Stable and Metastable Phase Equilibria in the Salt-Water Systems

Tianlong Deng

Tianjin Key Laboratory of Marine Resources and Chemistry

College of Marine Science and Engineering

Tianjin University of Science and Technology

TEDA, Tianjin,

CAS Key Laboratory of Salt Lake Resources and Chemistry

Institute of Salt Lakes

Chinese Academy of Sciences

Xining, Qinghai,

People Republic of China

1. Introduction

1.1 Salt lakes and the classification of hydrochemistry

Salt lakes are widely distributed in the world, and some famous salt lake resources are shown in Tables 1 and 2. In China, salt lakes are mainly located in the area of the Qinghai-Xizang (Tibet) Plateau, and the Autonomous Regions of Xinjiang and Inner Mongolia (M.P. Zheng et al., 1989). The composition of salt lake brines can be summarized to the complex salt-water multi-component system (Li - Na - K - Ca - Mg - H - Cl - SO₄ - B₄O₇ - OH- HCO₃ - CO₃ - H₂O).

According to the chemical type of salt lake brines, it can be divided into five types, i.e. chloride type, sulphate type, carbonate type, nitrite type, and borate type among those salt lake resources in the world (Gao et al., 2007).

Chloride type: the component of brines in Death Sea, Mideast and Caerhan Salt Lake in China belongs to the system of chloride type (Na - K - Mg - Cl - H₂O), and the main precipitation of salts are halite (NaCl), sylvite (KCl), carnallite (KCl•MgCl₂•7H₂O), and bischofite (MgCl₂•6H₂O).

Sulphate type: this kind of salt lake resources is similar with the sea water system (Na - K - Mg - Cl - SO₄ - H₂O), and it can be divided into two kinds of hypotypes i.e. sodium sulphate and magnesium sulphate. As to sodium sulphate hypotype, the Great Salt Lake in America, the gulf of Kara-Bogaz-Golin Urkmenistan, and Da-Xiao Qaidan in China belong to this hypotype with the main deposit of glauberite (Na₂SO₄•CaSO₄), glauber salt (Na₂SO₄•10H₂O), halite, galserite (Na₂SO₄•3K₂SO₄), schonenite (K₂SO₄•MgSO₄•6H₂O), and so on. As to magnesium sulphate hypotype, there are Yunchen Salt Lake in Shanxi Province and Chaka Salt Lakes in Qinghai Province, China, especially Salt Lakes of the Qaidam Basin in Qinghai Province are a sub-type of magnesium sulphate brines famous for their

abundance of lithium, potassium, magnesium and boron resources (Zheng et al., 1989). The main precipitation of salts are halite, glauber salt, blodite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), and epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$).

Carbonate type: this type belongs to the system ($\text{Na} - \text{K} - \text{Cl} - \text{CO}_3 - \text{SO}_4 - \text{H}_2\text{O}$), and Atacama Salt Lake in Chile and Zabuye Salt Lake in Tibet are the famous carbonate type of salt lake. The main precipitated minerals are thermonatrite ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), baking soda (NaHCO_3), natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), glauber salt, and halite.

Nitrite type: the brine composition of this type salt lake can be summarized as the system ($\text{Na} - \text{K} - \text{Mg} - \text{Cl} - \text{NO}_3 - \text{SO}_4 - \text{H}_2\text{O}$). The type salt lake main locates in the salt lake area in the northern of Chile among the salt lake group of Andes in the South-America, semi and dry salts in Luobubuo and Wuzunbulake Lakes in Xinjiang, the northern of China. There are natratite saltier (NaNO_3), niter (KNO_3), darapskite ($\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), POTASSIUM-darapskite ($\text{KNO}_3 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), humberstonite ($\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$).

Borate type: it can be divided into carbonate-borate hypotype and sulphate-borate hypotype. Searles Salt Lake in America, Banguo Lake and Zabuye Salt Lakes in Tibet, China belong to the former, and the brines mostly belong to the system ($\text{Na} - \text{K} - \text{Cl} - \text{B}_4\text{O}_7 - \text{CO}_3 - \text{HCO}_3 - \text{SO}_4 - \text{H}_2\text{O}$). In order to prove the industrial development of Searles Lake brines, Teeple (1929) published a monograph after a series of salt-water equilibrium data on Searles lake brine containing carbonate and borate systems. The latter includes Dong-xi-tai Lake, Da-xiao-chaidan Lake and Yiliping Lake in Qinghai Province, Zhachangchaka Lake in Tibet, China. In those lake area, the natural borate minerals of raphite ($\text{NaO} \cdot \text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$), pinnoite ($\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), chloropinnoite ($2\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot \text{MgCl}_2 \cdot 14\text{H}_2\text{O}$), inderite ($2\text{MgO} \cdot 3\text{B}_2\text{O}_3 \cdot 15\text{H}_2\text{O}$), hungchanoite ($\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), mcallisterite ($\text{MgO} \cdot 3\text{B}_2\text{O}_3 \cdot 7.5\text{H}_2\text{O}$), kurnakovite ($2\text{MgO} \cdot 3\text{B}_2\text{O}_3 \cdot 15\text{H}_2\text{O}$) and hydroborate were precipitated (Zheng et al., 1988; Gao et al., 2007). In addition, the concentration of lithium ion exists in the surface brine of salt lakes.

Salt lakes	Death Sea	Great lake, US	Searles lake, US	Atacama, Chile	Caerhan, China	Zabuye, Tibet
Altitude, /m	-400	1280	512	2300	2900	2677
Area, /km ²	1000	3600	1000	1400	5882	120
Dept, m	329	~5	Intragranular brine	Intragranular brine	Intragranular brine	~3
KCl	2×10^9	1×10^8	2.8×10^6	1.1×10^8	3×10^8	6.6×10^7
NaCl	1.2×10^{10}	3.2×10^9	—	—	4.3×10^{10}	2×10^8
MgCl ₂	2.2×10^{10}	1.2×10^9	—	1.2×10^8	2.7×10^9	5.7×10^8
MgSO ₄	—	1.7×10^7	—	—	—	—
LiCl	1.7×10^7	3.2×10^6	2.7×10^6	2.8×10^6	—	—
CaCl ₂	6×10^9	—	—	—	—	—
CaSO ₄	1×10^8	—	—	—	—	—
MgBr ₂	1×10^9	—	—	—	3.4×10^5	—
B ₂ O ₃	—	1.9×10^6	3×10^7	1.6×10^7	5.5×10^6	1.8×10^6
WO ₃	—	—	7.5×10^4	—	—	—

Table 1. Basic data of salt lakes and their salt reserves in the world. unit, /t (Song, 2000)

Type of lithium resources	Country and section	Lithium storage capacity, (Li ₂ O)
Salt lakes	Uyuni, Bolivia	More than 19 million tons
	Silver and Searles, US	More than 10 million tons
	Caerhan and Caida, China	10 million tons
	Kata Baca, Argentina	Sever million tons
Type of crystalline rocks	America	6.34 million tons
	Chile	4.3 million tons
	Canada	6.6 million tons
	Greenbusbse, Australian	6 million tons

Table 2. Statistical distribution of the lithium reserves in the world (Song, 2000; Zhao, 2003)

1.2 Phase equilibria of salt-water systems

It is essential to study the stable and metastable phase equilibria in multi-component systems at different temperatures for its application in the fields of chemical, chemical engineering such as dissolution, crystallization, distillation, extraction and separation.

1.2.1 The stable phase equilibria of salt-water systems

The research method for the stable phase equilibria of salt-water system is isothermal dissolution method. It is worthy of pointing out that the status of the stable phase equilibrium of salt-water system is the in a sealed condition under stirring sufficiently, and the speed of dissolution and crystallization of equilibrium solid phase is completely equal with the marker of no change for the liquid phase composition. As to the thermodynamic stable equilibrium studies aiming at sea water system (Na - K - Mg - Cl - SO₄ - H₂O), J.H. Vant'holff (1912) was in the earliest to report the stable phase diagram at 293.15 K with isothermal dissolution method.

In order to accelerate the exploiting of Qaidam Basin, China, a number of the stable phase equilibria of salt-water systems were published at recent decades (Li et al., 2006; Song, 1998, 2000; Song & Du, 1986; Song & Yao, 2001, 2003).

1.2.2 The metastable phase equilibria of salt-water systems

However, the phenomena of super-saturation of brines containing magnesium sulfate, borate is often found both in natural salt lakes and solar ponds around the world. Especially for salt lake brine and seawater systems, the natural evaporation is in a autogenetic process with the exchange of energy and substances in the open-ended system, and it is controlled by the radiant supply of solar energy with temperature difference, relative humidity, and air current, etc. In other word, it is impossible to reach the thermodynamic stable equilibrium, and it is in the status of thermodynamic non-equilibrium.

