Experimental and prediction studies on the phase equilibrium of the quinary system of $Li^+,Na^+,K^+/ Cl^-, CO_3^{2-},-H_2O$ at 298K[1]

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The phase equilibria of the system $Li^+,Na^+,K^+/ Cl^-, CO_3^{2-},-H_2O$ at 298K were studied with the isothermal dissolution method. The physico-chemistry properties of corresponding equilibrium solutions such as density, viscosity, refractive index, conductivity and pH value were determined. The dried salt diagram of the system consists of five crystallization fields for $LiCl·H_2O$, KCl, Li_2CO_3, $NaKC03·6H_2O$ $Na2C03·7H_2O$, all saturated with sodium chloride and seven solubility isotherms. No solid solutions or trona minerals were found. Pitzer's theory of aqueous electrolyte solutions was used for fitting Pitzer parameters that not previously reported in literature. Using these parameters the solubilities for the quinary system were predicted. The calculated solubilities are in fair agreement with the experimental values.

1. INTRODUCTION

Zabuye Salt Lake, Tibet, China, is unrivalled in the world for its brine with high ion concentrations of lithium, potassium, berate, carbonate etc. These brine resources have not been developed in industrial since there are no reports about phase relations of the salt lake brines in the literature, though Chen [1] reported his results on isothermal evaporation study of the brine at 298K.

In order to promote the industrial development and utilization of the brine, as a part of the whole work to clarify genesis of ore-deposit of brines and salts and to design an effective process for the separation of the components contained in the brine, the phase equilibrium for the quinary system of $Li^+,Na^+,K^+/ Cl^-, CO_3^{2-},-H_2O$ are studied in the present work.

2. EXPERIMENTAL

2.1. Reagents

Analytically pure NaCl, KCl, $LiCl·H_2O$, Na_2CO_3, K_2CO_3, Li_2CO_3 and distilled water (conductivity less than 1.0 X 10' $s.cm^{-1}$, pH 6.6) were used.

2.2. Experimental method

The isothermal dissolution method was used. Twenty six samples of different compositions were prepared and transferred to closed plastic bottles, which were kept at a constant temperature 298±0.03K by means of a constant temperature air bath oscillator (Model HZQ-C). The samples were stirred at regular intervals (120 rpm) to accelerate equilibration. When the composition of the liquid phase of sample in the bottle was constant phase equilibrium was considered to be achieved. Generally, it took about 40 to 50 days to reach equilibrium. After thatperiod, the solubilities and the physico-chemistry properties of the corresponding equilibrium solution (density, viscosity, refractive index, conductivity and pH value) were determined at 298 ± 0.2K.

2.3. Assay determination

The liquid phase concentrations of Cl^- and CO_3^{2-} are determined by precipitation titration and acid-base titration, respectively. The liquid phase composition of K^+ is determined by indirect titration, i.e. the K^+ ion is quantitatively precipitated with sodium tetraphenylbron prior to titration analysis of the excess of the precipitant [2].The ionic concentrations of Li^+ is determined by Atomic Absorption Spectrometry (AAS). The remaining deficit of cations is assumed to be Na^+. The sodium concentration is at the same time verified by AAS determination.

The physicochemistry properties of the equilibrium solution such as density, viscosity, refractive index, conductivity and pH value are determined by weighing bottle method, Ubbelode viscometer, Abbe refractometer (Model WZS-1), conductivity detector (Model DDS-1 IA, measuring range 2 X 10-6_10

[1] Project supported by The National Natural Science Foundation of China to YIN (No.49773200) and The Key Discipline Growing Point of the National Land and Resources Ministry of China to YIN.

S.CMA), digital acido-meter(Model PH-3C,precision 1/100) respectively.

The equilibrium solid phases are determined by chemical analysis (with the Schreinemakers Wet Residue Method) combined with polarization microscopy and X-ray power diffraction.

3. RESULTS AND DISCUSSION

The physico-chemistry property data of the relevant equilibrium solution such as pH value, conductivity, viscosity, density, refractivity index and solubilities of the system mentioned above are shown in Table 1 and Table 2, respectively. Based on the Jänecke index Q,(J_B) in Table 2, i.e. J_B/[mol /100mol ($2Li^+ + 2K^+ + CO_3^{2-}$)], the solubility isothermal stereoscopic diagram and the dried salt phase diagram of the quinary are plotted in Fig.1 and Fig.2, respectively.

The phase diagrams in Figure 1 and Figure 2 consist of five crystallization phase regions, all saturated with sodium chloride, corresponding to potassium chloride, lithium carbonate, lithium chloride mono hydrate, sodium carbonate hepta hydrate and the double salt of sodium potassium carbonate hexahydrate ($NaKCO3{\cdot}6H_2O$). There are three invariant points, i.e. K, H, G and five invariant isotherms of solubility, i.e. AH, BH, HK, KG, GC, G1), KE. The crystallization area of lithium carbonate in the dried salt diagram is the largest one in the system. These results are very important for separating products like, for instance, lithium carbonate using the salt lake brine as a raw material. There are no solid solutions and trona minerals are formed in the quinary systems.

