A Study on the Phase Equilibrium and Solution Properties of the Quinary System Li^+, Na^+, K^+ // CO_3^{2-}, $B_4O_7^{2-}$ - H_2O at 298K

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The phase equilibria of the quinary system Li^+, Na^+, K^+ // CO_3^{2-}, $B_4O_7^{2-}$ - H_2O corresponding to the composition of the brine in Zabuye saline lake,Ti'bet,China, were studied at 298K using the isothermal method. The solubility and the physicochemical properties (density,viscosity,refractive index,conductivity and pH value) of the equilibrium solutions were determined at 298K.The isothermal solubility diagram of the quinary system consists of thirteen univariant curves, four invariant points, and seven crystallization regions including one that belongs to the new double salt $Na_2CO_3 \cdot K_2CO_3 \cdot H_2O$.

The Pitzer theory was used for theoretically describing relations of the highly concentration multicomponent systems in the study. Using solubility data of ternary sub-systems, the single salt parameters of Li_2CO_3, Na_2CO_3, K_2CO_3, $Li_2B_4O_7$and $K_2B_4O_7$, the solubility product of each solid phase being in equilibrium with the related solution, and the corresponding ion-interaction parameters θ_{ij} and ψ_{ijk} were fitted with the multiple linear regression method. Using the Fitted parameters the solubilities in the quinary system were predicted. The results indicate that the calculated solubilities are in agreement with the experimental data.

1. INTRODUCTION

The brine of ZabuYe saline take,Tibet, P.R.China, belong to the carbonate-type alkaline brine system. The main components are Li^+, Na^+, K^+, CO_3^{2-}, $B_4O_7^{2-}$, HCO_3^-,Cl^- and SO_4^{2-} [1]. The concentrations of lithium, potassium and boron in the brine are so high and the proven reserves of these are so great that the lake is unique in the world. Unfortunately.no study on the phase equilibria corresponding to the composition of the brine of the lake have been reported in literature except for an isothermal evaporation experminet performed by Chengl [2]. Therefore the phase equilibrium of the quinary system Li^+, Na^+, K^+ // CO_3^{2-}, $B_4O_7^{2-}$ - H_2O and the physicochemical properties of the equilibrium solutions were determined at 298K in the present work. Also a study on the prediction of the solubilities of all salts in the quinary system was carried out.

2. EXPERIMENT

2.1. Reagent

De-ionized water: pH ≈ 6.6,with conductivity less than $1.5 \cdot 10^{-4}$ S/m The used reagents Li_2CO_3, Na_2CO_3, K_2CO_3, $Li_2B_4O_7$, $Na_2B_4O_7 \cdot 10H_2O$ and $K_2B_4O_7$ were analytically pure. Special care has been taken to calcine sodium carbonate and potassium carbonate at 470 K in order to remove sodium bicarbonate and potassium bicarbonate before use.

2.2. Experimental method

The isothermal method was used in this study. The experimental solutions were prepared by adding the other salt in different quantities to one of the invariant quaternary sub-systems The complexes were kept sealed hard plastic bottles. The plastic bottles were put into a temperature controlled agitator and kept at 298±0.1 K. The samples of the solution were analysed at regular intervals. When the composition of liquid phase did not change anymore, the system was assumed to be at equilibrium. The equilibrated solid-phases were identified by X-Ray diffraction and micropolariscope.

2.3. Analytical methods

The analytical methods are described in [3].