For the thermodynamic non-equilibrium phase diagram of the sea water system as called "solar phase diagram" in the first, N.S. Kurnakov (1938) was in the first to report the experimental diagrams based on the natural brine evaporation, and further called

“metastable phase diagram” for the same system (Na - K - Mg - Cl - SO₄ - H₂O) at (288.15, 298.15, and 308.15) K was reported on the basis of isothermal evaporation method (Jin, et al., 1980, 2001, 2002; Sun, 1992). Therefore, the metastable phase equilibria research is essential to predict the crystallized path of evaporation of the salt lake brine.

The isothermal evaporation phase diagrams of the sea water system at different temperature show a large difference with Vant’hoff stable phase diagram. The crystallization fields of leonite (MgSO₄.K₂SO₄.4H₂O), and kainite (KCl.MgSO₄.3H₂O) are all disappear whereas the crystallization field of picromerite (MgSO₄.K₂SO₄.6H₂O) increases by 20-fold, which is of great importance for producing potassium sulfate or potassium-magnesium fertilizer.

Therefore, in order to separate and utilize the mixture salts effectively by salt-field engineering or solar ponds in Qaidam Basin, studies on the phase equilibria of salt-water systems are focused on the metastable phase equilibria and phase diagrams at present years (Deng et al., 2011; Deng et al., 2008a-g; Deng, et al., 2009a-c; Wang & Deng, 2008, 2010; Li & Deng, 2009; Li et al., 2010; Liu et al., 2011; Meng & Deng, 2011; Guo et al., 2010; Gao & Deng, 2011a-b; Wang et al., 2011a-b).

1.2.3 Solubility prediction for the phase equilibria of salt-water systems

Pitzer and co-workers have developed an ion interaction model and published a series of papers (Pitzer, 1973a-b, 1974a-b, 1975, 1977, 1995, 2000; Pabalan & Pitzer, 1987) which gave a set of expressions for osmotic coefficients of the solution and mean activity coefficient of electrolytes in the solution. Expressions of the chemical equilibrium model for conventional single ion activity coefficients derived are more convenient to use in solubility calculations (Harvie & Weare, 1980; Harvie et al.1984; Felmy & Weare, 1986; Donad & Kean, 1985).

In this chapter, as an example, the stable and metastable phase equilibria in the salt-water system (NaCl - KCl - Na₂B₄O₇ - K₂B₄O₇ - H₂O), which is of great importance to describe the metastable behavior in order to separate and purify the mixture salts of borax and halosylvite were introduced in detail. The stable phase diagrams of the sub-ternary systems (NaCl - Na₂B₄O₇ - H₂O), (KCl -K₂B₄O₇ - H₂O), (Na₂B₄O₇ - K₂B₄O₇ - H₂O) at 298.15 K and the metastable phase diagrams of the sub-ternary systems (NaCl - Na₂B₄O₇ - H₂O) at 308.15 K for the mentioned reciprocal quaternary system were systematically studied on our previous researches under several scientific funding supports. The theoretical prediction for the stable solubility of this reciprocal quaternary system was also briefly introduced based on the ion-interaction model.

2. Apparatus

2.1 Apparatus for the stable phase equilibria in the salt-water system

Stable phase equilibria are the thermodynamic equilibria. In order to reach the isothermal dissolve equilibrium, the apparatus mainly contains two parts i.e. constant temperature installing and equilibrator. Therefore, experimental apparatus depends on the target of temperature. Generally, thermostatic water-circulator bath is used under normal atmospheric temperature, and thermostatic oil-circulator bath is chosen at higher level

temperature. Under low temperature, the refrigerator or freezing saline bath is commonly used. Figure 1 shows the common used equalizer pipe with a stirrer. The artificial synthesis complex put in the pipe to gradually reach equilibria under vigorous stirring. In order to avoid the evaporation of water, the fluid seal installing is needed, and the sampling branch pipe is also needed to seal. Usually, for aqueous quaternary system study, a series of artificial synthesis complex, normally no less than 30, was needed to be done one by one the experimental time consume is equivalence large. At present, a thermostatic shaker whose temperature could controlled with temperature precision of ± 0.1 K can be used for the measurement of stable phase equilibrium (Deng et al., 2002; Deng, 2004). The advantage is that a series artificial synthesis complexes which is loading in each sealed bottle can be put in and vigorous shaking together.

In this study, the stable phase equilibria system ($\text{NaCl} - \text{KCl} - \text{Na}_2\text{B}_4\text{O}_7 - \text{K}_2\text{B}_4\text{O}_7 - \text{H}_2\text{O}$) at 298.15 K, a thermostatic shaker (model HZQ-C) whose temperature was controlled within 0.1 K was used for the measurement of phase equilibrium.

2.2 Apparatus for the metastable phase equilibria in the salt-water system

The isothermal evaporation method was commonly used, and Figure 2 is our designed isothermal evaporation device in our laboratory (Guo et al., 2010). The isothermal evaporation chamber was consisted of evaporating container, precise thermometer to keep the evaporating temperature as a constant and electric fan to simulate the wind in situ, and the solar energy simulating system with electrical contact thermograph, electric relay and heating lamp. The temperature controlling apparatus is made up of an electric relay, an electrical contact thermograph and heating lamps.

Fig. 1. Apparatus of equalizer pipe. 1, thermostatic water-circulator bath; 2, pipe body; 3, assay; 4, stirrer; 5, fluid seal; 6, rubber seal lock; 7, sampling branch pipe.

In this example of the metastable phase equilibria system ($\text{NaCl} - \text{KCl} - \text{Na}_2\text{B}_4\text{O}_7 - \text{K}_2\text{B}_4\text{O}_7 - \text{H}_2\text{O}$) at 308.15 K, the isothermal evaporation box was used. In an air-conditioned laboratory, a thermal insulation material box (70 cm long, 65 cm wide, 60 cm high) with an apparatus to

control the temperature was installed. When the solution temperature in the container was under (308.15 ± 0.2) K, the apparatus for controlling the temperature formed a circuit and the heating lamp began to heat. Conversely, the circuit was broken and the heating lamp stopped working when the temperature exceeded 308.15 K. Therefore, the temperature in the box could always be kept to (308.15 ± 0.2) K. An electric fan installed on the box always worked to accelerate the evaporation of water from the solutions.

Fig. 2. The schematic diagram of the isothermal evaporation chamber. 1, electrical contact thermograph; 2, precise thermometer; 3, electric relay; 4, electric fan; 5, heating lamp; 6, evaporating container; 7, isothermal container.

Of course, the experimental conditions of an air flow velocity, a relative humidity, and an evaporation rate were controlled as similar as to those of the climate of reaching area in a simulative device.

3. Experimental methods

3.1 Reagents

For phase equilibrium study, reagents used should be high-purity grade otherwise the re-crystallized step was needed. For the stable and metastable phase equilibria in the salt-water system ($\text{NaCl} - \text{KCl} - \text{Na}_2\text{B}_4\text{O}_7 - \text{K}_2\text{B}_4\text{O}_7 - \text{H}_2\text{O}$), the chemicals used were of analytical grade, except borax which was a guaranteed reagent (GR), and were obtained from either the Tianjin Kermel Chemical Reagent Ltd. or the Shanghai Guoyao Chemical Reagent Co. Ltd: sodium chloride (NaCl , ≥ 0.995 in mass fraction), potassium chloride (KCl , ≥ 0.995 in mass fraction), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, ≥ 0.995 in mass fraction), potassium borate tetrahydrate ($\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, ≥ 0.995 in mass fraction), and were re-crystallized before use. Doubly deionized water (DDW) with conductivity less than $1.2 \times 10^{-4} \text{ S m}^{-1}$ and pH 6.60 at 298.15 K was used to prepare the series of the artificial synthesized brines and chemical analysis.

3.2 Analytical methods

3.2.1 The chemical analysis of the components in the liquids

For phase equilibrium study in this phase equilibrium system ($\text{NaCl} - \text{KCl} - \text{Na}_2\text{B}_4\text{O}_7 - \text{K}_2\text{B}_4\text{O}_7 - \text{H}_2\text{O}$), the composition of the potassium ion in liquids and their corresponding wet

solid phases was analyzed by gravimetric methods of sodium tetraphenyl borate with an uncertainty of $\leq \pm 0.0005$ in mass fraction; Both with an uncertainty of $\leq \pm 0.003$ in mass fraction, the concentrations of chloride and borate were determined by titration with mercury nitrate standard solution in the presence of mixed indicator of diphenylcarbazone and bromphenol blue, and by basic titration in the presence of mannitol, respectively (Analytical Laboratory of Institute of Salt Lakes at CAS, 1982). The concentration of sodium ion was calculated by subtraction via charge balance.

