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Metastable equilibrium for the quaternary system containing with lithium+potassium+magnesium+chloride in aqueous solution at 323 K

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Abstract−The metastable equilibrium of the system contained with lithium, potassium, magnesium, and chloride in aqueous system was investigated at 323 K using an isothermal evaporation method. The isothermal experimental data and physicochemical properties, such as density and refractive index of the equilibrated solution, were determined. With the experimental results, the stereo phase diagram, the projected phase diagram, the water content diagram and the physicochemical properties versus composition diagrams were constructed. The projected phase diagram consists of three invariant points, seven univariant curves and five crystallization fields corresponding to single salts potassium chloride (KCl), lithium chloride monohydrate ($LiCl\cdot H_2O$), bischofite ($MgCl_2\cdot 6H_2O$) and two double salts lithium carnallite ($LiCl\cdot MgCl_2\cdot 7H_2O$) and potassium carnallite ($KCl\cdot MgCl_2\cdot 6H_2O$). Salt KCl has the largest crystallization region; it contains almost 95% of the general crystallization field.

Keywords: Phase Equilibrium, Lithium, Potassium, Double Salt, Solubility

INTRODUCTION

A huge volume of natural salt lakes and underground brine with high concentrations of sodium, potassium, lithium, and chloride is widely distributed in China, such as Zabuye salt lake, Chaidamu saline lake, Pingluoba underground brine, and Jianglin underground brine [1,2]. Commonly, salt lakes and underground brine contain abundant mineral resources. To comprehensively utilize the brine resource, phase equilibrium studies about the different types of brines are necessary. For example, the phase diagram of Na^+, K^+ // Cl^-, CO_3^{2-}, SO_4^{2-} - H_2O at 293-373 K which was finished by Teeple has been used to comprehensively utilize the Searles Salt Lake [3], and the phase diagram of Na^+, K^+, Mg^{2+} // Cl^-, and SO_4^{2-} - H_2O at 288 K, 298 K, and 308 K which was done by Jin et al. have been used to extract $MgSO_4\cdot K_2SO_4\cdot 6H_2O$ or K_2SO_4 from Chaidamu Saline Lake [4-6]. Furthermore, a series of studies has been done on the phase equilibrium aimed at different types of brine, including our researches focused on the component characteristics of the Zabuye Salt Lake [7-11] and Pingluoba underground brine [12-18].

Pingluoba underground brine largely consists of sodium, potassium, chloride, and borate, and its main content can be included in the hexa component system $Li^++K^++Rb^++Mg^{2+}+Cl^-$+borate+$H_2O$. The phase equilibria of some subsystems of this hexa component system have been investigated in our previous researches [12-18]. Research results show that the ternary subsystem $KCl+MgCl_2+H_2O$ at 323 K is a complex type with the double salt $KCl\cdot MgCl_2\cdot 6H_2O$ formed; the ternary subsystem $LiCl+KCl+H_2O$ is a simple type without double salt or solid solution formed. The present paper is a continuation of previous research. To date, the phase equilibrium of the quaternary system $LiCl+KCl+MgCl_2+H_2O$ at 323 K has not been reported. Accordingly, the metastable equilibrium of the quaternary system at 323 K is presented in detail.

EXPERIMENTAL SECTION

1. Materials

Potassium chloride (KCl, molecular weight 74.55, CAS No. 7447-40-7), lithium chloride (LiCl, molecular weight 42.39, CAS No. 7447-41-8), and magnesium chloride hexahydrate ($MgCl_2\cdot 6H_2O$, molecular weight 203.30, CAS No. 7791-18-6) were obtained from Chengdu Kelong Chemical Reagent Plant at purity of 99.5%, 99.0%, and 98.0%, respectively. All materials were used directly from the manufacturers without further purification. Deionized water, with an electrical conductivity less than $1\cdot 10^{-4}\ S\cdot m^{-1}$ and pH≈6.60, was used in the experiments.

