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Solubility Measurement and Prediction of Phase Equilibria in the Quaternary System LiCl + NaCl + KCl + H_2O and Ternary Subsystem LiCl + NaCl + H_2O at 288.15 K

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Abstract: Using isothermal dissolution method, the phase equilibrium relationship in quaternary system LiCl + NaCl + KCl + H_2O and the ternary subsystem LiCl + NaCl + H_2O at 288.15 K were investigated. Each phase diagram of two systems was drawn. The phase diagram of LiCl + NaCl + H_2O system contains two solid phase regions of crystallization $LiCl\cdot 2H_2O$ and NaCl. In the phase diagram of LiCl + NaCl + KCl + H_2O system, there are three crystallization regions: $LiCl\cdot 2H_2O$, NaCl and KCl respectively. In this paper, the solubilities of phase equilibria in two systems were calculated by Pitzer's model at 288.15 K. The predicted phase diagrams generally agree with the experimental phase diagrams.

Keywords: Underground brine; Phase diagram; Pitzer model; Solubility prediction; Lithium chloride

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1 Introduction

The Sichuan Basin is rich in underground brine, including the Xuanhan area in Dazhou in northeast Sichuan. The K^+ content in this brine is up to 25.955 g/L, which is accompanied by strategic scarce salt resources such as Br^-, I^-, B^{3+}, Li^+, Sr^{2+}, and Rb^+ [1]. It also generally meets or exceeds comprehensive utilization and individual mining grade standards, and the quality is excellent and is conducive to industrial mining.

Although there are large reserves of potassium-rich brine with high economic value, the degree of geological exploration is relatively low. First, the enrichment methods, reserve calculations, and evaluation methods of brine must be further improved. Secondly, the brine is more than 3000 meters underground with a high degree of mineralization, making it difficult to develop. Brine, a non-renewable resource, has relatively fixed reserves and decreases as it is mined. Overall, the comprehensive utilization of brine resources in China generally has the problems of single product variety, low technology content, difficulties in the comprehensive utilization of multi-component mixtures, resource waste, and environmental pollution. Therefore, in order to use the brine resources effectively, reasonably and scientifically, there is a need to establish a complete set of comprehensive utilization techniques.

Rational exploitation of brine resources often depend on phase diagrams at multiple temperatures and is performed by series of phase separation processes. To describe the salting-out laws and ore-forming rules of brine, phase diagram can represent the solubility of salts as geometric shapes in graphical form. Salt lake brine is a naturally existing complex multi-component system and is a kind of salt deposit in which solids and liquids coexist. The experiment, calculation, and simulation of the thermodynamic properties and phase equilibrium of brine systems have been studied. The phase equilibrium of solid-liquid systems mainly include information about changes in the salt component concentration and phase changes at different temperatures, which are only slightly affected by pressure. Carrying out research related to phase equilibrium research of water-salt systems under multiple temperatures and drawing the corresponding phase diagram allows us to directly observe various phase changes, predict the crystallization sequence, and change the rule of each salt during production, in order to determine the process flow. This is a necessary basic research for integrated use of brine resources [2]. According to the annual average temperature of the Xuanhan area in Northeast Sichuan, which is about 15 ℃ (288.15 K), phase equilibrium research would be carried out on a lithium and potassium-containing system Li + Na + K + Mg + Cl + SO_4 + H_2O at this temperature. In our previous work, relevant research of its quaternary subsystems Li_2SO_4 + Na_2SO_4 + K_2SO_4 + H_2O, LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O, LiCl + NaCl + $MgCl_2$ + H_2O, LiCl + KCl + $MgCl_2$ + H_2O and Li_2SO_4 + K_2SO_4 + $MgSO_4$ + H_2O have been completed [3-5]. This paper does the study about phase equilibria of LiCl + NaCl + H_2O and LiCl + NaCl + KCl + H_2O systems at 288.15 K in detail. In the following study, we will further expand the research to include multiple components systems.

2 Experimental Section

All the chemical reagents used in this study have been recrystallized, as shown in Table 1. The water for sample preparation and analysis was ultrapure water, and the resistivity was more than 17 MΩ·cm after final testing.

The systems of this article adopt isothermal solution equilibrium method. According to the solubility of each single salt and existing solubility data at co-saturated point of its subsystem, another new salt was added gradually, and then add the proper quantity of ultrapure water to the mixed salt. The each group of mixture was placed in ground glass stoppered bottles separately, and put bottles into a thermostatic water-bathing oscillator at 288.15 K ± 0.02 K (A SW23 type shaking water bath thermostat made by Julobo technology Co. Ltd.). After oscillating and dissolving for 20 days, the sample was left to rest. After the sample was clarified, the supernatant was analyzed periodically. When the difference of the mass fraction of lithium ion content between two consecutive measurements is less than 0.5%, the system is considered to reach the solid-liquid equilibrium. After reaching equilibrium, the supernatant was weighed and diluted to a constant volume for chemical analysis.

The specific analysis method of each ion is as follows: the lithium ion concentration, ICP-OES method; the chloridion ion concentration, mercury nitrate capacity method; the sulfate ion concentration, gravimetric method; the sodium ion concentration, ion balanced method.