3.2.2 The measurements of the physicochemical properties

For the physicochemical properties determinations, a PHS-3C precision pH meter supplied by the Shanghai Precision & Scientific Instrument Co. Ltd was used to measure the pH of the equilibrium aqueous solutions (uncertainty of ± 0.01). The pH meter was calibrated with standard buffer solutions of a mixed phosphate of potassium dihydrogen phosphate and sodium dihydrogen phosphate (pH 6.84) as well as borax (pH 9.18); the densities (ρ) were measured with a density bottle method with an uncertainty of $\pm 0.2 \text{ mg}\cdot\text{cm}^{-3}$. The viscosities (η) were determined using an Ubbelohde capillary viscometer, which was placed in a thermostat at $(308.15 \pm 0.1) \text{ K}$. No fewer than five flow times for each equilibrium liquid phase were measured with a stopwatch with an uncertainty of 0.1 s to record the flowing time, and the results calculated were the average. An Abbe refractometer (model WZS-1) was used for measuring the refractive index (n_D) with an uncertainty of ± 0.0001 . The physicochemical parameters of density, refractive index and pH were also all placed in a thermostat that electronically controlled the set temperature at $(308.15 \pm 0.1) \text{ K}$.

3.3 Experimental methods of phase equilibria

3.3.1 Stable phase equilibria

For the stable equilibrium study, the isothermal dissolution method was used in this study. The series of complexes of the quaternary system were loaded into clean polyethylene bottles and capped tightly. The bottles were placed in the thermostatic rotary shaker, whose temperature was controlled to $(298.15 \pm 0.1) \text{ K}$, and rotated at 120 rpm to accelerate the equilibrium of those complexes. A 5.0 cm^3 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 cm^3 final volumes in a volumetric flask filled with DDW. If the compositions of the liquid phase in the bottle became constant, then equilibrium was achieved. Generally, it takes about 50 days to come to equilibrium.

3.3.2 Metastable phase equilibria

The isothermal evaporation method was used in metastable phase equilibria study. According to phase equilibrium composition, the appropriate quantity of salts and DDW calculated were mixed together as a series of artificial synthesized brines and loaded into clean polyethylene containers (15 cm in diameter, 6 cm high), then the containers were put into the box for the isothermal evaporation at $(308.15 \pm 0.2) \text{ K}$. The experimental conditions with air flowing velocity of 3.5-4.0 m/s, relative humidity of 20-30%, and evaporation rate of 4-6 mm/d are presented, just like the climate of the Qaidam Basin. For

metastable evaporation, the solutions were not stirred, and the crystal behavior of solid phase was observed periodically. When enough new solid phase appeared, the wet residue mixtures were taken from the solution. The solids were then approximately evaluated by the combined chemical analysis, of XP-300D Digital Polarizing Microscopy (Shanghai Caikon Optical Instrument Co., Ltd., China) using an oil immersion, and further identification with X-ray diffraction (X'pert PRO, Spectris. Pte. Ltd., The Netherlands). Meanwhile, a 5.0 cm³ sample of the clarified solution was taken from the liquid phase of each polyethylene container through a filter pipette, and then diluted to a 250.0 cm³ final volume in a volumetric flask filled with DDW for the quantitative analysis of the compositions of the liquid phase. Some other filtrates were used to measure the relative physicochemical properties individually according to the analytical method. The remainder of the solution continued to be evaporated and reached a new metastable equilibrium.

4. Experimental results

4.1 Mineral identification for the solid phase

For mineral identification when enough new solid phase appeared either in the stable equilibrium system or in the metastable equilibrium system, the wet residue mixtures were taken from the solution according to the experimental method. Firstly, as to the minerals of Na₂B₄O₇·10H₂O and K₂B₄O₇·4H₂O, the former belongs to monoclinic system, and the dual optical negative crystal i.e. 2v(-) whereas the later belongs to trimetric system, and the dual optical positive crystal i.e. 2v(+). Secondly, to the minerals NaCl and KCl, they can be identified through the property of refractive index. The refractive index of NaCl is higher than that of KCl. Observed with a XP-300D Digital Polarizing Microscopy using an oil immersion method, the crystal photos of the single and orthogonal polarized light on representative solid phases in the invariant points (NaCl + KCl + Na₂B₄O₇·10H₂O) and (Na₂B₄O₇·10H₂O + K₂B₄O₇·4H₂O + KCl) are presented in Figure 3.

single polarized light (10×10) orthogonal polarized light (10×10)

(a) Invariant point (NaCl + KCl + Borax)

Fig. 3. Identification of the invariant points for the solid phase in the reciprocal system ($NaCl - KCl - Na_2B_4O_7 - K_2B_4O_7 - H_2O$) with a polarized microscopy using an oil-immersion method. (a), the invariant point ($NaCl + KCl + Na_2B_4O_7 \cdot 10H_2O$); (b), the invariant point ($KCl + Na_2B_4O_7 \cdot 10H_2O + K_2B_4O_7 \cdot 4H_2O$).

The metastable equilibria solid phases in the two invariant points are further confirmed with X-ray diffraction analysis, and listed in Figure 4, except in the invariant points ($NaCl + KCl + Borax$) in Figure 4a which shows that the minerals KCl , $NaCl$, $Na_2B_4O_7 \cdot 10H_2O$ and a minor $Na_2B_4O_7 \cdot 5H_2O$ are existed. The minor of $Na_2B_4O_7 \cdot 5H_2O$ maybe is formed due to the dehydration of $Na_2B_4O_7 \cdot 10H_2O$ in the processes of transfer operation and/or grinding.

No.	Visible	Ref. Code	Chemical Formula	Score	Scale Factor	Semi-Quant/%
1	True	01-075-0296	KCl	49	0.369	22
2	True	01-075-0296	NaCl	45	0.732	57
3	True	01-075-0296	$B_4O_5(OH)_4(Na_2(H_2O)_8)$	39	0.030	20
4	True	01-075-0296	$Na_2B_4O_7(H_2O)_5$	13	0.007	1

(a), the X-ray diffraction photograph and the analytical data for the invariant point ($NaCl + KCl + Borax$)

No.	Visible	Ref. Code	Chemical Formula	Score	Scale Factor	Semi-Quant/%
1	True	01-072-1540	KCl	39	0.650	72
2	True	01-076-0753	$K_2(B_4O_5(OH)_4)(H_2O)_2$	37	0.011	22
3	True	01-074-0339	$B_4O_5(OH)_4(Na_2(H_2O)_8)$	10	0.004	5

(b), the X-ray diffraction photograph and the analytical data for the invariant point (KCl + Borax + $K_2B_4O_7 \cdot 4H_2O$)

Fig. 4. The X-ray diffraction data of the invariant points. (a), the invariant point (NaCl + KCl + $Na_2B_4O_7 \cdot 10H_2O$); (b), the invariant point ($Na_2B_4O_7 \cdot 10H_2O$ + $K_2B_4O_7 \cdot 4H_2O$ + KCl).

4.2 Stable phase equilibrium of the quaternary system (NaCl - KCl - $Na_2B_4O_7$ - $K_2B_4O_7$ - H_2O) at 298.15 K

The stable phase equilibrium experimental results of solubilities of the quaternary system (NaCl - KCl - $Na_2B_4O_7$ - $K_2B_4O_7$ - H_2O) at 298.15 K were determined, and are listed in Table 3, respectively. On the basis of the Jänecke index (J_B , $J_B/[mol/100 mol(2Na^+ + 2K^+)]$) in Table 3, the stable equilibrium phase diagram of the system at 298.15 K was plotted and shown in Figure 5.

4.3 Metastable phase equilibrium of the quaternary system (NaCl - KCl - $Na_2B_4O_7$ - $K_2B_4O_7$ - H_2O) at 308.15 K

The experimental results of the metastable solubilities and the physicochemical properties of the quaternary system (NaCl - KCl - $Na_2B_4O_7$ - $K_2B_4O_7$ - H_2O) at 308.15 K were determined, and are listed in Tables 4 and 5, respectively. On the basis of the Jänecke index (J_B , $J_B/[mol/100 mol(2Na^+ + 2K^+)]$) in Table 4, the metastable equilibrium phase diagram of the system at 308.15 K was plotted (Figure 6).

