · 4H ₂ O
24.34	22.68	52.98	11.06	43.35	45.59	CaCl ₂ · 4H ₂ O
24.97	22.28	52.75	21.75	27.55	50.70	(CaCl ₂ · 4H ₂ O + LiCl · CaCl ₂ · 5H ₂ O)
25.01	22.27	52.72	25.89	23.03	51.08	(CaCl ₂ · 4H ₂ O + LiCl · CaCl ₂ · 5H ₂ O)
29.98	17.04	52.98	29.66	17.75	52.59	LiCl · CaCl ₂ · 5H ₂ O
31.66	15.41	52.93	27.37	24.39	48.24	LiCl · CaCl ₂ · 5H ₂ O
34.41	12.94	52.65	39.45	9.93	50.62	(LiCl · CaCl ₂ · 5H ₂ O + LiCl · 2H ₂ O)
34.35	12.95	52.70	35.86	13.09	51.05	(LiCl · CaCl ₂ · 5H ₂ O + LiCl · 2H ₂ O)
34.34	12.97	52.69	38.42	10.45	51.13	(LiCl · CaCl ₂ · 5H ₂ O + LiCl · 2H ₂ O)
35.49	11.16	53.35	38.53	9.32	52.15	LiCl · 2H ₂ O
37.41	8.11	54.48	40.42	6.64	52.94	LiCl · 2H ₂ O
42.64	0	57.36				LiCl · 2H ₂ O

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