4.PREDICTION OF SOLUBILITIES

Pitzer's electrolyte solution model [3] is adopted to calculate the solubilities of the brine systems mentioned above. The single salt Pitzer parameters of Li_2CO_3 including β_{MX}^0, β_{MX}^1, C_{MX}^Φ (where MX represents the salt of Li_2CO_3) and the Pitzer's mixing parameters $\Psi_{Li,Cl,CO3}$, $\Psi_{Li,K,CO3}$ and $\Psi_{Li,Na,CO3}$ which are not reported in the literature are fitted using the reliable solubility data in relevant ternary systems [4,5]. The parameters are: $\beta_{MX}^0 = 0.389335$, $\beta_{MX}^1 = -2.72267$, $C_{MX}^\Phi = -0.162859$, $\Psi_{Li,Cl,CO3} = 0.135066$, $\Psi_{Li,K,CO3} = 0.135066$ and $\Psi_{Li,Na,CO3} = 0.202563$, respectively. The other Pitzer's parameters needed are taken from literature [6,7]. The activity products of salts are used as basis for the

Table 1: Determined results of the solution physicochemical properties of the quinary systems at 298 K

No.	pH value	Refractive index D25	Conductivity K./(s.m^{-1})	Viscosity [N_{25}/(Pa·s) x 10^{-3}	Density [d_{25}/(kg.m^{-3})] x 10^{-3}
1,H	5.83	1.4071	3.18	2.7720	1.2255
2	5.52	1.4100	2.70	3.2249	1.2260
3	5.47	1.4137	3.20	3.6454	1.2418
4	5.48	1.4111	2.70	3.5087	1.2413
5	9.92	1.3520	6.00	0.8829	1.0676
6	9.96	1.3859	6.05	1.0665	1.2450
7	10.39	1.3878	6.41	1.2244	1.2600
,K	11.16	1.3922	6.10	1.7847	1.2918
9	11.44	1.3918	5.68	2.8929	1.3293
10	10.75	1.3915	5.60	1.7163	1.2822
11	11.44	1.3970	5.40	2.8723	1.3295
12	11,77	1.3971	4.80	3.1272	1.3267
13	11.41	1.3960	5.10	2.9259	1.3304
14	11,42	1.3978	5.12	3.4062	1.5022
15	11.43	1.3938	5.08	2.0664	1.3031
16	11.83	1.3971	4.60	2.7446	1.3110
17	11.82	1.3973	4.30	2.8232	1.3279
18	11.84	1.3975	4.60	2.9472	1.3296
9,G	11.81	1.3969	4.36	2.8181	1.3285
20	10.70	1.3875	5.52	1.7543	1.2555
21	11.74	1.3969	4.10	3.2133	1.3240
22	11.59	1.3955	4.98	2.3295	1.3149
23	11.82	1.3979	4.98	2.9069	1.3352
24	11.82	1.3980	4.22	-2.9258	1.3421
25	11.85	1.3979	4.21	2.8548	1.3257
26	11.84	1.3974	4.40	2.8912	1.3305

dissociating equilibria and the solubilities of the quinary system at 298K are calculated by using the Harie-Weare Equations based on Pitzer Model [8] and the above Pizter parameters. The calculated results of the solubility are shown in Table 3 and the dash line in Figure 2. The calculated solubility data are basically in agreement with the experimental ones.

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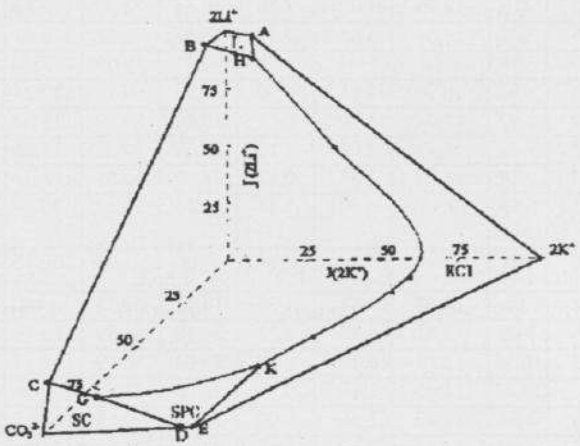
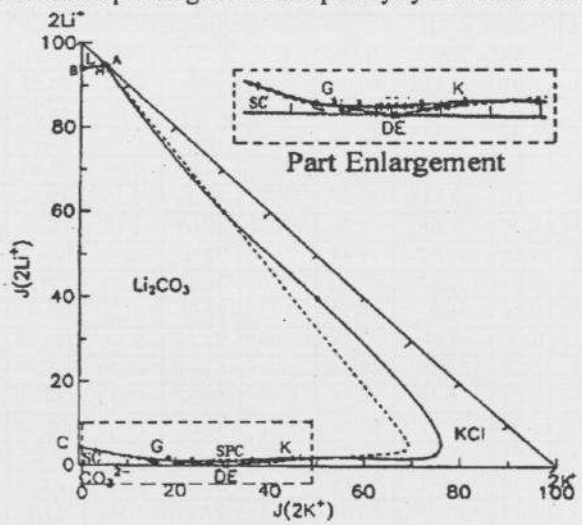