2. Experimental Apparatus and Procedure

The isothermal evaporation method was employed in this study. The component of the invariant points of the ternary subsystems (saturated with two salts) was taken as the composition of initial samples. The desired samples were compounded by adding the different quantities' third salt to the initial samples. When the composition of the solution remained constant, the system reached the dissolution equilibrium and the synthesized sample for evaporation was accomplished. Then, evaporation of the synthesized solutions proceeded in the SHH-250 type thermostatic evaporator, inside which the temperature of the solutions was (323±0.1) K. The solutions were observed periodically and newly appeared solids were separated from them by filtration. In the meantime, the concentrations of the components of the clarified solutions were measured by chemical or instrument analysis method. The densities of solution were

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Table 1. The isothermal experimental values corresponding to the invariant points of the binary and ternary subsystems in the quaternary system LiCl+KCl+MgCl$_2$+H$_2$O at 323 K[a]

No.	System	Composition of solution				Jänecke index of dry salt				Equilibrated solid phase
		w(B)×10^2				J(Li$_2$Cl$_2$)+J(K$_2$Cl$_2$)+J(MgCl$_2$)=100				
		w(LiCl)	w(KCl)	w(MgCl$_2$)	w(H$_2$O)	J(Li$_2$Cl$_2$)	J(K$_2$Cl$_2$)	J(MgCl$_2$)	J(H$_2$O)	
a	LiCl-H$_2$O	47.51	0.00	0.00	52.49	100.0	0.00	0.00	520.4	LiI
b	KCl-H$_2$O	0.00	28.99	0.00	71.01	0.00	100.0	0.00	2029	KI
c	MgCl$_2$-H$_2$O	0.00	0.00	37.35	62.65	0.00	0.00	100.0	888.1	Bis
A	KMgCl	0.00	4.60	25.68	69.72	0.00	10.27	89.73	1290	KI+K-Car
B	KMgCl	0.00	0.20	37.11	62.69	0.00	0.34	99.66	891.3	Bis+K-Car
C	LiMgCl	23.76	0.00	20.11	56.13	57.05	0.00	42.95	634.7	LiI+LiI-Car
D	LiMgCl	39.98	0.00	8.75	51.27	83.70	0.00	16.30	505.6	Bis+LiI-Car
E	LiKCl	44.77	5.14	0.00	50.09	93.87	6.13	0.00	494.7	LiI+KI
H$_1$	LiKMgCl	2.10	0.22	34.64	63.04	6.36	0.37	93.27	898.6	KI+K-Car+Bis
H$_2$	LiKMgCl	21.70	0.25	20.50	57.55	54.14	0.36	45.50	676.3	Bis+LiI-Car+KI
H$_3$	LiKMgCl	40.70	0.48	8.66	50.16	83.61	0.56	15.83	485.3	KI+LiI-Car+LiI

Note: w(B): mass fraction of B; LiI: LiCl·H$_2$O; K-Car: KCl·MgCl$_2$·6H$_2$O; LiI-Car: LiCl·MgCl$_2$·7H$_2$O; Bis: MgCl$_2$·6H$_2$O; KI: KCl; KMgCl-KCl+MgCl$_2$+H$_2$O; LiKCl-KCl+LiCl+H$_2$O; LiMgCl-MgCl$_2$+LiCl+H$_2$O; LiKMgCl-LiCl+KCl+MgCl$_2$+H$_2$O

Table 2. The isothermal experimental values of the quaternary system LiCl+KCl+MgCl$_2$+H$_2$O at 323 K