CO_3^{2-}: acid-base titration

$B_4O_7^{2-}$: basic titration with mannitol existing

K^+: sodium tetraphenylborate-hexadecyl trimethyl ammonium bromide titration

Li^+: atomic absorption spectrophotometry

Na^+: equivalent minus according to ion balance

Table 1: Compositions of equilibrium saturated solutions in the quinary system Li^+, Na^+, K^+ // CO_3^{2-}, $B_4O_7^{2-}$ - H_2O at 298K

No.	composition of solution (mass fraction W_B)x 10^2						$n(K_2^{2+})+n(Na_2^{2+})+n(B_4O_7^{2-})$=100mol					Equilibrium solid-phase*
	Li^+	Na^+	K^+	CO_3^{2}	$B_4O_7^{2}$	H_2O	$n(K_2^{2+})$	$n(Na_2^{2+})+$	$n(B_4O_7^{2-})$	$N(Li_2^{2+})$	$n(H_2O)$	
1	0.109	9.560	0,650	12.66	2.040	74.98	3.610	90.67	5.720	3.530	1858	NaB + NaC + LiC
2	0.183	6.350	2.870	10.34	2.400	77.86	19.29	72.58	8.130	6.830	2274	
3	0.201	5.580	4.140	10.26	2.750	77.07	27.57	63.21	9.220	7.500	2269	NaB+NaC+LiC+KB
4	0.073	0.000	32.41	24.57	1.600	41.35	97.57	0.000	2.430	1.240	540,8	KC + KB + LiC
5	0.074	1.080	28.11	22,60	1.790	46.34	92.73	6.060	2.980	1.370	664.3	
6	0.077	1.680	27.25	22,73	1.820	46.44	87.84	9.210	2.950	1.410,	650.4	
7	0.074	1.720	25.62	21.53	1.800	49.26	86.99	9.930	3.080	1.420	726.6	KC+KB+LiC+NaK
8	0.068	2.600	27.96	25.01	0.320	43.41	85.92	13.59	0.490	0.530	579.6	LiC + KC + NaK
9	0.078	2.120	27.45	23.54	1.630	45.18	86.12	11.31	2.570	1.390	615.7	
10	0.082	3.040	26.50	24.62	0.000	45.76	83.68	16.32	0.000	1.340	627.9	LiC + NaC + NaK
11	0.120	4.010	18.74	19.74	1.020	56.37	71.87	26.15	1.980	2.590	939.0	
12	0.110	3.730	17.28	17.84	2.000	59.04	70.16	25.75	4.090	2.520	1041	LiC+KB+NaC
13	0.170	4.580	12.27	15.46	1.740	65.78	58.61	37.21	4.180	4.510	1365	LiC+KB+NaC
14	0.183	4.970	7.930	12.65	1.810	72.46	45.86	48.87	5.270	5.860	1820	
15	0.070	1.910	2530	21.54	1.730	49.45	86.00	11.03	2.970	1.340	730.3	LiC+KB+NaK
16	0.091	3.150	20.83	19.75	1.910	54.27	76.72	19.74	3.540	1.880	868.4	
17	0.184	0.000	29.18	22.59	1.550	46.50	97.34	0.000	2.6 10	3.460	674.2	LiB+LiC+KB
Is	0.134	1.270	10.11	7.870	5.480	75.14	67.25	14.37	18.38	5.030	2172	
19	0,225	1.780	4.120	3.730	7.080	83.06	38.49	29.14	33.27	11.84	3366	NaB+LiB+LiC+KB
20	0.322	1.650	2.710	2.930	6.960	85.43	30.03	31.11	38,86	20.11	4114	NaB+LiB+LiC
21	0.374	1.140	0.250	1.550	4.520	92.17	5.570	43.43	51.00	47.25	8969	
22	0.206	2.150	4.340	4.590	6-300	82.41	38,87	32.72	28.41	10.39	3204	NaB+KB+LiC
23	0.193	3.720	4.440	7.340	4.550	79.96	34.01	48.43	17.56	8.320	2652	
24	0.224	1.730	4.120	3.560	7.370	83.00						NaB+KB+LiB
25	0.217	1.430	4.070	1.380	10.16	82.74						
26	0.077	1.630	25.97	21.55	1.780	48.99						
27	0.031	1.600	26.06	21.59	1.730	48.99						KC+NaK+KB
28	0.091	3.850	18.77	19.77	1.950	55.57						NaC + NaK + KB
29	0-197	5.930	4.360	11.31)	2.770	75.44						NaC+KB+NaB
30	0.177	6.860	5.130	13.21	3.130	71.49						
31	0.085	8.240	6.000	15.07	3.500	67.10						

