Experimental and Predictive Phase Equilibrium of the Li^+, Na^+/Cl^-, $CO_3^{2-}-H_2O$ System at 298.15 K

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The solubility of the quaternary system of lithium, sodium, chloride, and carbonate and the densities, viscosities, refractive indexes, conductivities, and pH at 298.15 K have been studied. On the basis of the Jãneche index values, the isothermal phase diagram of the system was plotted. The phase diagram of the system includes three invariant points, seven univariant curves, and five crystallization zones corresponding to sodium chloride, lithium chloride monohydrate, lithium carbonate, sodium carbonate heptahydrate, and natron ($Na_2CO_3{\cdot}10H_2O$). No solid solution and double salts were found. On the basis of Pitzer's semiempirical theory for mixed electrolytes, the chemical equilibrium model of Harvie was used for fitting the single-salt pitzer parameters of lithium carbonate, $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ}, and two Pitzer's mixing triplet parameters, Ψ_{Li,Na,CO_3} and Ψ_{Li,Cl,CO_3}, in this system, which are not reported in the literature. The prediction of solubilities for the quaternary system was then demonstrated. The calculated solubilities agree well with the experimental values.

Introduction

Alkaline lakes are widely distributed in the area of Qinghai-Xizang Plateau and the Inner Mongolia Autonomous Region, China. Zabuye Salt Lake, located in Tibet, is one of the alkaline lakes famous for its high concentrations of sodium, lithium, potassium, and carbonate, as well as borate and sulfate.[1] When the metallic lithium storage capacities in the lakes around the world are compared, that of Zabuye Salt Lake is in third place, preceded by those of Atacama Lake in Chile and Pastos Grandes Lake in Bolivia.[2] Crystallized lithium carbonate mineral can be found in the salt sediments of the lake. Although these salt lake brine resources are very valuable, nothing has been reported on the multipurpose utilization, as the relevant phase relations are lacking, although Chen[3] mentioned his results on the isothermal evaporation study of the surface water at 298.15 K.

Because the solubilities of salts in a multicomponent saltwater system are generally a few molal, it is necessary to use a reliable theory for aqueous solution of electrolytes in calculating solubilities.[4] On the basis of the semiempirical equations of Pitzer,[5,6] Harvie and co-workers have developed a chemical equilibrium model capable of high ionic strength.[7,8] This model was successfully utilized in the major seawater ions of the $Na-K-Mg-Cl-SO_4-H_2O$ five-component system[6,8] and the ternary and quaternary subsystems of the $Na-K-Ca-Mg-H-Cl-SO_4-CO_2-B(OH)_4-H_2O$ in Searles Lake, California.[9] For the Li^+, Na^+/Cl^-, $CO_3^{2-}-H_2O$ system at 298.15 K, there is no report on the relative Pitzer parameters of the single salt lithium carbonate and the two mixing triplet parameters Ψ_{Li,Na,CO_3} and Ψ_{Li,Cl,CO_3}.

In this paper, the solubility and physicochemical property data of the quaternary system at 298.15 K were measured. On the basis of the subsystems of the quaternary,[10−13] the Pitzer single-salt parameters for lithium carbonate and the two mixing triplet parameters Ψ_{Li,Na,CO_3} and Ψ_{Li,Cl,CO_3} were fitted, and the calculated solubility of the quaternary system is presented.

Experimental Section

Apparatus and Reagents. A thermostatic shaker (Model HZQ-C) with a precision of 0.1 K was used for the experimental phase equilibrium. A SIEMENS D500 X-ray diffraction analyzer was used for the X-ray diffraction analysis of the solid phase.

The chemicals used were of analytical grade and obtained from either the Chengdu Chemical Reagent Manufactory or the Shanghai Chemical Plant: sodium chloride (NaCl, 99.5 mass %), lithium chloride ($LiCl{\cdot}H_2O$, 99 mass %), sodium carbonate (Na_2CO_3 99.8 mass %), and lithium carbonate (Li_2CO_3, 99.9 mass %). Double deionized water was used to prepare the series of saturated solutions.