No.	Composition of the solution				Jänecke index			Equilibrium solid phase**
	100 w_B^*				$J_{Br} / [\text{mol}/100\text{mol}(2\text{Na}^{++}2\text{K}^{+})]$			
	Na ⁺	K ⁺	Cl ⁻	B ₄ O ₇ ²⁻	$J(2\text{Cl}^-)$	$J(2\text{K}^+)$	$J(\text{H}_2\text{O})$	
1	10.25	0.00	15.80	0.00	100.00	0.00	1807.5	NaCl
2	0.00	13.87	12.58	0.00	100.00	100.00	2310.8	KCl
3	0.72	0.00	0.00	2.41	0.00	0.00	34623.3	N10
4	0.00	4.74	0.00	9.42	0.00	100.00	7864.1	K4
5, E ₁	8.02	5.85	17.68	0.00	100.00	30.03	1526.2	NaCl+KCl
6, E ₂	9.60	0.00	14.33	1.04	96.79	0.00	1997.5	NaCl+N10
7, E ₃	0.00	15.87	12.35	4.48	85.85	100.00	1807.8	KCl +K4
8, E ₄	1.15	4.36	0.00	12.54	0.00	69.24	5649.7	N10 + K4
9	1.38	6.11	0.92	14.77	11.98	72.33	3947.5	N10 + K4
10	1.57	11.74	12.35	1.59	24.64	72.41	3496.9	N10 + K4
11	1.59	7.55	3.83	11.97	41.25	73.74	3181.6	N10 + K4
12	3.50	11.39	12.24	7.62	96.67	45.60	1427.4	N10 + K4
13, E	4.72	9.62	14.55	3.17	90.05	54.55	1672.8	KCl + N10 + K4
14	1.13	13.44	12.65	2.78	90.59	88.46	2123.7	KCl+K4
15	1.57	11.74	12.35	1.59	94.45	81.45	2191.0	KCl+K4
16	4.18	10.56	14.96	2.33	93.36	59.79	1670.9	KCl+K4
17	4.15	9.65	13.96	2.61	92.13	57.77	181.0	KCl+K4
18	5.27	9.43	15.50	2.58	93.83	51.84	1602.8	KCl + N10
19	6.11	9.83	17.52	1.79	95.55	48.48	1386.6	KCl + N10
20	6.40	9.10	17.52	1.32	96.67	45.60	1427.4	NaCl + KCl
21	7.50	7.13	17.73	0.67	98.30	35.89	1462.7	NaCl + KCl
22, F	6.16	9.64	17.55	1.52	96.19	47.94	1406.5	NaCl+KCl+N10
23	9.73	1.05	15.35	1.35	96.05	6.12	1830.4	NaCl+N10

* w_B is in mass fraction; ** K4, $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$; N10, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

Table 3. Stable solubilities of the system (NaCl - KCl - $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{K}_2\text{B}_4\text{O}_7$ - H_2O) at 298.15 K

Fig. 5. Stable phase diagram of the quaternary system (NaCl - KCl - $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{K}_2\text{B}_4\text{O}_7$ - H_2O) at 298.15 K. (a), dry-salt phase diagram; (b), water-phase diagram.

No.	Composition of the solution				Jänecke index			Equilibrium solid phase*
	100w _B				J _B / [mol/100mol(2Na ⁺ +2K ⁺)]			
	Na ⁺	K ⁺	Cl ⁻	B ₄ O ₇ ²⁻	J(2Cl ⁻)	J(2K ⁺)	J(H ₂ O)	
A	1.30	0.00	0.00	4.40	0.00	0.00	2090.17	N10
B	10.47	0.00	16.15	0.00	100.00	0.00	1788.31	NaCl
C	0.00	14.87	13.49	0.00	100	100	18468.05	KCl
D	0.00	3.87	0.00	19.26	0.00	100	4311.59	K4
1, E ₁ '	7.85	6.56	18.06	0.00	100	32.94	1471.69	NaCl+KCl
2	7.84	6.54	17.76	0.58	98.54	32.89	1469.10	NaCl+KCl
3	7.85	6.60	17.66	0.95	97.6	33.09	1456.10	NaCl+KCl
4, E'	7.87	6.56	17.17	1.99	94.98	32.89	1445.77	NaCl+KCl+N10
5, E ₂ '	10.62	0.00	15.80	1.28	96.47	0.00	1736.76	NaCl +N10
6	9.88	1.51	15.89	1.59	95.63	8.25	1684.84	NaCl +N10
7	9.36	2.87	16.24	1.74	95.33	15.27	1612.49	NaCl +N10
8	9.10	3.62	16.50	1.81	95.22	18.97	1566.69	NaCl +N10
9	8.15	5.38	16.57	1.94	94.92	27.96	1532.30	NaCl+N10
10, E ₃ '	0.00	15.22	11.83	4.34	85.66	100	1955.76	KCl+K4
11	0.49	14.75	12.16	4.34	85.99	94.61	1899.70	KCl+K4
12	0.54	14.73	12.29	4.15	86.66	94.16	1894.74	KCl+K4
13	1.22	13.68	12.51	3.88	87.60	86.86	1893.49	KCl+K4
14	1.86	12.88	12.45	4.60	85.56	80.30	1844.98	KCl+K4
15	2.65	12.41	12.51	6.19	81.57	73.39	1699.85	KCl+K4
16, F'	2.84	12.36	12.06	7.74	77.34	71.90	1641.11	KCl+K4+N10
17, E ₄ '	2.01	8.65	0.00	24.00	0.00	71.66	2346.01	N10+K4
18	1.89	9.86	1.78	22.09	15.03	75.41	2134.79	N10+K4
19	1.74	9.55	4.49	15.01	39.58	76.36	2000.89	N10+K4
20	1.66	10.78	6.11	13.66	49.49	79.22	2160.56	N10+K4
21	1.79	12.05	8.55	11.27	62.43	79.81	1906.21	N10+K4
22	1.87	12.73	9.48	10.86	65.66	79.97	1773.28	N10+K4
23	2.28	12.65	10.89	8.97	72.68	76.57	1712.53	N10+K4
24	2.78	12.61	8.30	11.95	75.94	72.72	1838.60	N10+K4
25	3.11	11.86	12.46	6.78	80.09	69.15	1664.48	N10+KCl
26	3.26	11.41	13.13	4.90	85.45	67.31	1723.59	N10+KCl
27	3.64	10.91	13.59	4.20	87.64	63.8	1717.14	N10+KCl
28	4.06	10.43	14.15	3.45	89.98	60.17	1699.65	N10+KCl
29	4.45	10.17	14.57	3.30	90.62	57.36	1652.70	N10+KCl
30	5.27	9.25	15.16	2.97	91.80	50.79	1604.93	N10+KCl
31	6.17	8.23	15.94	2.27	93.91	43.95	1562.35	N10+KCl

* K4, K₂B₄O₇·4H₂O; N10, Na₂B₄O₇·10H₂O; w_B, in mass fraction.

Table 4. Metastable solubilities of the quaternary system (NaCl - KCl - Na₂B₄O₇ - K₂B₄O₇ - H₂O) at 308.15 K

No.*	Density $\rho, /(\text{g cm}^{-3})$	pH	Refractive index	Viscosity $\eta/(\text{mPa s})$
A	1.0441	—**	1.3405	—
B	1.1935	—	1.3800	—
C	1.1857	—	1.3742	—
D	1.2003	—	1.3678	—
1, E' ₁	1.2300	5.63	1.3869	1.1241
2	1.2414	7.29	1.3872	1.1452
3	1.2433	7.72	1.3880	1.1930
4, 'E	1.2524	7.81	1.3890	1.2620
5, E' ₂	1.2060	—	1.3802	—
6	1.2172	8.22	1.3836	1.3023
7	1.2274	8.66	1.3860	1.2865
8	1.2313	9.21	1.3862	1.2829
9	1.2398	8.51	1.3879	1.2729
10, E' ₃	1.2270	9.55	1.3782	0.8499
11	1.2347	9.43	1.3798	0.8443
12	—	—	—	—
13	—	—	1.3792	0.8844
14	1.2433	9.02	1.3814	1.0625
15	1.2536	9.10	1.3840	1.0876
16, F'	1.2700	9.30	1.3863	1.1963
17, E' ₄	1.3040	10.36	1.3868	2.8279
18	1.3206	10.12	1.3868	2.8032
19	1.2533	9.94	1.3803	1.5661
20	1.2600	9.62	1.3823	1.4548
21	1.2636	9.58	1.3840	—
22	1.2764	9.53	—	1.3900
23	1.2784	9.47	1.3856	—
24	—	—	—	—
25	1.2555	9.08	1.3857	1.1682
26	1.2484	9.51	1.3842	1.0812
27	1.2409	9.48	1.3828	1.0480
28	1.2348	9.02	1.3827	1.0252
29	1.2366	9.04	1.3835	1.0421
30	1.2404	8.65	1.3841	1.0809
31	1.2381	8.38	1.3849	1.0130

* Corresponding to the no. column in Table 4; ** not determined.

Table 5. Physicochemical properties of the metastable reciprocal quaternary system (NaCl - KCl - Na₂B₄O₇ - K₂B₄O₇ - H₂O) at 308.15 K

Fig. 6. Metastable phase diagram of the quaternary system (NaCl - KCl - Na₂B₄O₇ - K₂B₄O₇ - H₂O) at 308.15 K. (a), dry-salt phase diagram; (b), water-phase diagram.