W^B-the rnass fraction of B
+ n(B)-the amount of the substance B
* NaC- $Na_2CO_3 \cdot 10\ H_2O$, LiC - Li_2CO_3, KC - K_2CO_3 3/2 H_2O, NaB - $Na_2B_4O_7 \cdot 10H_2O$, LiB - $Li_2B_4O_7 \cdot 3H_2O$, KB - $K_2B_4O_7 \cdot 3H_2O$

2.4. The methods for the determination of physicochemical properties.

Density. specific gravity bottle method with correction for the floating force of air;

Viscocity: determined by capillary viscosimeter

Refractive index: determined with WS-1 Abei refractometer

Conductivity: determined with DDS-11A conductometer

pH value: determined with PHS-3C digital pH meter

3. RESULTS AND DISCUSSION

3.1. Experimental

The determined solubility data of equilibrium solutions of the quinary system Li^+, Na^+, K^+ // CO_3^{2-}, $B_4O_7^{2-}$ - H_2O at 298K are listed in Table 1, 1, and the physicochemical properties of the corresponding equilibrium solutions are listed In Table 2. Figure 1 is the stereo-diagram and Figure 2 is the projected-diagram for the quinary systeem saturated with Li_2CO_3. The isothermal solubility diagrams (Fig.1 and Fig.2) of the quinary system consist of thirteen univariant curves, four invariant points, and seven crystallization regions corresponding to lithium carbonate (Li_2CO_3),

Lithium borate trihydrate ($Li_2B_4O_7 \cdot 3H_2O$), potassium borate tetrahydrate ($K_2B_4O_7 \cdot 4H_2O$), borax ($Na_2B_4O_7 \cdot 10H_2O$),Potashite ($K_2CO_3 \cdot 3/2\ H_2O$), natron ($Na_2CO_3 \cdot 10H_2O$), and the new double salt $Na_2CO_3 \cdot K_2CO_3 \cdot H_2O$, respectivelY. A double salt like this has only been found in Teeple's studies on Searles lake [4], where anhydrous type $Na_2CO_3 \cdot K_2CO_3$ was found at 35 ^{0}C and above. The crystallization regions of trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) and sodium carbonate heptahydrate ($Na_2CO_3 \cdot 7H_2O$) were not found in the present work.

In the phase diagram of the quinary system, the crystallization fields of lithium carbonate and lithium, sodium and potassum borate minerals are larger, but the crystallization fields of potashite, natron, and the double salt $Na_2CO_3 \cdot K_2CO_3 \cdot H_2O$ are smaller. This feature is very important for the extraction of lithium and borate from the salt lake brine.

For the system mentioned above, it is found that physicochernical properties of the equilibrium solutions saturated with the double salt $Na_2CO_3 \cdot K_2CO_3 \cdot H_2O$ show abnormal changes with the solution composition.

3.2. Prediction of solubilities

3.2.1. Theory for calculations

In this study, we used the chemical model of Harvie et. al [5],which is based upon the semiempirical equation of Pitzer and Magorga [6], to calculate the solubility of the quinary system Li^+, Na^+, K^+ // CO_3^{2-}, $B_4O_7^{2-}$ - H_2O. The coexisting phases and their composition at equilibrium were identified by using the activity coefficient and the solubility product of equilibrium solid-phase. The necessary model parameters for the activity coefficient expressions were fitted from binary and ternary sub-systems utilising solubility data by multiple linear regression method.