3 Results and Discussion

3.1 Ternary system LiCl + NaCl + H_2O

For LiCl + NaCl + H_2O system at 288.15 K, the results of phase equilibrium studies at 288.15 K have been reported in the literature [6], but the relevant Pitzer parameters in this literature were not consistent with the current calculation in this paper. Therefore, this system was also studied to verify the experimental results and test the veracity of parameter $\Psi_{Li,Na,Cl}$ fitted by us before. And relative comparison has been added in the revised manuscript. The stable phase equilibrium experiments were conducted, and results of experiments including the detailed compositions of liquid phase, solid phase, and wet residue were shown in Table 2. And in which the concentration in equilibrium liquid phase and wet residue were given in the form of mass percentage (w(B)). Meanwhile, the isothermal equilibrium phase diagram of LiCl + NaCl + H_2O system at 288.15 K was plotted through adoption of data in Table 2, as shown in Fig. 1. The solid phase was identified by the wet residue method and single crystal analysis [4]. To connect a straight line between the liquid phase point and its corresponding wet residue point, and then to extend it, the point of intersection of these lines is the solid phase point. Combined with the analysis the trend of the phase field and univariant curve in the phase diagram, the equilibrium solid phase could be identified.

Based on what shown in Fig. 1, the phase diagram is covered with two isothermal solubility univariate curves, one co-saturated point, and two equilibrium solid crystallization fields. The specific compositions of the point, lines, as well as regions are as follows: (1) two univariate curves, corresponding to equilibrium solid phases: NaCl and $LiCl·2H_2O$; (2) one co-saturated point (point A), saturated with NaCl and $LiCl·2H_2O$, accompanying with the compositions of liquid phase: w(LiCl) = 43.09, w(NaCl) = 0.37; (3) two solid crystallization regions, corresponding to single salts NaCl and $LiCl·2H_2O$.

Table 4 shows the comparison with solubility data of the equilibrium liquid phase of ternary system LiCl + NaCl + H_2O at different temperatures [6-10]. In this system, no solid solution or complex salt is formed between the two original components. Meanwhile hydrous salt is also not dehydrated. There is only one invariant point and two crystallization fields in each phase diagram. All of these could be concluded that it is a simple co-satiation type from 273.15 K to 363.15 K. Lithium chloride hydrate is $LiCl_2·2H_2O$ at 273.15 K and 288.15 K, and it becomes $LiCl_2·H_2O$ at 298.15 K~363.15 K. It can be seen from Table 4 that the composition of LiCl clearly increases as the temperature increases and the composition of NaCl is always lower (less than 1%) for the corresponding liquid phase at invariant points of this system. The phase field of sodium chloride is far beyond that of lithium chloride hydrate among the equilibrium solid crystallization fields. This shows that lithium chloride has the salting-out effect on sodium chloride. The solubility of LiCl is much higher, and crystallization of NaCl becomes easy under the condition of the co-saturation.

3.2 Quaternary system LiCl + NaCl + KCl + H_2O

The liquid phase compositions (mass percentage) and the corresponding equilibrium solid phase of LiCl + NaCl + KCl + H_2O system 288.15 K were shown in Table 3, where J was the Jänecke dry salt index converted by the following formula J(LiCl) + J(NaCl) + J(KCl) = 100. Its phase diagram and water-content diagram were drawn by the converted Jänecke dry salt index, showing in Fig. 2 and Fig. 3.

According to the results shown in Fig. 3 and Table 2, the phase diagram has neither double salt nor solid solution existence, indicating that it should be the simple co-saturated type. The phase diagram of this quaternary system contains only one co-saturated point (point E), three isothermal solubility univariate curves (AE, BE, and CE), and three equilibrium solid crystallization regions (NaCl, $LiCl·2H_2O$, and KCl). Among them, the equilibrium solid phase compositions at the co-saturated point are NaCl, $LiCl·2H_2O$ and KCl, and the liquid compositions (mass fraction) are w(LiCl) = 0.4221, w(NaCl) = 0.033, and w(KCl) =0.0202. The three isothermal solubility univariate curves correspond to AE, BE, and CE in turn, in which the equilibrium solid phases are: (1) AE, NaCl + $LiCl·2H_2O$; (2) BE, KCl + $LiCl·2H_2O$; (3) CE, NaCl + KCl. Among the three equilibrium solid crystallization regions, compared with $LiCl·2H_2O$, the crystallization regions of NaCl and KCl are significantly larger. This indicates that $LiCl·2H_2O$ has a higher solubility, and is harder to crystallize. All types of equilibrium solid phases in the quaternary system appeared from its ternary subsystem, and no new solid phase formed. There was no new dehydration in the quaternary system.

Fig. 3 shows the changing rule of $J(H_2O)$ vs J(NaCl) on the solubility curve, the results indicated that the water content increases as J(NaCl) increased on univariate curve CE. The content is lowest at point B ($J(H_2O) = 119.35$), as well as highest at the point C ($J(H_2O) = 226.58$).

4 Prediction of Solubility

In this paper, the Pitzer electrolyte solution model was adopted to predict the solubility of two systems above. Pitzer model hypothesized that the anions and ions in the electrolyte solution were charged hard balls, with both electrostatic attraction and short-range repulsion. Pitzer classifies the interaction energy between ions into three parts: the long-range electrostatic potential energy between a pair of ions, the short-range hard-core effect potential energy (mainly the repulsive energy between two ions) and the interaction energy between three ions [11, 12]. For mixed electrolyte solutions, more concise HW formula made out by Harive and Weare are now commonly used [13, 14].