Experimental Method. The isothermal dissolution method was used in this study. The series of complexes of the quaternary system were loaded in the cleaned polyethylene bottles and capped tightly. The bottles were placed in the thermostatic rotary shaker, whose temperature was controlled at (298.15 ± 0.1) K, and rotated at 120 rpm to accelerate the equilibrium of those complexes. A 5.0 mL sample of the clarified solution was taken from the liquid phase of each polyethylene bottle with a pipet at regular intervals and diluted to 50.0 mL final solution in a volumetric flask filled with double distilled water. If the compositions of the liquid phase in the bottle became constant, it indicated that the equilibrium was achieved. Generally, it took about 40 to 50 days to be at equilibrium.

After equilibrium was achieved, the rotary system was allowed to rest for 1 h to separate the solid phase from the liquid phase before sampling. The liquid phases were taken out, and a quantitative analysis was performed. The solid phases were filtered through a 0.22 μm membrane by vacuum filtration at (298.15 ± 0.1) K. The filtrate was used

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Table 1. Solubility Data of the Li^+, Na^+/Cl^-, $CO_3^{2-}-H_2O$ System at 298.15 K

	composition of liquid phase (mass %)					Jãneck index/[mol/100 mol dry-salt]					equilibrium
no.	Li^+	Na^+	Cl^-	CO_3^{2-}	H_2O	$2Li^+$	$2Na^+$	$2Cl^-$	CO_3^{2-}	H_2O	solid phase[a]
1	0.20	12.30	0.17	16.77	70.56	5.11	94.89	0.85	99.15	1390.5	$C_A + L_B$
2	0.16	12.38	0.86	16.12	70.48	4.11	95.89	4.32	95.68	1394.6	$C_A + L_B$
3	0.0062	12.14	3.24	13.13	71.49	0.17	99.83	17.28	82.72	1501.7	$C_A + L_B$
4, E	0.092	13.92	8.76	11.15	66.08	2.14	97.86	39.94	60.06	1186.6	$C_A + C_B + L_B$
5	0.044	13.52	8.42	10.71	67.31	1.07	98.93	39.96	60.04	1258.2	$C_A + C_B$
6, F	0.044	13.20	10.66	8.39	67.70	1.09	98.91	51.80	48.20	1295.9	$C_A + L_B + NaCl$
7	0.00048	12.60	8.74	9.05	69.61	0.01	99.99	44.98	55.02	1411.1	$C_B + NaCl$
8	0.09	10.60	15.56	1.05	72.70	2.74	97.26	92.59	7.41	1704.0	$L_B + NaCl$
9	0.098	10.30	15.88	0.43	73.30	3.06	96.94	96.93	3.07	1762.2	$L_B + NaCl$
10	0.16	10.26	16.00	0.54	73.04	4.91	95.09	96.16	3.84	1729.2	$L_B + NaCl$
11	1.91	9.40	23.20	0.89	64.60	40.23	59.77	95.66	4.34	1049.2	$L_B + NaCl$
12, G	7.88	0.084	37.90	2.10	52.03	99.68	0.32	93.84	6.16	507.5	$L_A + L_B + NaCl$
13	8.16	0.086	37.68	3.50	50.57	99.68	0.32	90.10	9.90	476.3	$L_A + L_B$
14	7.36	0.026	36.52	0.95	55.15	99.89	0.11	97.02	2.98	577.1	$L_A + L_B$
15	7.76	0.03	34.70	4.22	53.29	99.88	0.12	87.43	12.57	528.8	$L_A + L_B$
16	7.96	0.082	38.48	1.96	51.52	99.69	0.31	94.33	5.67	497.5	$NaCl + L_A$
17	8.16	0.082	39.60	1.87	50.28	99.70	0.30	94.70	5.30	473.7	$NaCl + L_A$
18, H[11]	6.82	0.00	30.24	3.89	59.05	100.0	0.00	86.79	13.21	667.5	$L_A + L_B$
19, A[12]	0.17	10.15	0.00	13.98	75.70	5.26	94.74	0.00	100.0	1805.0	$C_A + L_B$
20, B[10]	0.00	9.72	8.64	5.37	76.27	0.00	100.0	57.65	42.35	2004.3	$C_A + C_B$
21, C[10]	0.00	11.11	11.34	4.90	72.65	0.00	100.0	66.19	33.81	1670.4	$NaCl + C_B$
22, D[13]	6.56	0.079	33.64	0.00	59.73	99.64	0.36	100.0	0.00	699.4	$NaCl + L_A$