3.2.2. Model parameters

The molecular formula of the equilibrium solid-phases which were adapted in the work are Li_2CO_3, K2CO3·3/2 H_2O, $Na_2[B_4O_5(OH)] \cdot 8H_2O$, $Li_2[B_4O_5(OH)_4] \cdot H_2O$, $K_2[B_4O_5(OH)_4] \cdot 2H_2O$ and $Na_2CO_3 \cdot 10H_2O$..The calculated parameters are given in Table 3 and 4.

Among these parameters, the single salt parameter of lithium carbonate, all the mixing parameters θ_{ij} and ψ_{ijk} of the systems and the solubility product of the equilibrium solid-phase were fitted for the first time.The single salt parameter values of lithium,sodium and potassium borate minerals and that of potashite and natron which were fitted in this study are very different from the ones in the literature [7,8].

Table 2: Physicochemicat property-composition values of equilibrium solutions in the quinary system at 298K

No	d* 10^{-3} (kg/m^3)	η (Pa.s)	K/(S/M)	D_{298}	pH
1	1.3244	1.3917	8.789	2.765	10.87
2.	1.5030	1.4144	14.22	4.229	11.46
3	1.5612	1.4189	15.17	6.070	12.73
4	1.5302	1.4199	15.84	6.052	13-04
5	1.5467	1.4207	16.68	4.726	12.11
6	1.5606	1.4211	18.99	3.372	13.97
7	1,5615	1.4216	21.85	3.230	13-99
8	1.5497	1.4210	15.93	3.819	13.99
9	1.5532	1.4211	17.35	4.791	14.10
10	1.5329	1.4203	16.91	5.140	14.21
11	1.5402	1.4190	14.85	6.051	13.89
12	1.5443	1.4177	13.99	6.260	13.85
13	1.5499	1.4181	14.19	6.175	13.14
14	1.5556	1.4196	14.85	6.110	12.89
15	1.5596	1.4211	18.47	3.781	13.%
16	1.5461	1.4193	14.70	5.924	13.89
17	1.5302	1.4173	10.25	6.251	12.84
19	1.4393	1.3981	6.229	5.228	11.18
19	1.2346	1.370	3,340	4.418	9.95
20	1.2239	1.3746	2.937	3.919	9.87
21	1.1059	1.3482	1.606	1.275	9.70
22	1.2817	1.3798	4.693	4.7265	10.63
23	1.4893	1.4096	11.29	5.824	11.79
24	1.2331	1.3759	3.066	4.228	9.43
25	1.1800	1.3654	2.469	3.249	8.55
26	1.5602	1.4216	18.37	3.306	13.93
27	1.5583	1.4218	17.30	4.028	13.25
28	1.5573	1.4213	15.11	5.5869	13.30
29	1.5093	1.4180	12.73	5.%6	12.70
30	1.4371	1,4102	8,192	5.871	12.21
31	1.1900	1.3698	2.929	5.337	10.78

Note: (1) Numbers in Table 2 and in Table I correspond with each other

(2) d-density, η -viscosity, K-conductivity, D -refractive index

3.2.3. Calculated solubilities

Using the parameters above, we have made the prediction of the solubilities of the quinary system at 298K.The calculated values are shown in Table 5

Table 3: Pitzer single salt parameters and solubility products

Salt	InK	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Source
Li_2CO_3	-8.963	-1.236	-2.655	-0.004661	this study
Na_2CO_3, $10H_2O$	3.065	-0.2930	2.156	-0.0(9256	this study
$K_2CO_3 \cdot 3/2\ H_2O$	14.30	0.5077	-0.8203	-0.02081	this study
$Li_2B_4O_7 \cdot 3H_2O$	-7.357	-3.031	-3.024	-0.2909	this study
$Na_2B_4O_7 \cdot 10H_2O$	-7.478	-0.1100	-0.4000	0.00	[7]
$K_2B_4O_7 \cdot 4H_2O$	-5.769	-0.1129	0.3370	-0.1030	this study
$Na_2CO_3 \cdot K_2CO_3 \cdot H_2O$	21.10				this Study