In China, Song Pengsheng, Yao Yan, and other scholars in my unit have built thermodynamic models of Li + Na + K + Mg + Cl + SO_4 + H_2O system at T = 298.15

K [15]. The main difference between this system and the classical seawater system was the introduction of lithium ion. Through the comprehensive processing of its experimentally determined osmotic coefficient, activity coefficient, solubility, and literature data, all Pitzer parameters of this system (applicable to the concentration range up to saturation, i.e. the ionic strength can be as high as 20), and standard molar Gibbs free energy of lithium salts were obtained, and the parameterization of the model was completed. And further use of this model to predict the solubility of the multi-component system, calculate the isothermal evaporation process of lithium-rich brine, and describe metathesis and conversion and so on. Based on the previous research, relevant studies on predicting the liquid-solid phase equilibrium of quaternary systems LiCl + NaCl + KCl + H_2O and LiCl + NaCl + Li_2SO_4 + Na_2SO_4 + H_2O at 288.15 K would be carried out.

The relevant parameters about LiCl +NaCl + KCl + H_2O system at 288.15 K were reported in the literature [4, 5, 16-19] (see Table 5 to 7 for details). First, the phase equilibrium solubility of ternary system LiCl +NaCl + H_2O was predicted by the Pitzer model. The solubility of a salt in water was calculated according to the principle that the free energy of the solution process system is the minimum, i.e., mathematically solving nonlinear equations.

The calculated results were shown in the Figure 4. In this figure, the experimental phase diagram is shown by solid points and solid lines, and the calculated phase diagram is shown by dotted lines. The calculated results correspond with the experimental data. We further predicted the solubility of salts in the quaternary system. The corresponding calculated and experimental phase diagram was drawn in Figure 5 and the values of each co-saturation point of this system and its ternary subsystem were compared and analysed, as listed in Table 8 (for a convenient comparison, they were uniformly expressed by mass percentage). It can be seen from the comparison that the calculated results were satisfactory.

5 Conclusions

The solid-liquid phase equilibrium of ternary system (LiCl + NaCl + H_2O) and quaternary system (LiCl + NaCl + KCl + H_2O at 288.15 K were studied. The equilibrium solid phases in the phase diagrams of LiCl + NaCl + H_2O and LiCl + NaCl + KCl + H_2O systems corresponded to the original components. No double salts or solid solution was found, and no dehydration of the original components occurred. Two systems are all of the simple co-saturated type. Combined with relevant parameters found in the literature, the solubility of above two systems at 288.15 K was obtained using the Pitzer model. However, the theoretically calculated solibility was essentially consistent with that of the experimental data.

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Reference

1. Y. T. Lin, Y. C. Yao, Z. H. Kang, N. J. Wang. Study on the geochemical characteristics and resource significance of the highly mineralized potassium-rich brine in the Sichuan Xuanda salt basin (in Chinese). J. Salt Lake Res. 12 (2004) 8-18.
2. P. S. Song, The Phase Diagram of Salt-Water Systems and Utilization of Salt Lake resources (in Chinese). J. Salt Lake Res. 3 (2016) 35-49.
3. R. Z. Cui, L. Yang, W. Wang, S. H. S, Measurements and calculations of solid-liquid equilibria in the quaternary system Li_2SO_4–Na_2SO_4–K_2SO_4–H_2O at 288 K. Chem. Res. Univ. 33 (2017) 460-465.
4. R. Z. Cui, W. Li, Y. P. Dong, Measurement and prediction of solid + liquid equilibria in the quaternary system LiCl–KCl–Li_2SO_4–K_2SO_4–H_2O at 288.15 K. J. Chem. Eng. Data 64 (2019) 4206-4213.
5. R. Z. Cui, W. Li, Y. P. Dong, Z. Nie, Mineral solubilities of salts in the three quaternary systems: LiCl–NaCl–$MgCl_2$–H_2O, LiCl–KCl–$MgCl_2$–H_2O and Li_2SO_4–K_2SO_4–$MgSO_4$–H_2O

at 288.15 K. J. Chem. Thermodyn. 138 (2019) 127-139.