On the basis of physicochemical property data of the metastable system (NaCl - KCl - Na₂B₄O₇ - K₂B₄O₇ - H₂O) at 308.15 K in Table 5, the diagram of physicochemical properties versus composition was drawn and shows in Figure 7. The physicochemical properties of the metastable equilibrium solution vary regularly with the composition of borate mass fraction. The singular point on every curve of the composition versus property diagram corresponds to the same invariant point and on the metastable solubility.

Fig. 7. Diagram of physicochemical properties versus composition for the metastable quaternary system ($\text{NaCl} - \text{KCl} - \text{Na}_2\text{B}_4\text{O}_7 - \text{K}_2\text{B}_4\text{O}_7 - \text{H}_2\text{O}$) at 308.15 K

4.3 Comparison of the stable and metastable phase diagram of the quaternary system ($\text{NaCl} - \text{KCl} - \text{Na}_2\text{B}_4\text{O}_7 - \text{K}_2\text{B}_4\text{O}_7 - \text{H}_2\text{O}$)

A comparison of the dry-salt diagrams of the metastable phase equilibrium at 308.15 K and the stable phase equilibrium at 298.15 K for the same system is shown in Figure 8. The metastable crystallization regions of borax and potassium chloride are both enlarged while the crystallized area of other minerals existed is decreased. When compared with the stable system, the solubility of borax in water in the metastable system is increased from 3.13 % to 5.70 %. The metastable phenomenon of borax is obvious in this reciprocal quaternary system.

Fig. 8. Comparison of the metastable phase diagram at 308.15 K in solid line and the stable phase diagram at 298.15 K in dashed line for the quaternary system ($\text{NaCl} - \text{KCl} - \text{Na}_2\text{B}_4\text{O}_7 - \text{K}_2\text{B}_4\text{O}_7 - \text{H}_2\text{O}$). -●-, metastable experimental points; -○-, stable experimental points.

5. Solubility theoretic prediction of salt-water system

5.1 Ion-interaction model

As to any electrolyte, its thermodynamic prosperity varied from weak solution to high concentration could be calculated through 3 or 4 Pitzer parameters. Pitzer ion-interaction model and its extended HW model of aqueous electrolyte solution can be briefly introduced in the following (Pitzer, 1975, 1977, 2000; Harvie & Wear, 1980; Harvie et al., 1984; Kim & Frederich, 1988a-b).

As to the ion-interaction model, it is a semiempirical statistical thermodynamics model. In this model, the Pitzer approach begins with a virial expansion of the excess free energy of the form to consider the three kinds of existed potential energies on the ion-interaction potential energy in solution.

$$G^{\text{ex}} / (n_w RT) = f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k + \dots \quad (1)$$

Where n_w is kilograms of solvent (usually in water), and m_i is the molality of species i (species may be chosen to be ions); i, j , and k express the solute ions of all cations or anions; I is ion strength and given by

$$I = \frac{1}{2} \sum m_i z_i^2, \text{ here } z_i \text{ is the number of charges on the } i\text{-th solute.}$$

The first term on the right in equation (1) is the first virial coefficients. The first virial coefficients i.e. the Debye-Hückel limiting law, $f(I)$, is a function only of ionic strength to express the long-range ion-interaction potential energy of one pair of ions in solution and not on individual ionic molalities or other solute properties.

Short-range potential effects are accounted for by the parameterization and functionality of the second virial coefficients, λ_{ij} , and the third virial coefficients, μ_{ijk} . The quantity λ_{ij} represents the short-range interaction in the presence of the solvent between solute particles i and j . This binary interaction parameter of the second virial coefficient does not itself have any composition dependence for neutral species, but for ions it is dependent it is ionic strength.

The quantity μ_{ijk} represents short-range interaction of ion triplets and are important only at high concentration. The parameters μ_{ijk} are assumed to be independent of ionic strength and are taken to be zero when the ions i, j and k are all cations or all anions.

Taking the derivatives of equation ? with respect to the number of moles of each components yields expressions for the osmotic and activity coefficients.

5.1.1 For pure electrolytes

For the pure single-electrolyte MX, the osmotic coefficient defined by Pitzer (2000):

$$\phi - 1 = |z_M z_X| f^\phi + m \frac{2v_M v_X}{v} B_{MX}^\phi + m^2 \frac{2(v_M v_X)^{3/2}}{v} C_{MX}^\phi \quad (2)$$

ϕ is the osmotic coefficient; Z_M and Z_X are the charges of anions and cations in the solution. m is the molality of solute; ν_M , ν_X , and ν ($\nu = \nu_M + \nu_X$) represent the stoichiometric coefficients of the anion, cation, and the total ions on the electrolyte MX.

In equation (1), f^ϕ , B_{MX}^ϕ and C_{MX}^ϕ are defined as following equations. In equation (1a), here b is a universal empirical constant to be equal $1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$.

$$f^\phi = -\frac{A^\phi I^{1/2}}{1 + bI^{1/2}} \quad (2a)$$

For non 2-2 type of electrolytes, such as several 1-1-, 2-1-, and 1-2-type pure salts, the best form of B_{MX}^ϕ is following (Pitzer, 1973):

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha\sqrt{I}} \quad (2b)$$

For 2-2 type of electrolytes, such as several 3-1- and even 4-1-type pure salts, an additional term is added (Pitzer, 1977):

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha_1\sqrt{I}} + \beta_{MX}^{(2)} e^{-\alpha_2\sqrt{I}} \quad (2c)$$

$$A^\phi = \frac{1}{3} \left(\frac{2\pi N_0 \rho_w}{1000} \right)^{1/2} \left(\frac{e^2}{DkT} \right)^{3/2} \quad (2d)$$

A^ϕ is the Debye-Hückel coefficient for the osmotic coefficient and equal to 0.3915 at 298.15 K. Where, N_0 is Avogadro's number, d_w and D are the density and static dielectric constant of the solvent (water in this case) at temperature and e is the electronic charge. k is Boltzmann's constant. In equation (1b), $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, C_{MX}^ϕ are specific to the salt MX, and are the single-electrolyte parameters of MX. The universal parameters $\alpha = 2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ and omit $\beta_{MX}^{(2)}$ for several 1-1-, 2-1-, and 1-2-type salts at 298.15 K. As salts of other valence types, the values $\alpha_1 = 1.4 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, and $\alpha_2 = 12 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ were satisfactory for all 2-2 or higher valence pairs electrolytes at 298.15 K. The parameter $\beta_{MX}^{(2)}$ is negative and is related to the association equilibrium constant.

The mean activity coefficient $\gamma_\pm$ is defined as:

$$\ln \gamma_\pm = |z_M z_X| f^\gamma + m \frac{2\nu_M \nu_X}{\nu} B_{MX}^\gamma + m^2 \frac{2(\nu_M \nu_X)^{3/2}}{\nu} C_{MX}^\gamma \quad (3)$$

$$f^\gamma = -A^\phi [I^{1/2} / (1 + bI^{1/2}) + (2/b) \ln(1 + bI^{1/2})] \quad (3a)$$

$$B_{MX}^\gamma = B_{MX} + B_{MX}^\phi \quad (3b)$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} g(\alpha_2 I^{1/2}) \quad (3c)$$

$$g(x) = 2[1 - (1+x)\exp(-x) / x^2] \quad (3d)$$

$$C_{MX}^{\gamma} = 3C_{MX}^{\phi} / 2 \quad (3e)$$

5.1.2 For mixture electrolytes

In order to treat mixed electrolytes, the following sets of equations are identical with the form used by Harvie & Weare (1984) for modeling the osmotic coefficient and the activity coefficient of a neutral electrolyte based on Pitzer Equations:

$$\begin{aligned} \sum_i m_i(\phi - 1) = & 2(-A^{\phi} I^{3/2} / (1 + 1.2I^{1/2}) + \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a (B_{ca}^{\phi} + ZC_{ca}) \\ & + \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} (\Phi_{cc'}^{\phi} + \sum_{a=1}^{N_a} m_a \psi_{cc'a}) + \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} (\Phi_{aa'}^{\phi} \\ & + \sum_{c=1}^{N_c} m_c \psi_{aa'c}) + \sum_{n=1}^{N_n} \sum_{c=1}^{N_c} m_n m_c \lambda_{nc} \end{aligned} \quad (4)$$

$$\begin{aligned} \ln \gamma_M = & z_M^2 F + \sum_{a=1}^{N_a} m_a (2B_{Ma} + ZC_{Ma}) + \sum_{c=1}^{N_c} m_c (2\Phi_{Mc} + \sum_{a=1}^{N_a} m_a \psi_{Mca}) + \\ & \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} \psi_{aa'M} + |z_M| \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} + \sum_{n=1}^{N_n} m_n (2\lambda_{nM}) \end{aligned} \quad (5)$$

$$\begin{aligned} \ln \gamma_X = & z_X^2 F + \sum_{c=1}^{N_c} m_c (2B_{cX} + ZC_{cX}) + \sum_{a=1}^{N_a} m_a (2\Phi_{Xa} + \sum_{c=1}^{N_c} m_c \psi_{Xac}) + \\ & \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} \psi_{cc'X} + |z_X| \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} + \sum_{n=1}^{N_n} m_n (2\lambda_{nX}) \end{aligned} \quad (6)$$

$$\ln \gamma_N = \sum_{c=1}^{N_c} m_c (2\lambda_{nc}) + \sum_{a=1}^{N_a} m_a (2\lambda_{na}) \quad (7)$$