Table 4 Pitzer mixing ion-interaction parameters

Parameter	$\theta_{Li,Na}$	$\theta_{Na,K}$	$\theta_{Li,K}$	$\theta_{B,C}$	$\psi_{Li,Na,C}$	$\psi_{Li,K,C}$	$\psi_{Na,K,C}$
Value	1.042	0.03510	0.6287	-2.630	-0.06391	-0.02789	0.003000
Parameter	$\psi_{Li,Na,B}$	$\psi_{Li,K,B}$	$\psi_{Na,K,B}$	$\psi_{Li,C,B}$	$\psi_{Na,C,B}$	$\psi_{K,C,B}$	
Value	0.4936	0.3232	0.05381	-0.4784	0.3062	0.6075	

Note: C-CO_3^{2-}, B- $[B_4O_5(OH)_4]^{2-}$

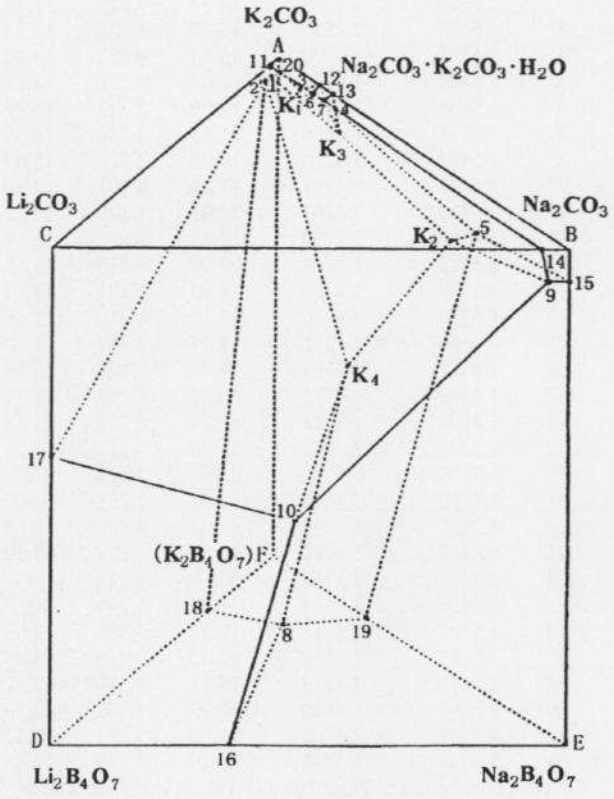

Fig.1 Stereo-diagram of the quinary system at 298K

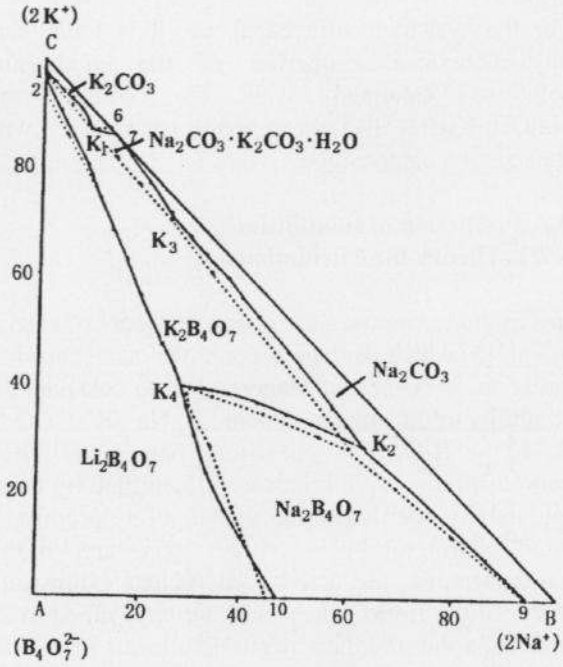

Fig.2 Projected-diagram of the quinary system at 298K(saturated with Li_2CO_3)
Solid lines—experimental
Dotted lines—calculated