6. J. A. Lovera, T. A. Graber, H. R. Galleguillos, Correlation of solubilities for the NaCl + LiCl + H_2O system with the Pitzer model at 15, 25, 50, and 100℃. Calphad 33 (2009) 388-392.
7. X. W. Jiang, X. M. Zhang, Z. X. Li, A study on ternary system LiCl–NaCl–H_2O at 0°C (in Chinese). J. Northwest Univ. 1 (1985) 40-43.
8. A. Zdanovskii, E. Solovea, E. Liahovskaia, N. Shestakov, P. Shleimovich, L. Abutkova, Spravochnik po rastvorimosti solevykh system. Trehkomponentnye systemy, vols. I-1 and I-2, Khimyua, St. Petersbug, 1973.
9. F. Farelo, C. Fernandes, A. Avelino, Solubilities for six ternary systems: NaCl + NH_4Cl + H_2O, KCl + NH_4Cl + H_2O, NaCl + LiCl + H_2O, KCl + LiCl + H_2O, NaCl + $AlCl_3$ + H_2O, and KCl + $AlCl_3$ + H_2O at T = (298 to 333) K. J. Chem. Eng. Data 50 (2005) 1470-1477.
10. S. Q. Wang, Y. F. Guo, D. F. Liu, T. L. Deng, Phase equilibria in system LiCl–NaCl–H_2O at 308 and 348 K. Russ. J. of Phys. Chem. A 90 (2016) 2532-2537.
11. K. S. Pitzer, Thermodynamics of electrolytes. I. Theoretical basis and general equations. J. Phys. Chem. 77 (1973) 268-277.
12. K. S. Pitzer, J. Simonson, Thermodynamics of multicom-ponent, miscible, ionic system: theory and equations. J. Phys. Chem. 90 (1986) 3005-3009.
13. C. E. Harvie, J. H. Weare, The prediction of mineral solubilities in natural waters: the Na–K–Mg–Ca–Cl–SO_4–H_2O system from zero to high concentrationat 25°C. Geochim. Cosmochim. Acta 44 (1980) 981-997.
14. C. E. Harvie, N. Moller, J. H. Weare, The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system to high ionic strengths at 25°C. Geochim. Cosmochim. Acta 48 (1984) 723-751.
15. P. S. Song, Y. Yao, B. Sun, W. Li, Pitzer model of thermodynamics for the Li^+, Na^+, K^+, Mg^{2+}//Cl^-, SO_4^{2-}–H_2O system (in Chinese). Sci. China-Chem. 40 (2010) 1286-1296.
16. H. F. Gibbard, G. Scatchard, Liquid–vapor equilibrium of aqueous lithium chloride, from 25 °C to 100 °C and from 1.0 to 18.5 Molal and related properties. J. Chem. Eng. Data 18 (1973) 293-298.
17. J. P. Greenberg, N. Moller, The Prediction of mineral solubilities in natural water: A chemical equilibrium model for the Na–K–Ca–Cl–SO_4–H_2O system to high concentration from 0 to

250 °C. Geochim. Cosmochim. Acta 53 (1989) 2503-2518.

18. Y. F. Guo, Y. H. Liu, Q. Wang, C. X. Lin, S. Q. Wang, T. L. Deng, Phase Equilibria and Phase Diagrams for the Aqueous Ternary System (Na_2SO_4 + Li_2SO_4 + H_2O) at (288 and 308) K. J. Chem. Eng. Data 58 (2013) 2763-2767.
19. S. Q. Wang, Y. F. Guo, D. C. Li, P. Tang, T. L. Deng, Experimental determination and modeling of the solubility phase diagram of the ternary system (Li_2SO_4 + K_2SO_4 + H_2O) at 288.15 K. Thermochim. Acta 601 (2015) 75-81.

Table 1 CAS registry numbers, source and purity of chemicals

Chemical name	CAS numbers	Suppliers	Mass fraction [a]
Lithium chloride	7447-41-8	Shanghai Aladdin Reagent Company	0.999
Sodium chloride	7647-14-5	Shanghai Aladdin Reagent Company	0.9999
Potassium chloride	7447-40-7	Shanghai Macklin Biochemical Co., Ltd	0.995

[a] Provided by suppliers.

Table 2 Experimental results of phase equilibria in the ternary system LiCl + NaCl + H_2O at 288.15 K and 0.077 MPa [a]

No.	Composition of liquid phase 100·*w*(B)		Composition of wet residue 100·*w*(B)		Equilibrium phase solids
	w(LiCl)	*w*(NaCl)	*w*(LiCl)	*w*(NaCl)	
1	0	26.35	–	–	NaCl
2	3.75	22.22	1.26	80.05	NaCl
3	10.33	15.78	2.48	81.3	NaCl
4	16.48	10.8	4.18	78.53	NaCl
5	25.37	4.62	5.33	80.25	NaCl
6	35.41	1.24	8.43	77.42	NaCl
7, A	43.09	0.37	30.41	46.78	$LiCl \cdot 2H_2O$ + NaCl
8	43.64	0.21	–	–	$LiCl \cdot 2H_2O$
9	44.08	0	–	–	$LiCl \cdot 2H_2O$

[a] w(B) means mass fraction of component B in saturated solution. $u(T)$ = 0.02 K, $u(p)$ = 0.002 MPa, $u_r[w(\mathrm{LiCl})]$ = 0.005, $u_r[w(\mathrm{NaCl})]$ = 0.005.