In equations (3), (4), (5) and (6), the subscripts M, c, and c' present cations different cations; X, a, and a' express anions in mixture solution. N_c , N_a and N_n express the numbers of cations, anions, and neutral molecules; r_M , Z_M , m_c and r_X , Z_X , m_a , Φ present the ion activity coefficient, ion valence number, ion morality, and the permeability coefficient; γ_n , m_n , λ_{nc} and λ_{na} express activity coefficient of neutral molecule, morality of neutral molecule the interaction coefficient between neutral molecules with cations c and anion a.

In equations from (3) to (6), the function symbols of $F, C, Z, A^{\phi}, \psi, \Phi, B^{\phi}, B$ are as following, respectively:

1. The term of F in equations (4) to (5) depends only on ionic strength and temperature. The defining equation of F is given by equation (7).

$$\begin{aligned} F = & -A^{\phi} [I^{1/2} / (1 + 1.2I^{1/2}) + 2 / 1.2 \ln(1 + 1.2I^{1/2})] + \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a B_{ca}' \\ & + \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} \Phi_{cc'}' + \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} \Phi_{aa'}' \end{aligned} \quad (8)$$

- The single-electrolyte third virial coefficient, C_{MX} , account for short-range interaction of ion triplets and are important only at high concentration. These terms are independent of ionic strength. The parameters C_{MX} and C_{MX}^ϕ , the corresponding coefficients for calculating the osmotic coefficient, are related by the equation (1-6) (Pitzer & Mayorga, 1973):

$$C_{MX} = C_{MX}^\phi / (2|Z_M Z_X|^{1/2}) \quad (9)$$

- The function Z in the equation (8) is defined by:

$$Z = \sum_i |z_i| m_i \quad (10)$$

Where, m is the molality of species i , and z is its charge.

- $A\varphi$ is the Debye-Hückel coefficient for the osmotic coefficient and equal to 0.3915 at 298.15 K, and it is decided by solvent and temperature as equation (1d).
- The third virial coefficients, $\psi_{i,j,k}$ in equations (3) to (5) are mixed electrolyte parameters for each cation-cation-anion and anion-anion-cation triplet in mixed electrolyte solutions.
- The parameters B_{CA}^ϕ, B, B'_{CA} which describe the interaction of pair of oppositely charged ions represent measurable combinations of the second virial coefficients. They are defined as explicit functions of ionic strength by the following equations (Kim & Frederick, 1988).

$$B_{CA}^\phi = \beta_{CA}^{(0)} + \beta_{CA}^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta_{CA}^{(2)} \exp(-\alpha_2 I^{1/2}) \quad (11)$$

$$B_{CA} = \beta_{CA}^{(0)} + \beta_{CA}^{(1)} g(\alpha_1 I^{1/2}) + \beta_{CA}^{(2)} g(\alpha_2 I^{1/2}) \quad (12)$$

$$B'_{CA} = [\beta_{CA}^{(1)} g'(\alpha_1 I^{1/2}) + \beta_{CA}^{(2)} g'(\alpha_2 I^{1/2})] / I \quad (13)$$

Where the functions g and g' in equations (10), (11) and (12) are defined by

$$g(x) = 2[1 - (1+x)\exp(-x)] / x^2 \quad (14)$$

$$g'(x) = -2[1 - (1+x+x^2/2)\exp(-x)] / x^2 \quad (15)$$

In equations (13) and (14), $x = \alpha_1 I^{1/2}$ or $= \alpha_2 I^{1/2}$.

In Pitzer's model expression in Eqns. (10) to (12), α is a function of electrolyte type and does not vary with concentration or temperature. Following Harvie et al. (1984), when either cation or anion for an electrolyte is univalent, the first two terms in equations (10) to (12) are considered, $\beta_{CA}^{(2)}$ can be neglect and $\alpha_1 = 2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, $\alpha_2 = 0$ at 298.15 K. For higher valence type, such as 2-2 electrolytes for these higher valence species accounts for their increased tendency to associate in solution, the full equations from (10) to (12) are used, and $\alpha_1 = 1.4 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ and $\alpha_2 = 12 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ at 298.15 K.

7. $\Phi_{ij}^\phi, \Phi_{ij}, \Phi_{ij}'$ which depend upon ionic strength, are the second virial coefficients, and are given the following form (Pitzer, 1973).

$$\Phi_{ij}^\phi = \theta_{ij} + {}^E\theta_{ij} + I {}^E\theta_{ij}' \quad (16)$$

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij} \quad (17)$$

$$\Phi_{ij}' = {}^E\theta_{ij}' \quad (18)$$

In equations (15), (16) and (17), $\theta_{i,j}$ is an adjustable parameter for each pair of anions or cations for each cation-cation and anion-anion pair, called triplet-ion-interaction parameter. The functions, ${}^E\theta_{ij}$ and ${}^E\theta_{ij}'$ are functions only of ionic strength and the electrolyte pair type. Pitzer (1975) derived equations for calculating these effects, and Harvie and Weare (1981) summarized Pitzer's equations in a convenient form as following:

$${}^E\theta_{ij} = (Z_i Z_j / 4I) [J(x_{ij}) - J(x_{ii}) / 2 - J(x_{jj}) / 2] \quad (19)$$

$${}^E\theta_{ij}' = -({}^E\theta_{ij} / I) + (Z_i Z_j / 8I^2) [x_{ij} J'(x_{ij}) - x_{ii} J'(x_{ii}) / 2 - x_{jj} J'(x_{jj}) / 2] \quad (20)$$

$$x_{ij} = 6Z_i Z_j A^\phi I^{1/2} \quad (21)$$

In equations (18) and (19), $J(x)$ is the group integral of the short-range interaction potential energy. $J'(x)$ is the single-order differential quotient of $J(x)$, and both are independent of ionic strength and ion charges. In order to give the accuracy in computation, $J(x)$ can be fitted as the following function:

$$J(x) = 1 / 4x - 1 + 1 / x \int_0^\infty [1 - \exp(-x / y) C_1 x^{-C_2} \cdot \exp(-C_3 x^{C_4})] y^{-1} dy \quad (22)$$

$$J'(x) = [4 + C_1 x^{-C_2} \cdot \exp(-C_3 x^{C_4})]^{-1} + [4 + C_1 x^{-C_2} \exp(-C_3 x^{C_4})]^{-2} [C_1 x \exp(-C_3 x^{C_4}) (C_2 x^{-C_2-1} + C_3 C_4 x^{C_4-1} x^{-C_2})] \quad (23)$$

In equations (21) and (22), $C_1 = 4.581$, $C_2 = 0.7237$, $C_3 = 0.0120$, $C_4 = 0.528$.

Firstly, x_{ij} can be calculated according to equation (20), and $J(x)$ and $J'(x)$ were obtained from equations (21) and (22), and then to obtained ${}^E\theta_{ij}$ and ${}^E\theta_{ij}'$ from equations (18) and (19); finally, $\Phi_{ij}^\phi, \Phi_{ij}, \Phi_{ij}'$ can be got through equations from (15) to (17). Using the values of $\Phi_{ij}^\phi, \Phi_{ij}, \Phi_{ij}'$, the osmotic and activity coefficients of electrolytes can be calculated via equations from (3) to (6).

Using the osmotic coefficient, activity coefficient and the solubility products of the equilibrium solid phases allowed us to identify the coexisting solid phases and their compositions at equilibrium.

On Pitzer ion-interaction model and its extended HW model, a numbers of papers were successfully utilized to predict the solubility behaviors of natural water systems, salt-water

systems, and even geological fluids (Felmy & Weare, 1986; Kim & Frederich, 1988a, 1988b; Fang et al., 1993; Song, 1998; Song & Yao, 2001, 2003; Yang, 1988, 1989, 1992, 2005).