Figure 1. The stereoscopic-diagram of the quinary system saturated with NaCl at 298K



L—LiCl·H$_2$O; SC—Na$_2$CO$_3$·7H$_2$O; SPC—NaKCO$_3$·6H$_2$O

Figure 2. The dried-salt diagram of the quinary system saturated with NaCl at 298K

—— Experimental value; ---- Calculated value; L—LiCl·H$_2$O; SC—Na$_2$CO$_3$·7H$_2$O; SPC—NaKCO$_3$·6H$_2$O

Table 2: _Experimental solubility data of the quinary system at **298K**

No	Mass percent comp. of liquid phase, w_B10^2						Jänecke Index, J_B					Solid phase
	Li^+	K^+	Cl^-	CO_3^{2-}	Na^+	H_2O	$2Li^+$	$2K^+$	CO_3^{2-}	$2Na^+$	H_2O	
1,H	4.46	1,40	29.88	0.02	3.79	60.45	94.62	5.29	0.10	20.28	988.9	$NaCl+LiCl·H_2O+Li_2CO_3+KCl$
2	4.60	0.06	30.86	0,01	4.75	59.72	99.72	0.23	0.05	31.05	989.4	$NaCl+LiCl·H_2O+Li_2CO_3$
3	5.12	1,40	31.89	0.01	2.90-	58.68	95.32	4.64	0.04	16.30	842,4	
4	4.83	1.35	3177	0,02	3.82	58.21	95.18	4.73	0.09	22.73	884.5	
5	0.30	4.64	24.40	0.82	12.72	57.18	22.81	62.79	14.40	292.0	3349.3	$NaCl+Li_2CO_3+KCl$
6	0.074	6.36	20.53	1.85	10.73	60.45	4.53	69.30	26.16	198.42	3139.4	
7	0.035	5.62	16.45	2.94	9.49	65.47	2.04	58.35	39.61	167.09	2945.2	
8,K	0.032	4.99	14.01	5.25	10.05	65.66	1.50	41.64	56.86	142.33	2374.5	$NaCl+Li_2CO_3+KCl+NaKCO_3·6H_2O$
9	0.035	5.39	11.16	9.19	10.97	63.25	1,12	30.78	68.10	106.30	1556.0	$NaCl+Li_2CO_3+NaKCO_3·6H_2O$
10	0.040	4.75	11.41	10.04	12.15	61.61	1.25	26.38	72.31	114.45	1482.8	
11	0.04.	3.25	11.18	9.60	12.55	63.38	1,41	20.40	78.19	13.3.57	1723.8	
12	0.034	4.58	11.74	9.72	12.24	61.69	1.10	26.34	72.56	119.40	1537.6	
13	0.031	4.11	10.46	8.21	10.54	66.65	1.17	27.51	71.32	119.67	1933.3	
14	0.025	5.14	13.23	5.78	9.89	65.94	1.10	40.21	58.69	131324	2235.4	
15	0.00	4.81	11,55	8.02	10.79	64.83	0.00	31.16	68.39	120.27	1846.0	
16	0.018	4.89	11.90	8.97	11.64	62.58	0.61	29.40	69.99	118.69	1630.5	
17	0.034	4.75	11.68	9.22	11.72	62.60	1.13	28.09	70.78	117.55	1604.5	
18	0.026	4.81	11.82	9.14	11.74	62.47	0.87	28.60	70.53	118.37	1609.5	
19,G	0.033	5.55	13.81	5.06	9.45	66.10	1.51	15.11	53.38	130.24	2328.3	$NaCl+Li_2CO_3+NaKCO_3·6H_2O+Na_2CO_3·7H_2O$
20	0.043	0.23	13.10	5.21	12.20	69.21	3.34	3.18	93.48	286.18	4146.4	$NaCl+Li_2CO_3+NaKCO_3·6H_2O$
21	0.040	2.38	11.08	10.98	14.05	61.47	1.33	14.12	84.55	1414.41	1580.4	
22	0.015	1.68	12.55	7.46	12.81	65.49	0.74	14.68	84.59	189.79	2479.3	$NaCl+NaKCO_3·6H_2O+Na_2CO_3·7H_2O$
23	0.033	4.81	11.33	10.95	12.78	60.10	0.97	25.04	73.99	112.87	1355.9	
24	0.042	6.24	7.65	13.47	11.45	61.15	0.99	26.05	72.97	81.06	1106.0	
25	0.00	5.02	11.78	8.87	11.47	62.86	0.00	30.37	69.63	117.65	1647.8	
26	0.033	4.47	11.61	8.80	11.52	63.57	1.15	27.80	71.04	121.53	1713.5	$NaCl+KCl+NaKCO_3·6H_2O$