Table 3 Solubilities of solution in the quaternary system LiCl + NaCl + KCl + H_2O at 288.15 K and 0.077 MPa [a]

No.	Composition of liquid phase 100·w(B)			Jänecke index J/(g/100 g) J(LiCl) + J(NaCl) + J(KCl) = 100				Equilibrium solids
	LiCl	NaCl	KCl	LiCl	NaCl	KCl	H_2O	
1, A	43.09	0.37	0.00	99.15	0.85	0.00	130.10	LC2 + NC
2	42.84	0.35	0.97	97.01	0.79	2.20	126.45	LC2 + NC
3, E	42.21	0.33	2.02	94.73	0.74	4.53	124.42	LC2 + NC + KC
4, B	43.49	0.00	2.10	95.39	0.00	4.61	119.35	LC2 + KC
5, C	0.00	21.05	9.57	0.00	68.75	31.25	226.58	NC + KC
6	4.21	17.50	9.12	13.66	56.76	29.58	224.36	NC + KC
7	7.88	15.17	8.24	25.18	48.48	26.33	219.59	NC + KC
8	11.05	12.86	7.33	35.37	41.17	23.46	220.10	NC + KC
9	15.47	9.84	6.04	49.35	31.39	19.27	218.98	NC + KC
10	22.03	5.70	4.66	68.01	17.60	14.39	208.74	NC + KC
11	28.54	3.60	3.28	80.58	10.16	9.26	182.33	NC + KC
12	36.18	1.32	2.37	90.74	3.31	5.94	150.82	NC + KC

[a] w(B) means mass fraction of component B in saturated solution. $u(T)$ = 0.02 K, $u(p)$ = 0.002 MPa, $u_r[w(\mathrm{LiCl})]$ = 0.005, $u_r[w(\mathrm{NaCl})]$ = 0.005, $u_r[w(\mathrm{KCl})]$ = 0.005. Abbreviations: LC2 = $LiCl\cdot 2H_2O$, NC = NaCl, KC = KCl.

Table 4 Compositions of liquid phase and equilibrium solid phase at invariant points of the ternary system LiCl–NaCl–H_2O at different temperatures

T	Composition of liquid phase		Equilibrium solids	Reference
	100w(LiCl)	100w(NaCl)		
273.13 K	38.99	0.98	$LiCl\cdot 2H_2O$ + NaCl	[7]
273.13 K	41.3	0.2	$LiCl\cdot 2H_2O$ + NaCl	[8]

288.15 K	43.61	0.15	$LiCl\cdot 2H_2O$ + NaCl	[6]
288.15 K	43.09	0.37	$LiCl\cdot 2H_2O$ + NaCl	This work
298.15 K	45.58	0.11	$LiCl\cdot H_2O$ + NaCl	[8]
298.15 K	45.54	0.19	$LiCl\cdot H_2O$ + NaCl	[9]
308.15 K	44.71	0.42	$LiCl\cdot H_2O$ + NaCl	[10]
323.15 K	48.41	0.33	$LiCl\cdot H_2O$ + NaCl	[8]
323.15 K	48.14	0.24	$LiCl\cdot H_2O$ + NaCl	[9]
333.15 K	49.96	0.32	$LiCl\cdot H_2O$ + NaCl	[9]
348.15 K	52.08	0.52	$LiCl\cdot H_2O$ + NaCl	[10]
363.15 K	54.67	0.75	$LiCl\cdot H_2O$ + NaCl	[8]

Table 5 Single–salt parameters in the solution of quaternary system quaternary system LiCl + NaCl + KCl + H_2O at 288.15 K

Salt	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Reference
LiCl	0.1500	0.3006	0.004211	16
NaCl	0.06698	0.2671	0.002636	17
KCl	0.04167	0.2022	–0.00009683	17

Table 6 Mixing ion-interaction parameters in the solution of quaternary system LiCl + NaCl + KCl + H_2O at 288.15 K

Parameter	$\theta_{Li,Na}$	$\theta_{Li,K}$	$\theta_{Na,K}$	$\Psi_{Li,Na,Cl}$	$\Psi_{Li,K,Cl}$	$\Psi_{Na,K,Cl}$
Value	0.05515	–0.008914	–0.001571	–0.02657	–0.02060	–0.004285
Reference	18	19	17	5	4	17

Table 7 Debye-Hückel constant (A^{ϕ}) and solubility equilibrium constants of salts of quaternary system LiCl + NaCl + KCl + H_2O at 288.15 K

Parameter	A^{ϕ}	$\ln K(LiCl\cdot 2H_2O)$	$\ln K(NaCl)$	$\ln K(KCl)$
Value	0.3851	12.1433	3.6010	1.8511
Reference	17	19	17	17

Table 8 Comparisons of the calculated and experimental values of co-saturated points for the quaternary system LiCl + NaCl + KCl + H_2O and its ternary subsystems at 288.15 K

System	Point	Exp/Cal	Composition of liquid phase $100 \cdot w(B)$			Equilibrium solids
			LiCl	NaCl	KCl	
LiCl + NaCl + H_2O	Point A	Experimental	43.09	0.37	0.00	$LiCl \cdot 2H_2O$ + NaCl
		Calculated	43.81	0.81	0.00	
LiCl + KCl + H_2O	Point B	Experimental	43.49	0.00	2.10	$LiCl \cdot 2H_2O$ + KCl
		Calculated	43.37	0.00	1.95	
NaCl + KCl + H_2O	Point C	Experimental	0.00	21.05	9.57	NaCl + KCl
		Calculated	0.00	21.57	9.20	
LiCl + NaCl + KCl + H_2O	Point E	Experimental	42.21	0.33	2.02	$LiCl \cdot 2H_2O$ + NaCl + KCl
		Calculated	42.76	1.09	2.39	