[a] L_A, $LiCl{\cdot}H_2O$; L_B, Li_2CO_3; C_A, $Na_2CO_3{\cdot}10H_2O$; C_B, $Na_2CO_3{\bullet}7H_2O$.

to measure the relative physicochemical properties individually. One part of the solid phases was qualitatively dissolved in water and analyzed by chemical methods. The other part was dried at (298.15 ± 0.1) K, pestled into powder, and then analyzed by X-ray diffraction.

Analytical Method. The liquid-phase concentrations of Na^+ and Li^+ were determined by atomic absorption spectrometry (precision ± 0.06 mass %, Medal WYD-YII). The Cl^- concentration was titrated with a standard solution of $AgNO_3$ in the presence of three drops of 0.1% (w/v) $KCrO_4$ as an indicator (precision: ±0.01 mass %). The CO_3^{2-} concentration was determined by neutralization titration with a precision of ±0.03 mass %.[14]

A PHS-3C precision pH meter supplied by the Shanghai Electromagnetic Instrumentation Manufactory was used to measure the pH of the equilibrium aqueous solutions. The pH meter was calibrated with standard buffer solutions of either mixing phosphate of potassium dihydrogen phosphate (pH = 6.863) or Borax (pH = 9.183), respectively; which one is used depends on the position of each complex with a precision of ±0.01. The densities (ρ) were measured with a specific weighing bottle method corrected for the floating force of air with a precision of ±0.2 mg. The viscosities (η) were determined using an Ubbelohde capillary viscometer. The viscometer was placed in a thermostat that electronically controlled the set temperature at (298.15 ± 0.1) K. No fewer than three flow times of each equilibrium liquid-phase solution were measured, and the results were averaged. The uncertainty of the flow time measurements was ±0.01 s. An Abbe refractometer (model WZS-1) was used for measuring the refractive index (n_D) with an accuracy of ±0.0001. The thermostat temperature was constant ± 0.1 K. Conductivities (Λ) were measured with a conductivity meter (DDS-11A) with an accuracy of ±0.01 $S{\cdot}m^{-1}$. Measurements were made in a water bath maintained at (298.15 ± 0.1) K.

Table 2. Physicochemical Property Data of the Li^+, Na^+/Cl^-, $CO_3^{2-} - H_2O$ System at 298.15 K

no.[a]	pH	n_D	$\Lambda/(S{\cdot}m^{-1})$	$\eta/(MPa{\cdot}s)$	$10^{-3}\rho/(kg{\cdot}m^{-3})$
1	9.97	1.3930	3.20	9.4495	1.3149
2	9.36	1.3939	2.79	8.8323	1.3142
3	9.11	1.3893	3.58	6.2198	1.2842
4, E	9.40	1.3965	3.78	7.0074	1.3136
5	9.16	1.3967	3.88	6.9310	1.3193
6, F	8.89	1.3922	3.79	4.7221	1.2850
7	9.34	1.3895	3.38	6.0213	1.2762
8	7.18	1.3801	4.45	2.0237	1.2214
9	7.16	1.3808	3.96	1.9575	1.2204
10	7.15	1.3799	3.82	1.9183	1.2040
11	7.17	1.3805	4.01	1.9133	1.2042
12, G	5.15	1.4320	2.00	13.8359	1.2842
13	5.21	1.4339	1.56	14.0697	1.2863
14	5.43	1.4241	2.23	10.1145	1.2583
15, H	5.47	1.4230	2.30	9.1814	1.2576
16	5.37	1.4340	1.98	15.4817	1.2962
17	5.40	1.4320	2.18	14.8030	1.2897
18	5.69	1.4097	2.45	5.1690	1.2092
19, H	ND[b]	ND	ND	ND	ND
20, A	ND	ND	ND	ND	ND
21, B	ND	ND	ND	ND	ND
22, C	ND	ND	ND	ND	ND

[a] The no. column corresponds to the no. column in Table 1. [b] ND, not detected at the ternary cosaturated points

Results and Discussion

The solubility data and the relevant physical chemical property data of the Li^+, Na^+/Cl^-, $CO_3^{2-}-H_2O$ system at 298.15 K were measured, and the results are shown in Tables 1 and 2, respectively. On the basis of the Jãneche index (J_B) in Table 1, the experimental solubility isothermal phase diagram of the system at 298.15 K was plotted, as shown in Figure 1.