By the way, additional work has centered on developing variable-temperature models, which will increase the applicability to a number of diverse geochemical systems. The primary focus has been to broaden the models by generating parameters at higher or lower temperatures (Pabalan & Pitzer, 1987; Spencer et al., 1990; Greenberg & Moller, 1989).

5.2 Model parameterization and solubility predictions

As to the borate solution, the crystallized behavior of borate salts is very complex. The coexisted polyanion species of borate in the liquid phase is difference with the differences of boron concentration, pH value, solvent, and the positively charged ions. The ion of $B_4O_7^{2-}$ is the general statistical express for various possible existed borates. Therefore, the structural formulas of $Na_2B_4O_7 \cdot 10H_2O$ and $K_2B_4O_7 \cdot 4H_2O$ in the solid phases of the quaternary system ($NaCl - KCl - Na_2B_4O_7 - K_2B_4O_7 - H_2O$) are $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ and $K_2[B_4O_5(OH)_4] \cdot 2H_2O$, respectively. Borate in the liquid phase corresponding to the equilibrium solid phase maybe coexists as $B_4O_5(OH)_4^{2-}$, $B_3O_3(OH)_4^-$, $B(OH)_4^-$, and son on due to the reactions of polymerization or depolymerization of boron anion.

Therefore, in this part of predictive solubility of the quaternary system ($NaCl - KCl - Na_2B_4O_7 - K_2B_4O_7 - H_2O$), the predictive solubilities of this system were calculated on the basis of two assumptions: Model I: borate in the liquid phase exists all in statistical form of $B_4O_7^{2-}$ i.e. $B_4O_5(OH)_4^{2-}$; Model II: borate in the liquid phase exists as various boron species of $B_4O_5(OH)_4^{2-}$, $B_3O_3(OH)_4^-$, $B(OH)_4^-$.

The necessary model parameters for the activity coefficients of electrolytes in the system at 298.15 K were fit from obtained osmotic coefficients and the sub-ternary subsystems by the multiple and unary linear regression methods.

5.2.1 Model I for the solubility prediction

Model I: Suppose that borate in solution exists as in the statistical expression form of $B_4O_7^{2-}$ i.e. $B_4O_5(OH)_4^{2-}$, and the dissolved equilibria in the system could be following:

So, the dissolved equilibrium constants can be expressed as:

$$K_{N10} = (m_{Na^+} \cdot \gamma_{Na^+})^2 \cdot (m_{B_4} \cdot \gamma_{B_4}) \cdot a_w^8 \quad (24)$$

$$K_{K4} = (m_{K^+} \cdot \gamma_{K^+})^2 \cdot (m_{B_4} \cdot \gamma_{B_4}) \cdot a_w^2 \quad (25)$$

$$K_{NaCl} = (m_{Na^+} \cdot \gamma_{Na^+}) \cdot (m_{Cl^-} \cdot \gamma_{Cl^-}) \quad (26)$$

$$K_{KCl} = (m_{K^+} \cdot \gamma_{K^+}) \cdot (m_{Cl^-} \cdot \gamma_{Cl^-}) \quad (27)$$

And the electric charge balance exists as:

$$m_{Na^+} + m_{K^+} = m_{Cl^-} + 2m_{B_4O_5(OH)_4^{2-}} \quad (28)$$

Where, K , r , m , and a_w express equilibrium constant, activity coefficient, and water activity, and N10, K4 instead of the minerals of $Na_2B_4O_7 \cdot 10H_2O$, $K_2B_4O_7 \cdot 4H_2O$ (the same in the following), respectively. Then, the equilibria constants K are calculated with μ^0/RT and shown in Table 6.

The single salt parameters $\beta^{(0)}$, $\beta^{(1)}$, $C^{(\varphi)}$ of NaCl, KCl, $Na_2[B_4O_5(OH)_4]$, and $K_2[B_4O_5(OH)_4]$, two-ion interaction Pitzer parameters of $\theta_{Na, K}$, $\theta_{Cl, B_4O_5(OH)_4}$ and the triplicate-ion Pitzer parameters of $\Psi_{Cl, B_4O_5(OH)_4, Na}$, $\Psi_{Cl, B_4O_5(OH)_4, K}$, $\Psi_{Na, K, Cl}$, $\Psi_{Na, K, B_4O_5(OH)_4}$ in the reciprocal quaternary system at 298.15 K were chosen from Harvie et al. (1984), Felmy & Weare (1986), Kim & Frederick (1988), and Deng (2001) and summarized in Tables 7 and 8.

According to the equilibria constants and the Pitzer ion-interaction parameters, the solubilities of the quaternary system at 298.15 K have been calculated though the Newton's Iteration Method to solve the non-linearity simultaneous equations system, and shown in Table 9.

5.2.2 Model II for the solubility prediction

Model II: Suppose that borate in solution exists as in various boron species of $B_4O_5(OH)_4^{2-}$, $B_3O_3(OH)_4^-$, $B(OH)_4^-$ to further describe the behaviors of the polymerization and depolymerization of borate anion in solution, and the dissolved equilibria in the system could be following:

So, the dissolved equilibrium constants can be expressed as:

$$K_{N10} = (m_{Na^+} \cdot \gamma_{Na^+})^2 \cdot (m_{B_4} \cdot \gamma_{B_4}) \cdot a_w^8 \quad (29)$$

$$K_{K4} = (m_{K^+} \cdot \gamma_{K^+})^2 \cdot (m_{B_4} \cdot \gamma_{B_4}) \cdot a_w^2 \quad (30)$$

$$K_{B_4B_3B} = \frac{(m_{B_3} \cdot \gamma_{B_3}) \cdot (m_B \cdot \gamma_B)}{(m_{B_4} \cdot \gamma_{B_4}) \cdot a_w^2} \quad (31)$$

$$K_{NaCl} = (m_{Na^+} \cdot \gamma_{Na^+}) \cdot (m_{Cl^-} \cdot \gamma_{Cl^-}) \quad (32)$$

$$K_{KCl} = (m_{K^+} \cdot \gamma_{K^+}) \cdot (m_{Cl^-} \cdot \gamma_{Cl^-}) \quad (33)$$

Where, B₄, B₃ and B to instead of B₄O₅(OH)₄²⁻, B₃O₃(OH)₄⁻, and B(OH)₄⁻ for short; $K_{B_4B_3B}$ expresses the equilibrium constant of the polymerized species reaction of B₄O₅(OH)₄²⁻, B₃O₃(OH)₄⁻, B(OH)₄⁻.

And the electric charge balance exists as:

$$m_{Na^+} + m_{K^+} = m_{Cl^-} + 2m_{B_4O_5(OH)_4^{2-}} + m_{B_3O_3(OH)_4^-} + m_{B(OH)_4^-} \quad (34)$$

From this reaction of B₄, B₃ and B, i.e. B₄O₅(OH)₄²⁻ + 2H₂O = B₃O₃(OH)₄⁻ + B(OH)₄⁻, the molalities of B₃ and B are in equal. In the meantime, we suppose that two-ion and triplicate-ion interaction of different boron species would be weak, and the mixture ions parameters of different boron species should be ignored.

Similar as in model I, then, the equilibrium constant K existed solid phase is calculated with μ^0/RT , and also shown in Table 6, where another four possible borate salts of NaB₃O₃(OH)₄, NaB(OH)₄, KB₃O₃(OH)₄, KB(OH)₄ were also listed. The single salt parameters, binary ion interaction parameters, triplet mixture parameters and more parameters of $\theta_{Cl,B_3O_3(OH)_4}$, $\theta_{Cl,B(OH)_4}$, $\Psi_{Cl,B_3O_3(OH)_4,Na}$, and $\Psi_{Cl,B(OH)_4,Na}$ were considered, and shown in Table 8. According to the equilibria constants and the Pitzer ion-interaction parameters, the solubilities of the quaternary system at 298.15 K have been calculated though the Newton's Iteration Method to solve the non-linearity simultaneous equations system, and shown in Table 10. In fact, this theoretic calculation for the reciprocal quaternary system is equivalence of the calculated solubilities for the six-component system (Na - K - Cl - B₄O₅(OH)₄²⁻ - B₃O₃(OH)₄⁻ - B(OH)₄⁻ - H₂O). It is worthy saying that although the concentrations of Na⁺, K⁺, Cl⁻, B₄O₅(OH)₄²⁻, B₃O₃(OH)₄⁻, B(OH)₄⁻ in molalities could be got (Table 10), the concentrations including B₄O₅(OH)₄²⁻, B₃O₃(OH)₄⁻, B(OH)₄⁻ should be all inverted into the concentration of B₄O₇²⁻ when the Jänecke index of B₄O₇²⁻ calculation.