No.	Density/ (g·cm^{-3})	Refractive index	Composition of equilibrium solution w(b)×10^2				Jänecke index of dry salt J(Li$_2$Cl$_2$)+J(K$_2$Cl$_2$)+J(MgCl$_2$)=100				Equilibrated solid phase
			w(LiCl)	w(KCl)	w(MgCl$_2$)	w(H$_2$O)	J(Li$_2$Cl$_2$)	J(K$_2$Cl$_2$)	J(MgCl$_2$)	J(H$_2$O)	
1, A	1.3767	1.4090	0.00	4.60	25.68	69.72	0.00	10.27	89.73	1290	KI+K-Car
2	1.3743	1.414	0.96	3.98	27.05	68.01	3.52	8.29	88.19	1174	KI+K-Car
3	1.3823	1.4141	1.24	3.36	27.37	68.03	4.51	6.95	88.54	1165	KI+K-Car
4	1.3921	1.4176	1.39	1.90	29.06	67.65	4.91	3.81	91.28	1125	KI+K-Car
5	1.4035	1.4224	1.60	0.82	29.93	67.65	5.58	1.62	92.80	1111	KI+K-Car
6, H$_1$	1.4213	1.4352	2.10	0.22	34.64	63.04	6.36	0.37	93.27	898.6	Bis+KI+K-Car
7, B	1.4883	1.4336	0.00	0.20	37.11	62.69	0.00	0.34	99.66	891.3	Bis+K-Car
8	1.4484	1.4351	0.58	0.26	37.78	61.38	1.69	0.43	97.88	841.9	Bis+K-Car
9	1.4253	1.4349	1.46	0.21	37.55	60.78	4.17	0.34	95.49	818.3	Bis+K-Car
10, H$_1$	1.4213	1.4352	2.10	0.22	34.64	63.04	6.36	0.37	93.27	898.6	Bis+KI+K-Car
11	1.4206	1.4325	2.79	0.22	34.42	62.57	8.32	0.37	91.31	878.8	Bis+KI
12	1.4216	1.4344	4.38	0.21	34.33	61.08	12.50	0.34	87.16	820.1	Bis+KI
13	1.4262	1.4328	5.47	0.25	33.28	61.00	15.53	0.40	84.07	815.8	Bis+KI
14	1.4272	1.4363	7.80	0.27	32.32	59.61	21.25	0.42	78.33	764.9	Bis+KI
15	1.4337	1.4346	8.42	0.21	30.11	61.26	23.83	0.34	75.83	816.8	Bis+KI
16	1.4369	1.4364	13.83	0.22	26.23	59.72	37.09	0.34	62.57	754.3	Bis+KI
17	1.4375	1.4382	19.11	0.24	22.71	57.94	48.44	0.35	51.21	691.8	Bis+KI
18,C	1.4095	1.4322	23.76	0.00	20.11	56.13	57.05	0.00	42.95	634.7	Bis+LiI-Car
19,H$_2$	1.4215	1.4386	21.70	0.25	20.50	57.55	54.14	0.36	45.50	676.3	Bis+KI+LiI-Car
20	1.4156	1.4387	24.35	0.35	20.59	54.71	56.80	0.47	42.73	601.1	KI+LiI-Car
21	1.4118	1.4323	28.85	0.44	18.89	51.82	62.85	0.54	36.61	531.7	KI+LiI-Car
22	1.4116	1.4329	33.36	0.45	14.59	51.60	71.60	0.55	27.85	521.6	KI+LiI-Car
23	1.4115	1.4327	35.36	0.46	12.59	51.59	75.52	0.56	23.92	519.0	KI+LiI-Car
24	1.4114	1.4358	40.70	0.48	8.66	50.16	83.61	0.56	15.83	485.3	KI+LiI-Car
25, D	1.4033	1.4476	39.98	0.00	8.75	51.27	83.70	0.00	16.30	505.6	LiI+LiI-Car
26, H$_3$	1.4111	1.4428	40.70	0.48	8.66	50.16	83.61	0.56	15.83	485.3	LiI+KI+LiI-Car
27, E	1.4069	1.4386	44.77	5.14	0.00	50.09	93.87	6.13	0.00	494.7	LiI+KI
28	1.4125	1.4403	43.96	4.82	2.51	48.71	89.84	5.60	4.56	468.3	LiI+KI
29	1.4132	1.4439	43.21	2.76	4.80	49.23	88.09	3.20	8.71	472.7	LiI+KI
30	1.4142	1.4449	41.32	1.85	5.91	50.92	86.75	2.21	11.04	503.5	LiI+KI
31, H$_3$	1.4111	1.4428	40.70	0.48	8.66	50.16	83.61	0.56	15.83	485.3	LiI+KI+LiI-Car

measured with a gravity bottle method with a precision of ±0.0002 $g\cdot cm^{-3}$ and used for the mass fraction calculation of liquid components. The refractive indices of solution were measured with a 2WAJ Abbe refractometer with a precision of ±0.0001.