Table 3: Calculated solubility data of the quinary system at 298K

No	Mass percent comp. of liquid phase, w_B10^2						Jänecke Index, J_B					Solid phase
	Li^+	K^+	Cl^-	CO_3^{2-}	Na^+	H_2O	$2Li^+$	$2K^+$	CO_3^{2-}	$2Na^+$	H_2O	
1	4.43	1.28	30.12	0.01	4.11	60.05	95.06	4.89	0.05	26.62	993.7	$NaCl+LiCl·H_2O+KCl$
2	4.52	1.06	30.86	0.01	4.42	59.13	95.95	4.00	0.05	28.33	967.9	
3	5.01	1.40	31.09	0.01	2.75	59.74	95.22	4.73	0.04	15.76	875,6	
4	4.93	1.33	31.77	0.02	3.50	58.45	95.33	4.58	0.09	20.44	871.5	
5	1.02	5.73	13.72	0.50	2.52	76.51	47.33	47.31	5.36	35.34	2737.5	$NaCl+Li_2CO_3+KCl$
6	1.36	5.23	13.23	0.40	1.30	78.48	57.07	39.05	3.88	16.43	2539.6	
7	0.073	7.68	25.32	1.86	16.62	48.44	3.97	73.05	22.98	269.0	2002.3	
8	0.035	12.94	21.10	2.94	20,13	432.86	1.16	76.26	22.57	201,8	1097.4	
9	0.074	4.80	17.02	0.14	10.21	67.76	7.73	88.95	3.32	321.85	5457.5	
10	0.074	6,36	20.53	0.14.	9.45	63.48	5.99	91.44	2.57	230.56	3961.6	
11	0.033	11.90	18.10	5.07	23.99	40.91	1.00	63.71	35.30	218.47	951.6	
12	0.035	12.36	15.05	9.21	26.59	36.76	0.80	50.37	48.83	184.22	650.6	
13	0.033	5.55	13.81	5,07	9.46	66.08	1.51	45.02	53.47	130.49	2328.7	
14	4.60	0.06	30.86	0.01	4.75	59.72	99.72	0.23	0.05	31.05	99.4	$NaCl+LiCl·H_2O+Li_2CO_3$
15	0.02	5.34	10.16	9.19	10.41	64.88	0.65	30.73	68.63	101.56	1617.8	$NaCl+KCl+NaKCO_3·6H_2O$
16	0.031	4.11	10.46	8.23	10.56	66.61	1.15	27.72	71.43	119.79	1930.4	$NaCl+Li_2CO_3+NaKCO_3·6H_2O$
17	0.035	5.39	11.16	9.21	11.00	63.20	1.12	30.67	68.20	106.45	1481.0	
18	0.025	5.14	13.23	5.78	9.90	65.92	1.10	40.14	58.76	131.46	2236.4	
19	0.033	4.81	11.33	10.97	12,80	60.06	0.97	24.97	74.06	113.00	1354.6	$NaCl+NaKCO_3·6H_2O+Na_2CO_3·7H_2O$
20	0.042	6.24	7.65	13.50	11.48	61.09	0.98	25.96	73.06	81.21	1104. 1	
21	0.043	0.23	13.10	5.22	12.21	69.20	3.34	3.17	93.50	285.99	4140.8	$NaCl+Li_2CO_3+Na_2CO_3·7H_2O$
22	0.015	1.68	12.55	7.47	12.82	65.46	0.74	14.62	84.64	189.76	2475.4	
23	0.034	4.58	11.74	9.74	12.26	61.65	1.10	26.26	72.65	119.52	1535.3	
24	4.46	0.098	28.61	0.02	3.73	63.04	99.51	0. 39	0.10	25.12	1084.5	$NaCl+KCl+LiCl·H_2O+Li_2CO_3$
25	0.032	5.00	14.27	10.05	10.05	38.67	.99	27.63	71.63	93.61	920.1	$NaCl+Li_2CO_3+Na_2CO_3·7H_2O+NaKCO_3·6H_2O$
26	0.030	5.00	17.01	5.25	10.00	51.25	1.40	41.67	56.93	141.7	1855.5	$NaCl+KCl+LiCl·H_2O+Li_2CO_3$