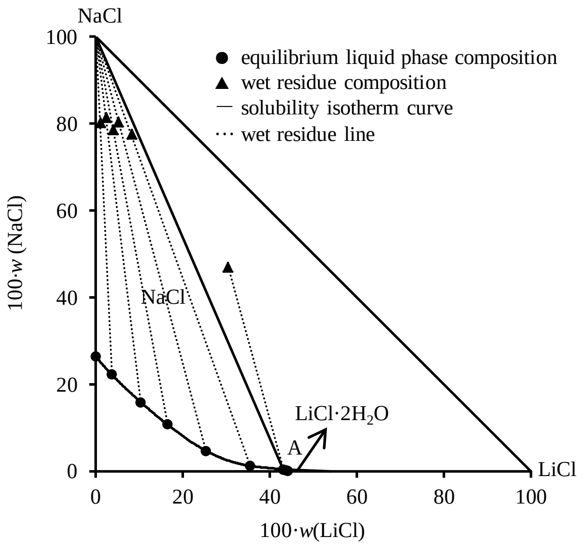


Fig. 1 Equilibrium phase diagram of the ternary system LiCl + NaCl + H_2O at 288.15 K.

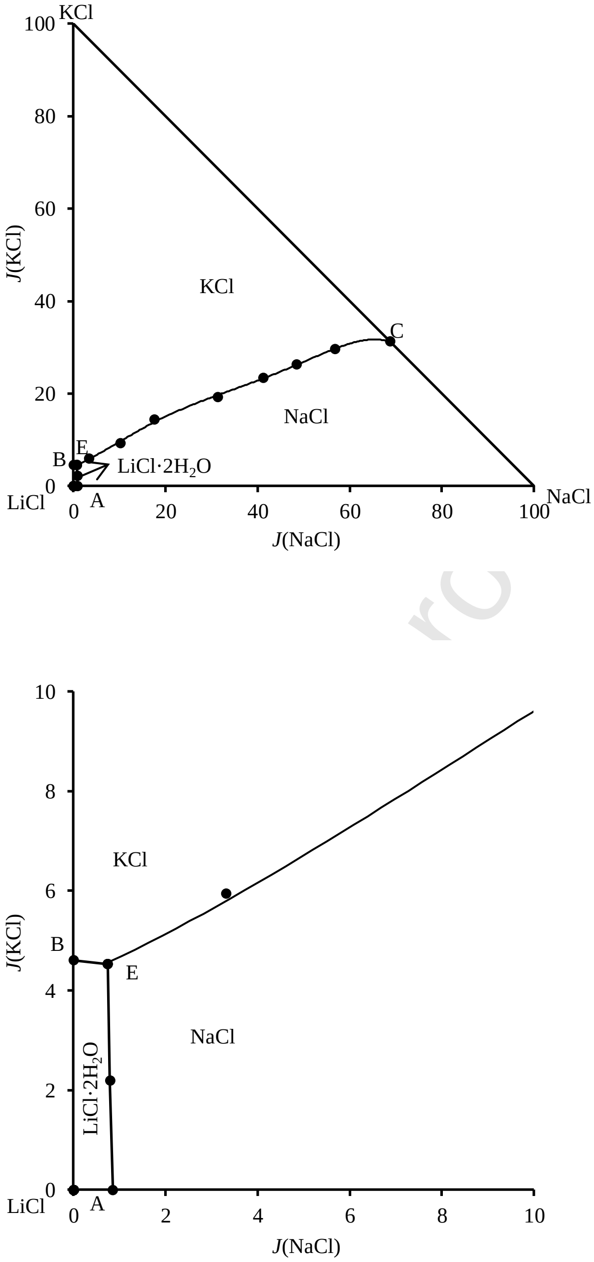


Fig. 2 Equilibrium phase diagram of the quaternary system LiCl + NaCl + KCl + H_2O at 288.15 K.

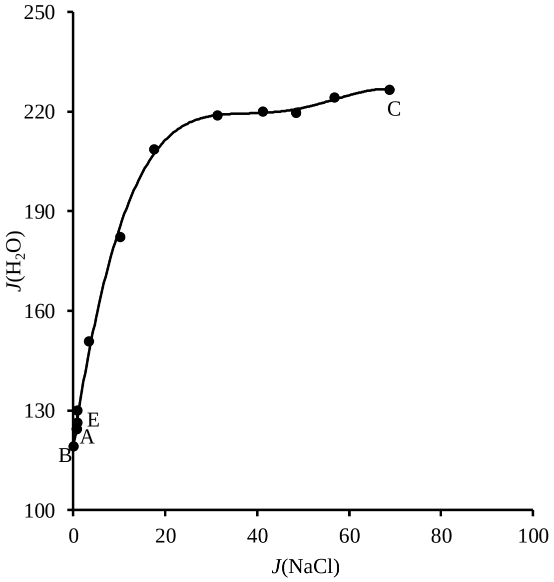


Fig. 3 Water contents of saturated solutions in the quaternary system LiCl + NaCl + KCl + H_2O at 288.15 K.