The solutions separated by filtration were continued to be evaporated and the next samples were taken as mentioned above. This operation was repeated and the whole procedure ended when the solutions evaporated to dryness.

3. Analytical Methods

The concentration of Cl^- was determined by $AgNO_3$ titration using K_2CrO_4 as an indicator with a precision of ±0.3%. The concentration of K^+ was measured by a sodium tetraphenylborate-cetyltrimethylammonium bromide titration using Titan yellow as an indicator with a precision of ±0.5% [19]. The Li^+ and Mg^{2+} concentration was measured by the ICP-OES method with a precision of ±1.0%.

RESULTS AND DISCUSSION

The data corresponding to the invariant points in the binary and ternary subsystems of this quaternary system are tabulated in Table 1. The isothermal experimental results of the quaternary system at 323 K are listed in Table 2. In Tables 1 and 2, the concentration of salts in solution is expressed in mass fraction w(M), and the component of dry salts is shown as Jänecke index J(M) (with $J(Li_2Cl_2)+J(K_2Cl_2)+J(MgCl_2)=100$). The Jänecke index values can be calculated according to the following equations:

$$\text{Letting } [B]=\frac{1}{2}\left[\frac{w(LiCl)}{42.39}+\frac{w(KCl)}{74.55}\right]+\frac{w(MgCl_2)}{95.21}$$

$$J(Li_2Cl_2)=\frac{1}{2}\times\frac{w(LiCl)}{42.39\times[B]}\times 100$$

$$J(H_2O)=\frac{w(H_2O)}{18.02\times[B]}\times 100$$

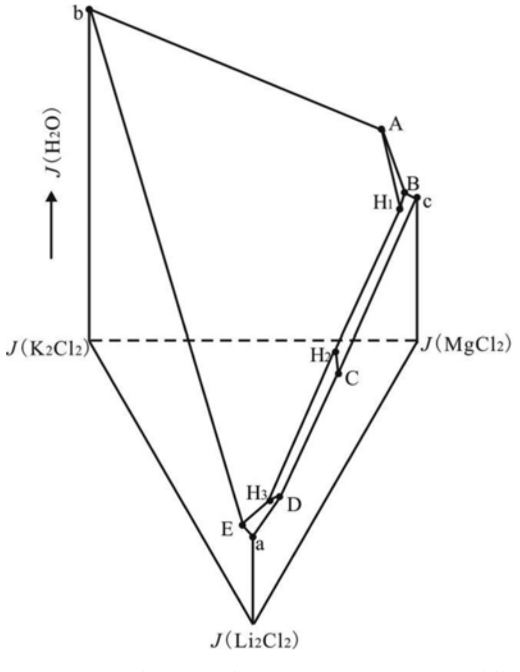

Fig. 1. The stereo - diagram of the quaternary system $LiCl+KCl+MgCl_2+H_2O$ at 323 K.

With the data of Jänecke index J(M) in Tables 1 and 2, the space diagram of the system at 323 K was constructed in Fig. 1. Fig. 2 is the projected phase diagram of Fig. 1. Fig. 3 is the partial enlarged diagram of Fig. 2. Figs. 1 and 2 show that the phase diagram consists of five crystallization fields, seven univariant curves, and three invariant points. The five crystallization fields correspond to single salts KCl, $LiCl\cdot H_2O$, $MgCl_2\cdot 6H_2O$ and double salts $LiCl\cdot MgCl_2\cdot 7H_2O$ and $KCl\cdot MgCl_2\cdot 6H_2O$. Salt KCl has the largest crystallization region; it contains almost 95% of the general crystallization field.