The phase diagram of the system in Figure 1 includes three invariant points, that is, G, E, and F, and seven univariant curves corresponding to curves HG, GD, GF, FC, EF, BE, and AE, indicating cosaturation of two salts. There are five crystallization zones corresponding to sodium chloride (NaCl), lithium chloride monohydrate ($LiCl{\cdot}H_2O$), hydrous lithium carbonate (Li_2CO_3), sodium carbonate heptahydrate ($Na_2CO_3{\cdot}7H_2O$), and natron ($Na_2CO_3{\cdot}10H_2O$). The crystallization area of lithium carbonate is the largest, and the crystallized zones of lithium chloride monohydrate and sodium carbonate heptahydrate are smaller. These results indicate that lithium carbonate is easy to saturate and crystallize from the solution. There are no solid solutions or double salts formed in the system.

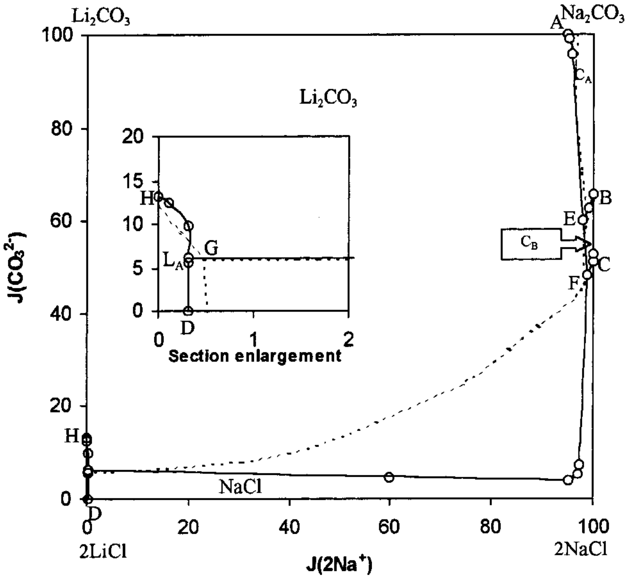

Figure 1. Dry-salt phase diagram of the Li^+, Na^+/Cl^-, $CO_3^{2-}-H_2O$ system at 298.15 K: J_B, Jãneche index, J_B/[mol/100 mol dry-salt]; ○, experimental value; —, experimental isotherm curve; - - -, predictive isotherm curve; L_A, $LiCl\cdot H_2O$ crystallization zone; C_A, $Na_2CO_3\cdot 10H_2O$ crystallization zone; C_B, $Na_2CO_3\cdot 7H_2O$ crystallization zone.

The physicochemical properties of the equilibrium solution changed regularly with the changing lithium concentration in the system. Table 2 indicates that the viscosities and refractive indexes of the equilibrium aqueous solutions gradually increase with the increase of lithium concentration, whereas the pH, conductivities, and densities of the equilibrium aqueous solutions have the opposite behavior.

Prediction of Solubilities

Ion-Interaction Model. Pitzer[5,6] has published a series of papers and given a set of expressions for the osmotic coefficient of the solution and the mean activity coefficient of electrolytes in the solution. But the expressions of the chemical equilibrium model for conventional single ion activity coefficients derived by Harvie[8] were used to calculate the solubilities of the Li^+, Na^+/ Cl^-, $CO_3^{2-}-H_2O$ system. A complete discussion of these equations can be found in the appendixes of refs 8 and 9. Using the activity coefficients and the solubility products of the equilibrium solid phases identified the coexisting solid phase and their compositions at equilibrium. The necessary model parameters for the activity coefficients of electrolytes in the system were fitted from its ternary subsystems by a multiple linear regression method.