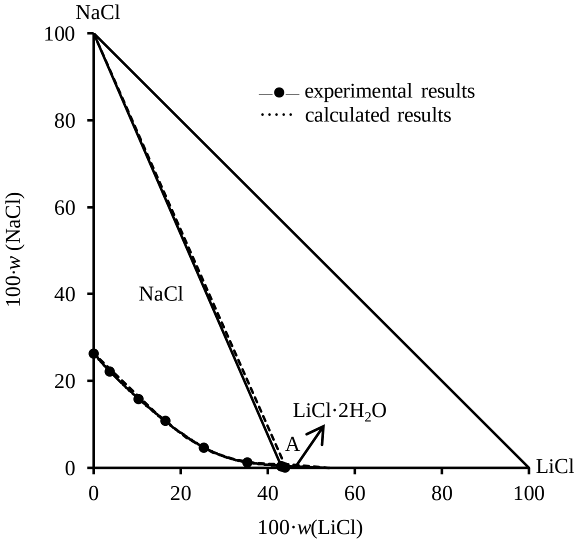


Fig. 4 The experimental and calculated phase diagram of the ternary system LiCl + NaCl + H_2O at 288.15 K.

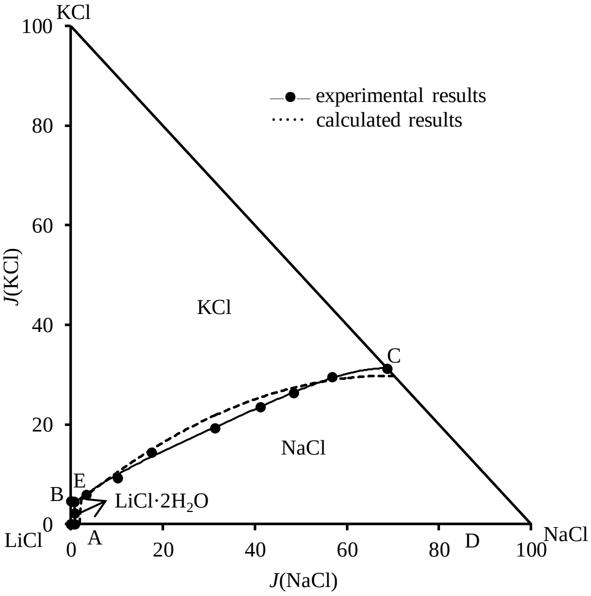
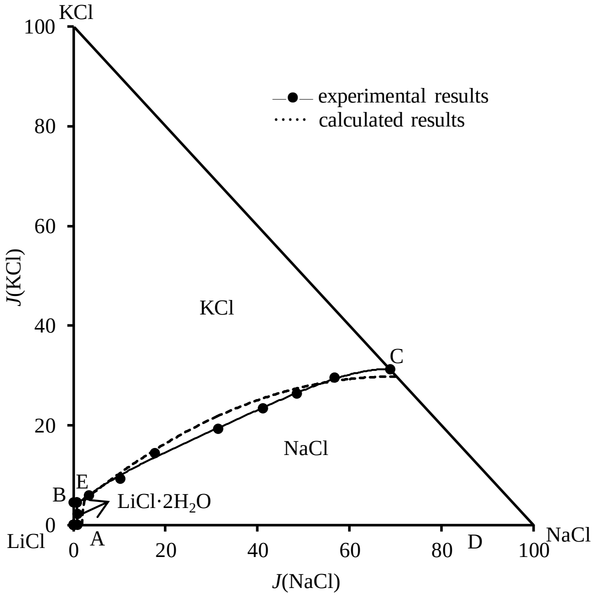


Fig. 5 The experimental and calculated phase diagram of the quaternary system LiCl + NaCl + KCl + H_2O at 288.15 K.

conflict of interest

I declare that I do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.



The experimental and calculated phase diagram of the quaternary system LiCl + NaCl + KCl + H_2O at 288.15 K.

Graphical abstract

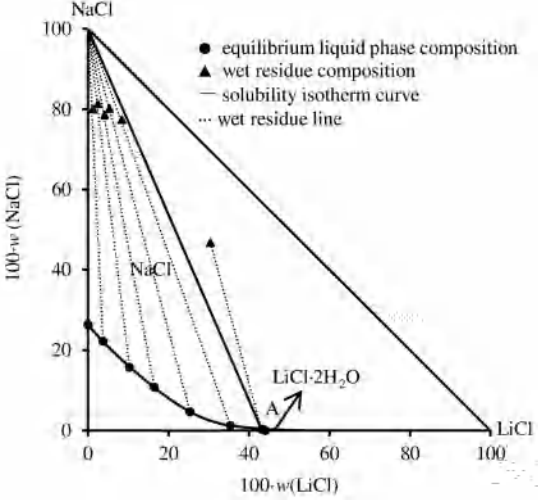

NaCl
100
80
60
40
20
0
100-w (NaCl)
● equilibrium liquid phase composition
▲ wet residue composition
— solubility isotherm curve
··· wet residue line
NaCl
LiCl·2H_2O
A
LiCl
0
20
40
60
80
100
100-w(LiCl)