In the previous researches [20-22], the researchers consider that a great variety of carnallite types can be obtained by isomorphic replacement of individual ions in the salts, that is, in the carnallite formula $KCl\cdot MgCl_2\cdot 6H_2O$, K^+ can be replaced by Rb^+, Cs^+, and NH_4^+ to form rubidium carnallite ($RbCl\cdot MgCl_2\cdot 6H_2O$), cesium carnallite ($CsCl\cdot MgCl_2\cdot 6H_2O$), and ammonium carnallite ($NH_4Cl\cdot MgCl_2\cdot 6H_2O$), respectively. Meantime, K^+ can also be replaced by $Li(H_2O)^+$

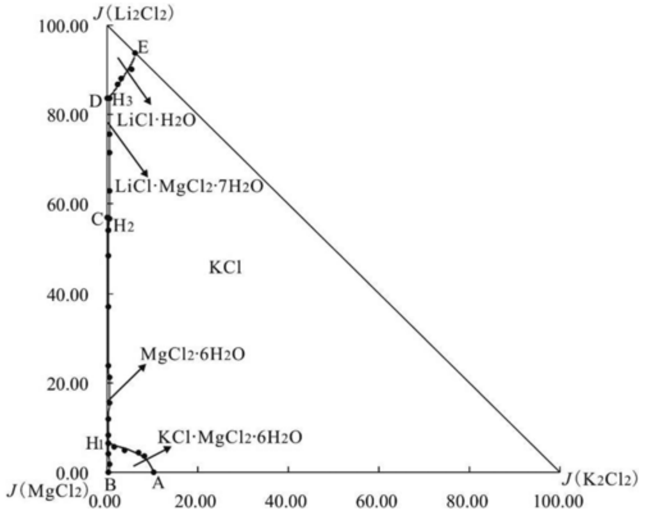

Fig. 2. The projected phase diagram of the quaternary system $LiCl+KCl+MgCl_2+H_2O$ at 323 K.

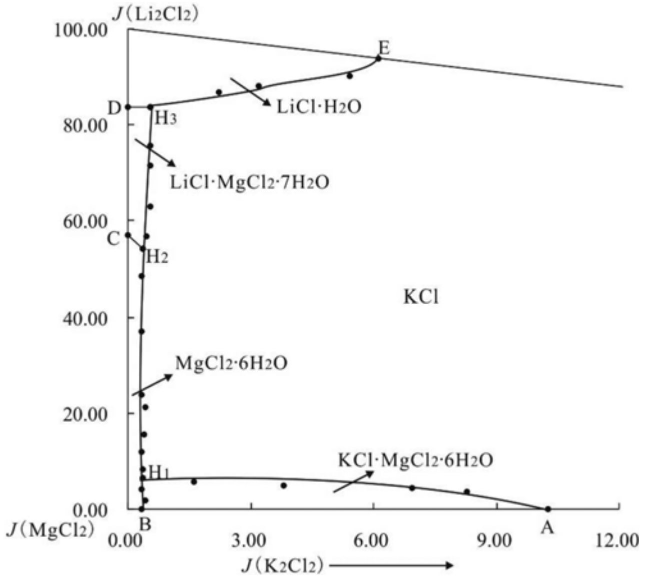

Fig. 3. Partial enlarged diagram of Fig. 2.