Table 5: Calculated values of solubility of the quinary system at 298 K

No.	Comp. of solution(mass fraction) W(Li)	W(Na)	W(K)	$W(CO_3)$	$W(B_4O_7)$	$n(K_2^{2+})+n(Na_2^{2+})+n(B_4O_7^{2-})=100mol$ $n(Na_2^{2+})$	$n(K_2^{2+})$	$n(B_4O_7^{2-})$	Equilibrium Solid-phase
1	0.112	10.96	0.000	13.97	2.170	94.46	0.000	5.540	NaB+NaC+LiC
2	0.157	7.850	1.930	11.48	2.390	80.99	11.71	7.300	NaB+NaC+LiC
3	0.197	6.630	3.380	10.97	2.930	69.88	20.95	9.170	NaB+NaC+LiC
4	0.211	5.030	4.210	9.610	2.830	60.28	29.67	9.500	NaB+NaC+LiC+KB
5	0.069	0.000	33.11	24.90	2.080	0.000	96.93	3.07	KC+KB+LiC
6	0.073	0.980	29.75	23.69	1.900	5.150	91.90	2.950	KC+KB+LiC
7	0.077	1.590	27.77	23.01	1.830	8.610	88.45	2.940	KC+KB+LiC
8	0.079	1.750	24.96	21.09	1.790	10.32	86.55	3.130.	KC+KB+LiC+NaK
9	0.077	2.120	25.75	22.25	1.580	11.96	85.40	2.640	LiC+KC+NaK
10	0.075	2.390	26.49	23.41	0.930	13.10	85.39	1.510	LiC+KC+NaK
11	0.069	2.580	27.51	24.78	0.000	13.76	86.24	0.00	LiC+KC+NaK
12	0.083	2.950	26.14	24.27	0.000	16.10	83.90	0.000	LiC+NaK+NaC+KB
13	0.092	3.080	25.45	23.82	0.320	16.98	82.50	0.520	LiC+NaK+NaC
14	0.109	3.160	23.73	22.44	0.950	18.17	80.22	1.610	LiC+NaK+NaC
15	0.111	3.730	20.85	20.68	1.730	22.60	74.29	3.110	LiC+NaK+NaC
16	0.113	3.890	17.95	18.52	2.110	25.81	70.04	4.150	LiC+NaK+NaC+KB
17	0.135	4.030	12.37	14.51	2.140	33.76	60.93	5.310	KB+LiC+NaC
18	0.178	4.610	9.380	13.07	2.370	42.58	50.94	6.480	KB+LiC+NaC
19	0.191	4.720	7.950	12.09	2.590	46.45	46.00	7.550	KB+LiC+NaC
20	0.200	4.970	5.630	10.61	2.750	54.65	36.40	8.950	KB+LiC+NaC
21	0.083	1.890	23.79	20.31	2.000	11.47	84.93	3.600	LiC+KB+NaK
22	0.094	2.770	21.36	19.68	1.910	17.43	79.01	3.560	LiC+KB+NaK
23	0.107	3.730	20.75	'20.55	1.830	22.64	74.07	3.290	LiC+KB+NaK
24	0.193	0.000	29.03	21.78	3.440	0.000	94.37	5.630	LiB+LiC+KB
25	0.198	0.730	22.51	17.36	4.460	4.780	86.58	8.640	LiB+LiC+KB
26	0.214	1.270	13.98	11.12	5.660	11.37	73.61	15.02	LiB+LiC+KB
27	0.229	1.460	9.450	7.760	6.170	16.51	62.83	20.56.	LiB+LiC+KB
28	0.237	1.790	4.050	3.790	6.920	28.77	38.28	32.95	LiB+LiC+KB+NaB
29	0.295	1.630	2.160	2.870	5.670	35.59	27.73	36.68	NaB+LiB+LiC
30	0.314	1.420	1.830	2.220	5.580	38.24	17.14	44.62	NaB+LiB+LiC
31	0.339	1.140	0.350	1.470	4.520	42.46	7.670	49.87	NaB+LiB+LiC
32	0.385	1.030	0.000	1.410	4.140	45.68	0.000	54.32	NaB+LiB+LiC
33	0.231	2.150	4.070	4.640	5.910	34.16	38.02	27.82	NaB+KB+LiC
34	0.229	3.070	4.130	6.190	5.120	43.76	34.62	21.62	NaB+KiB+LiC
35	0.220	4.310	4.150	8.220	3.990	54.33	30.76	14.91	NaB+KB+LiC
36	0.215	4.850	4.190	9.480	2.570	60.06	30.51	9.430	NaB+KB+LiC