Figure 1

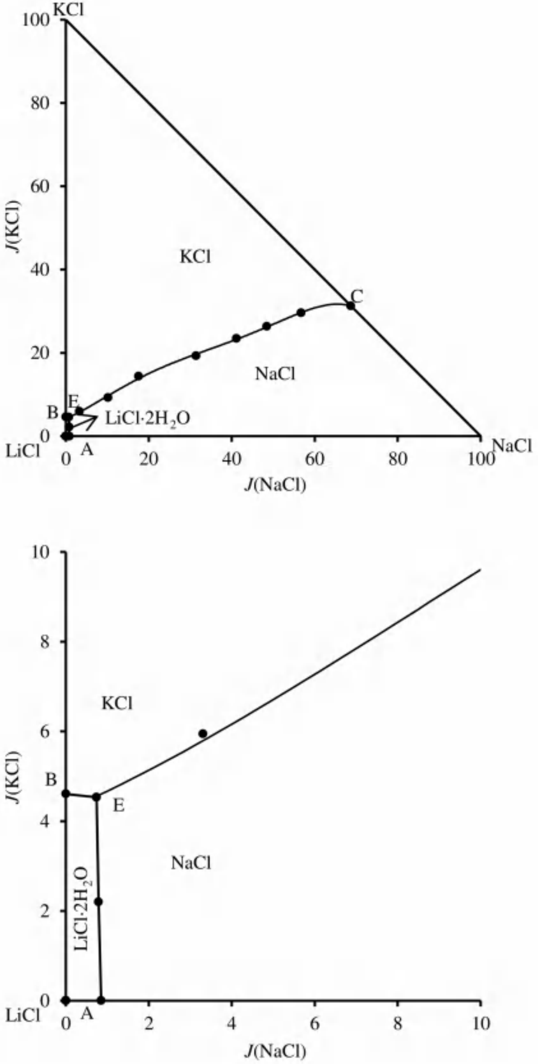

KCl
100
80
60
40
20
0
J(KCl)
KCl
C
NaCl
E
B
LiCl·2H$_2$O
LiCl
0
A
20
40
60
80
100
NaCl
J(NaCl)
10
8
6
4
2
0
J(KCl)
KCl
B
E
NaCl
LiCl·2H$_2$O
LiCl
0
A
2
4
6
8
10
J(NaCl)

Figure 2

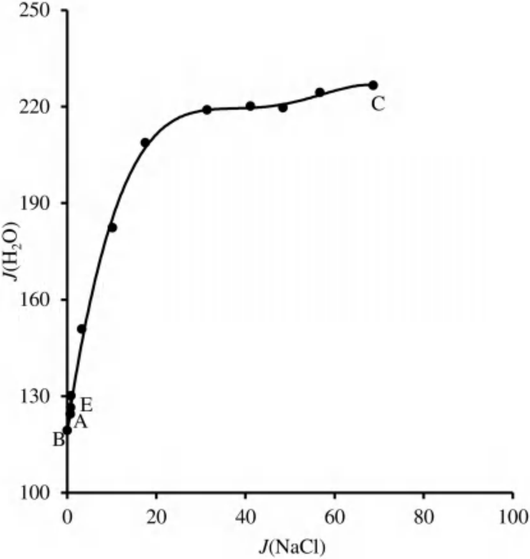


Figure 3

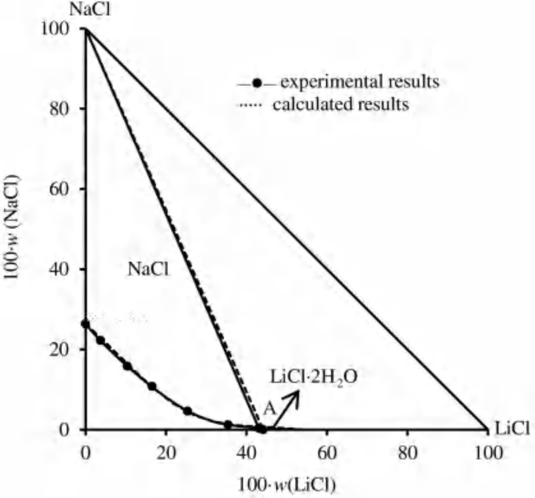

NaCl
100
80
60
40
20
0
100·w (NaCl)
—●— experimental results
····· calculated results
NaCl
LiCl·2H₂O
A
LiCl
0
20
40
60
80
100
100·w(LiCl)

Figure 4

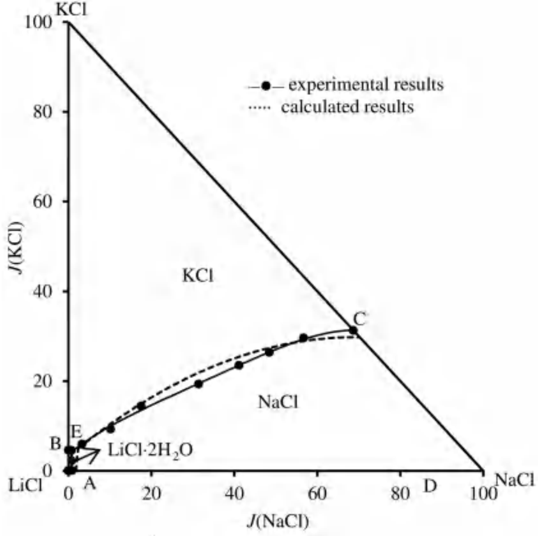

KCl
100
80
60
40
20
0
J(KCl)
—●— experimental results
····· calculated results
KCl
C
NaCl
E
B
LiCl·2H₂O
LiCl
A
0
20
40
60
80
D
100
NaCl
J(NaCl)

Figure 5