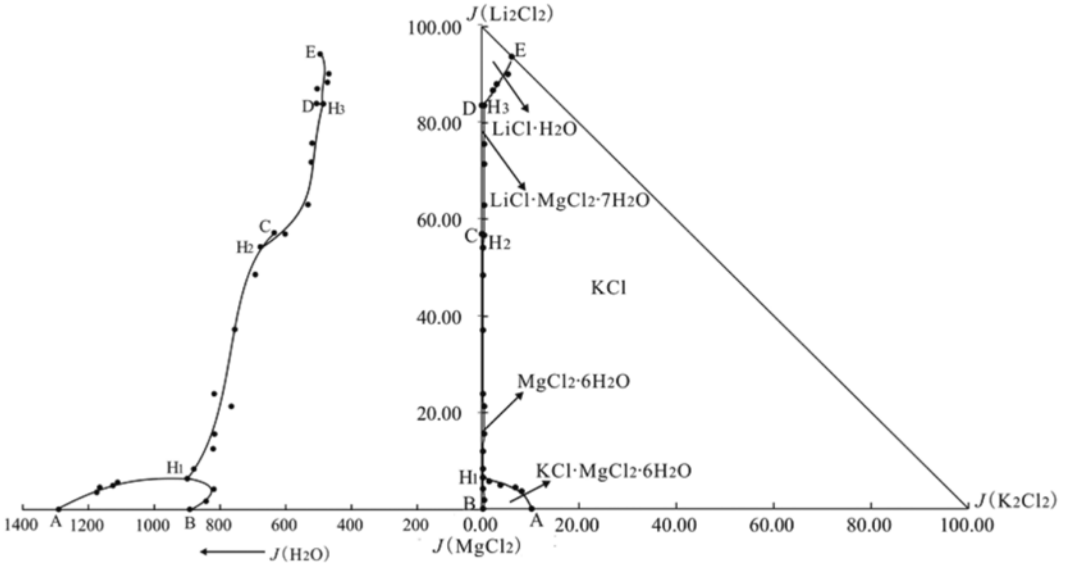

Fig. 4. Water-content diagram of the quaternary system LiCl+KCl+$MgCl_2$+H_2O at 323 K.

or H_3O^+ to form special carnallite $Li(H_2O)Cl·MgCl_2·6H_2O$ or $(H_3O)Cl·MgCl_2·6H_2O$, respectively. In these two special carnallites, one molecule water is bonding with a monovalent cation Li^+ or H^+ to form H_3O^+ or $Li(H_2O)^+$; therefore, the formulas of the lithium carnallite and hydrogen carnallite are $Li(H_2O)Cl·MgCl_2·6H_2O$ and $(H_3O)Cl·MgCl_2·6H_2O$, and can also be expressed as $LiCl·MgCl_2·7H_2O$ and $HCl·MgCl_2·7H_2O$.

In this quaternary system, besides single salts $MgCl_2·6H_2O$, KCl, $LiCl·H_2O$, two double salts $LiCl·MgCl_2·7H_2O$ and $KCl·MgCl_2·6H_2O$ are simultaneously formed at 323 K, which are consistent with previous research conclusions.

Point H_1 is cosaturated with three salts KCl+$KCl·MgCl_2·6H_2O$+$MgCl_2·6H_2O$, and an equilibrated solution. The composition of the corresponding equilibrated solution is w(LiCl)=2.10%, w(KCl)=0.22%, w($MgCl_2$)=34.64%, w(H_2O)=63.04%.

Point H_2 is cosaturated with three salts $MgCl_2·6H_2O$+KCl+$LiCl·MgCl_2·7H_2O$, and an equilibrated solution. The composition of the corresponding equilibrated solution is w(LiCl)=21.70%, w(KCl)=0.25%, w($MgCl_2$)=20.50%, w(H_2O)=57.55%.

Point H_3 is cosaturated with three salts KCl+$LiCl·H_2O$+$LiCl·MgCl_2·7H_2O$, and an equilibrated solution. The composition of corresponding equilibrated solution is w(LiCl)=40.70%, w(KCl)=0.48%, w($MgCl_2$)=8.66%, w(H_2O)=50.16%.

According to the experimental data in Table 2, the water content diagram is plotted in Fig. 4; the diagrams of the density and refractive index versus the composition of magnesium chloride in solu-