Model Parametrization. The single-salt parameters of lithium carbonate ($\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ}) and the mixing triplet parameters Ψ_{Li,Na,CO_3} and Ψ_{Li,Cl,CO_3}, all of which are not reported in the literature, are fitted using the reliable solubility data in the relative ternary subsystem.[10−13] The Pitzer single-salt parameters, Pitzer mixing ion-interaction parameters, and $\mu°/RT$ values of the species in the quaternary system at 298.15 K used in this study are presented in Tables 3 and 4. The standard deviation of the fit (SD) and the multiple correction coefficient (R) for the best values of these fitting ion-interaction parameters for the single electrolyte lithium carbonate, which are a measure of the closeness of the fit to a linear relationship, are 0.0411 and 0.9971, respectively, when the maximum molality of lithium carbonate dissolved in this study was 0.183 mol/kg of solvent. The $\mu°/RT$ value of lithium carbonate presented in Table 4 was calculated for the first time and combined the fitted single-salt parameters of lithium carbonate and the solubility of the binary system of lithium carbonate in water.

Table 3. Pitzer Ion-Interaction Parameters for the Quaternary System at 298.15 K

Single-Salt Parameters

cation	anion	$\beta_{MX}^{(0)}$	$\beta_{MX}^{(1)}$	C_{MX}^{ϕ}	ref
Li^+	Cl^-	0.20972	−0.34380	0.00433	15
Na^+	Cl^-	0.07722	0.25183	0.00106	15
Na^+	CO_3^{2-}	0.0399	1.389	0.0044	8
Li^+	CO_3^{2-}	−0.389335	−2.27267	−0.162859	this work[a]

Mixing Ion-Interaction Parameters

parameter	θ_{Cl,CO_3}	$\theta_{Li,Na}$	Ψ_{Na,Cl,CO_3}	$\Psi_{Li,Na,Cl}$	Ψ_{Li,Na,CO_3}	Ψ_{Li,Cl,CO_3}
value	−0.02	0.012	0.0085	0.1	0.202 563	0.135 066
ref	8	16	8	17	this work	this work

[a] The adjustable parameters are $\alpha_1 = 2.00$, $\alpha_2 = 0$, and $b = 1.20$.

Table 4. $\mu°/RT$ Values of the Species in the Quaternary System at 298.15 K

species	$\mu°/RT$	ref	wpecies	$\mu°/RT$	ref
H_2O	−95.6635	8	$LiCl\cdot H_2O$	−254.5962	4
Li^+	−118.0439	4	NaCl	−154.99	8
Na^+	105.651	8	$Na_2CO_3\cdot 7H_2O$	−1382.78	8
Cl^-	−52.955	8	$Na_2CO_3\cdot 10H_2O$	−1094.95	8
CO_3^{2-}	−212.944	8	Li_2CO_3	−458.06	this work

Calculated Solubilities. Using the chemical equilibrium model and the above parameters, the calculated results of the solubility are shown in Figure 1 with dashed lines. It is shown that the calculated and the determined values are in good agreement. This means that the parameters fitted in this work are reliable. Especially when either lithium ion or carbonate is the dominant component in the system, the predictive values using the chemical equilibrium model significantly coincided with experimental values. However, when the liquid composition is located in the univariant curve of lithium carbonate and sodium chloride, the discrepancy between the predictive values and the experimental measurements is relatively large, as shown in Figure 1 with the dashed line. The possible reason is that the fitted ion-interaction parameters for a single electrolyte of lithium carbonate were evaluated from the solubility data of the relative subsystems because of lacking osmotic coefficient data. Further work on the osmotic coefficient data should be carried out in order to improve the calculated accuracy of the solubility.

Conclusions

The experimental solubility data and the relevant physicochemical property data of the Li^+, Na^+/Cl^-, $CO_3^{2-}-H_2O$ system at 298.15 K were determined. According to the solubility data measured, the isothermal phase diagram was constructed. The single-salt Pitzer's parameter of lithium carbonate and the mixing ion-interaction parameters Ψ_{Li,Na,CO_3} and Ψ_{Li,Cl,CO_3} were fitted. The maximum molality of lithium carbonate fitted in this study was 0.183 mol/kg of solvent. The calculated solubilities agree well with the experimental values.

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