and also in Figure 2 (the dotted lines).The quantity symbols are the same as those in Table 1. It can be seen in Fig.2 that the calculated and the determined values are in good agreement, which means that the parameters obtained in this work are reliable.

3.3. Discussion

Usually, the aqueous carbonate system has (lie following equilibrium:

$$CO_3^{2-}(aq,)+ H_2O(1.) = HCO_3^-(aq.) +OH^-(aq.) \quad (1)$$

However.this quinary system is a strongly basic, so the crystallization area for bicarbonate isnon existent in our study. When we added carbonate to the invariant complex $Li_2B_4O_7{\cdot}3H_2O$ + $Na_2B_4O_7{\cdot}10H_2O$ + $K_2B_4O_7{\cdot}4H_2O$ plus the eqilibrium solution (that is on F→K, solubility curve of Fig. 1), it was found that the equilibrium liquid phase contained HCO_3^- and the amount of HCO_3^-, decreased gradually with the increase of the PH value of the solution. When the pH value of the solution is higherr than 9, HCO_3^- was transformed into CO_3^{2-} entirely. The trona salt was not found in the equilibrium solid-phase with X-Ray diffraction and micropolariscope. So it can be concluded that the emergence of HCO_3^- in the equilibrium solution is just a reflection of acid base equilibrium based on the formula (l). This character is very useful for justifying the neglection of the electrostatic effects of asymmetric mixing between CO_3^{2-} and HCO_3^- in the solubility prediction reasonable.

The behaviour of the dissolved borate in aqueous solution is very complex. Borate can exist as various forms in the solution, depending on hH value, concentration of the salts, and solvent characteristics. The main forms of borate are polyborate species, such as $B_3O_3(OH)_4^-$ and $B_4O_5(OH)_4^{2-}$ in the system with high borate concentration and a high pH value [9,10].

Unfortunately, the polymeric species $B_4O_5(OH)_4^2$ is only involved in the calculation part of the study, because the accurate concentration distribution between $B_3O_3(OH)_4^-$ and $B_4O_5(OH)_4^{2-}$ is unknown, and also because in the case of high borate concentration and high pH values the content of $B_3O_3(OH)_4^-$ is much higher than that of $B_4O_5(OH)_4^{2-}$ [10], which reduces the accuracy of the prediction for the solubility curves of borate.

The phenomena that the physicochemical properties of the equilibrium solutions saturated with the double salt $Na_2CO_3 \cdot K_2CO_3 \cdot H_2O$ abnormally vary with the solution composition will be studied further.

4. CONCLUSIONS

Based on the determined values of the solubility and the physicochemical properties of the system system Li^+, Na^+, K^+ // CO_3^{2-}, $B_4O_7^{2-}$ - H_2O, the phase diagram of the system is composed of seven crystallization regions including the-one for the new double salt $Na_2CO_3 \cdot K_2CO_3 \cdot H_2O$. Trona was not found in the experiment. The Pitzer equations were adapted to predict solubility in the quinary system. With the parameters fitted in this study,solubilities of this quinary salt - water system were predicted. The results indicate that the calculated values are in goodagreement with the determined ones.

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