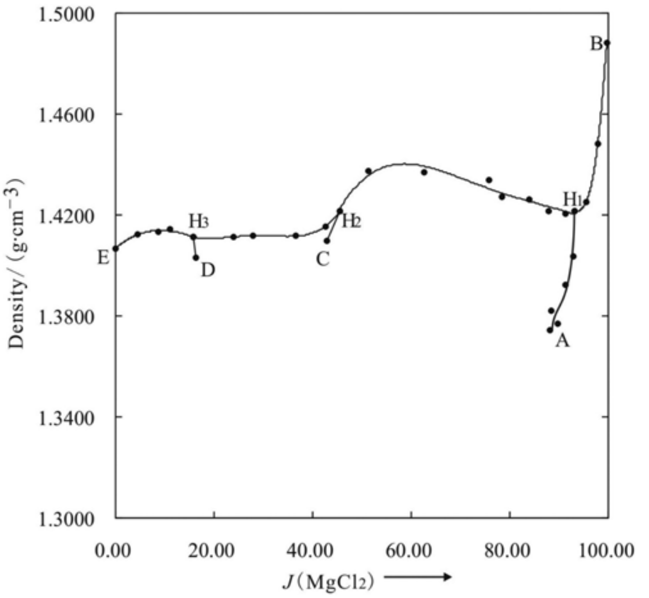

Fig. 5. Density vs. composition diagram for the quaternary system LiCl+KCl+$MgCl_2$+H_2O at 323 K.

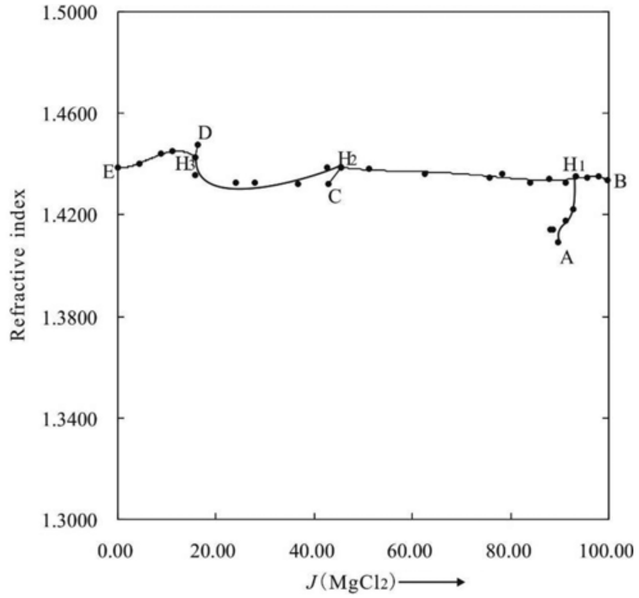

Fig. 6. Refractive index vs. composition diagram for the quaternary system LiCl+KCl+$MgCl_2$+H_2O at 323 K.

tion are in Fig. 5 and Fig. 6, respectively. Fig. 4 shows that the water content decreases with the increase of lithium chloride content at univariant curves AH_1, H_1H_2, and H_2H_3, while at univariant curves CH_2, DH_3, and EH_3, the water content slightly changes with the change of lithium chloride content. Fig. 5 shows that the densities sharply increase with the quick increasing of magnesium chloride at univariant curves AH_1, BH_1, and CH_2, while changing with the change of magnesium chloride at univariant curves EH_3 and H_2H_3. Fig. 6 shows that the refractive indices sharply increase with the rapid increasing of magnesium chloride at univariant curves AH_1 and CH_2, while slightly changing with the change of magnesium chloride at univariant curves EH_3, BH_1, and H_1H_2.

CONCLUSIONS

The metastable equilibrium data for the quaternary system $LiCl+KCl+MgCl_2+H_2O$ at 323 K were measured. The system is a complex type with two double salts $LiCl\cdot MgCl_2\cdot 7H_2O$ and $KCl\cdot MgCl_2\cdot 6H_2O$ formed at 323 K. The solid phase of the quaternary system is found as $LiCl\cdot H_2O$, KCl, $MgCl_2\cdot 6H_2O$, $LiCl\cdot MgCl_2\cdot 7H_2O$ and $KCl\cdot MgCl_2\cdot 6H_2O$, respectively. Salt KCl has the largest crystallization region; its crystallization area occupies almost 95% of the whole crystallization field, and the sequence of the crystallization fields size of slats is salt KCl>salt $LiCl\cdot H_2O$>salt $KCl\cdot MgCl_2\cdot 6H_2O$> salt $MgCl_2\cdot 6H_2O$>salt $LiCl\cdot MgCl_2\cdot 7H_2O$. The physicochemical property values sharply increase with the rapid increasing of magnesium chloride at univariant curves AH_1 and CH_2, while slightly changing with the change of magnesium chloride at univariant curves EH_3.

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