Species	μ^0/RT	Refs	Species	μ^0/RT	Refs
H ₂ O	-95.6635		B(OH) ₄ ⁻	-465.20	
Na ⁺	-105.651	Harvie et al., 1984	Na ₂ B ₄ O ₅ (OH) ₄ ·8H ₂ O	-2224.16	Felmy & Weare, 1986
K ⁺	-113.957		K ₂ B ₄ O ₅ (OH) ₄ ·2H ₂ O	-1663.47	
Cl ⁻	-52.955				
B ₄ O ₅ (OH) ₄ ²⁻	-1239.10	Felmy & Weare, 1986	NaCl	-154.99	Harvie et al., 1984
B ₃ O ₃ (OH) ₄ ⁻	-963.77		KCl	-164.84	

Table 6. μ^0/RT of species in the system (NaCl - KCl - Na₂B₄O₇ - K₂B₄O₇ - H₂O) at 298.15 K

On the basis of the calculated solubilities, a comparison diagram among model I, model II, experimental values for the reciprocal quaternary system at 298.15 K are shown in Figure 9.

Cation	Anion	$\beta_{MX}^{(0)}$	C_{MX}^{ϕ}	$\beta_{MX}^{(1)}$	$C_{MX}^{(\phi)}$	Refs
Na ⁺	Cl ⁻	0.07722	0.25183		0.00106	Kim & Frederick, 1988
Na ⁺	B ₄ O ₅ (OH) ₄ ²⁻	-0.11	-0.40		0.0	Felmy & Weare, 1986
Na ⁺	B ₃ O ₃ (OH) ₄ ⁻	-0.056	-0.91		0.0	
Na ⁺	B(OH) ₄ ⁻	-0.0427	0.089		0.0114	
K ⁺	Cl ⁻	0.04835	0.2122		-0.00084	Harvie et al., 1984
K ⁺	B ₄ O ₅ (OH) ₄ ²⁻	-0.022	0.0		0.0	Felmy & Weare, 1986
K ⁺	B ₃ O ₃ (OH) ₄ ⁻	-0.13	0.0		0.0	
K ⁺	B(OH) ₄ ⁻	0.035	0.14		0.0	

Table 7. Single-salt Pitzer parameters in the system (NaCl - KCl - Na₂B₄O₇ - K₂B₄O₇ - H₂O) at 298.15 K

Parameters	Values	Refs
θ_{Na^+, K^+}	-0.012	Harvie et al., 1984
$\theta_{Cl^-, B_4O_5(OH)_4^{2-}}$	0.074	Felmy & Weare, 1986
$\theta_{Cl^-, B_3O_3(OH)_4^-}$	0.12	
$\theta_{Cl^-, B(OH)_4^-}$	-0.065	
$\theta_{B_4O_5(OH)_4^{2-}, B_3O_3(OH)_4^-}$	—	—
$\theta_{B_4O_5(OH)_4^{2-}, B(OH)_4^-}$	—	—
$\theta_{B_3O_3(OH)_4^-, B(OH)_4^-}$	—	—
$\Psi_{Cl^-, B_4O_5(OH)_4^{2-}, Na^+}$	0.025	Felmy & Weare, 1986
$\Psi_{Cl^-, B_3O_3(OH)_4^-, Na^+}$	-0.024	
$\Psi_{Cl^-, B(OH)_4^-, Na^+}$	-0.0073	
$\Psi_{B_4O_5(OH)_4^{2-}, B_3O_3(OH)_4^-, Na^+}$	—	—
$\Psi_{B_4O_5(OH)_4^{2-}, B(OH)_4^-, Na^+}$	—	—
$\Psi_{B_3O_3(OH)_4^-, B(OH)_4^-, Na^+}$	—	—
$\Psi_{Cl^-, B_4O_5(OH)_4^{2-}, K^+}$	0.0185245	Deng, 2004
$\Psi_{Cl^-, B_3O_3(OH)_4^-, K^+}$	—	—
$\Psi_{Cl^-, B(OH)_4^-, K^+}$	—	—
$\Psi_{B_4O_5(OH)_4^{2-}, B_3O_3(OH)_4^-, K^+}$	—	—
$\Psi_{B_4O_5(OH)_4^{2-}, B(OH)_4^-, K^+}$	—	—
$\Psi_{B_3O_3(OH)_4^-, B(OH)_4^-, K^+}$	—	—
Ψ_{Na^+, K^+, Cl^-}	-0.0018	Harvie et al., 1984
$\Psi_{Na^+, K^+, B_4O_5(OH)_4^{2-}}$	0.289823	Deng, 2004
$\Psi_{Na^+, K^+, B_3O_3(OH)_4^-}$	—	—
$\Psi_{Na^+, K^+, B(OH)_4^-}$	—	—

Table 8. Mixing ion-interaction Pitzer parameters in the system (NaCl - KCl - Na₂B₄O₇ - K₂B₄O₇ - H₂O) at 298.15 K

Though the theoretical calculation on the basis of model II, it was found that the boron species are mainly existed B₃O₃(OH)₄⁻ and B(OH)₄⁻ while the concentration of B₄O₅(OH)₄²⁻ is very low when the total concentration of boron is low in weak solution. This result demonstrated that the polymerization or depolymerization behaviors of borate are complex.

No.	Composition liquid phase molality, / (mol/kgH ₂ O)				Jänecke index, J/(mol/100mol dry salts)		Equilibrium solid phases*
	Na ⁺	K ⁺	Cl ⁻	B ₄ O ₇ ²⁻	J/(2Na ⁺)	J/(B ₄ O ₇ ²⁻)	
1	0.2748	1.2843	0.00	0.7796	17.62	100.00	N10+K4
2	0.2768	1.3032	0.2000	0.6900	17.52	87.34	N10+K4
3	0.2804	1.3279	0.3500	0.6292	17.43	78.24	N10+K4
4	0.2863	1.3619	0.5000	0.5741	17.37	69.66	N10+K4
5	0.3014	1.4496	0.7800	0.4855	17.21	55.45	N10+K4
6	0.3177	1.5386	1.0000	0.4282	17.11	46.13	N10+K4
7	0.3603	1.7573	1.4400	0.3388	17.02	32.00	N10+K4
8	0.4297	2.0854	2.0000	0.2575	17.08	20.48	N10+K4
9	0.5028	2.4030	2.5000	0.2029	17.30	13.97	N10+K4
10	0.5858	2.7319	3.0000	0.1589	17.66	9.58	N10+K4
11	0.6774	3.0673	3.5000	0.1224	18.09	6.54	N10+K4
12	0.8903	3.7442	4.5000	0.06725	19.21	2.90	N10+K4
13,A1	1.0298	4.1687	5.1107	0.04392	19.81	1.69	N10+K4+KCl
14	0.00	4.8834	4.7149	0.08423	0.00	3.45	K4+KCl
15	0.1500	4.7688	4.7699	0.07444	3.05	3.03	K4+KCl
16	0.3000	4.6592	4.8262	0.06649	6.05	2.68	K4+KCl
17	0.4500	4.5534	4.8835	0.05996	8.99	2.40	K4+KCl
18	0.6000	4.4509	4.9418	0.05457	11.88	2.16	K4+KCl
19	0.7500	4.3511	5.0009	0.05009	14.70	1.96	K4+KCl
20	0.9000	4.2536	5.0609	0.04636	17.46	1.80	K4+KCl
21	4.8000	2.2523	7.0507	8.13E-4	68.06	0.023	N10+KCl
22	4.3000	2.4641	6.7621	9.67E-4	63.57	0.029	N10+KCl
23	3.6000	2.7821	6.3794	0.00139	56.41	0.044	N10+KCl
24	3.2000	2.9750	6.1713	0.00185	51.82	0.060	N10+KCl
25	2.8000	3.1758	5.9705	0.00263	46.86	0.088	N10+KCl
26	2.4000	3.3843	5.7762	0.00405	41.49	0.14	N10+KCl
27	2.0000	3.6007	5.5869	0.00686	35.71	0.25	N10+KCl
28	1.6000	3.8255	5.3992	0.01316	29.49	0.49	N10+KCl
29	5.2183	1.9000	7.1163	9.75E-4	73.31	0.027	N10+NaCl
30	5.4046	1.5000	6.9014	0.00159	78.28	0.046	N10+NaCl
31	5.6432	1.0000	6.6369	0.00313	84.95	0.094	N10+NaCl
32	5.8894	0.5000	6.3762	0.0066	92.17	0.21	N10+NaCl
33	6.1479	0.00	6.1178	0.01504	100.00	0.49	N10+NaCl
34,B1	5.1148	2.1256	7.2389	7.53E-4	70.64	0.021	N10+NaCl+K Cl
35	5.1147	2.1259	7.2394	6.00E-4	70.64	0.017	NaCl+KCl
36	5.1145	2.1264	7.2401	4.00E-4	70.63	0.011	NaCl+KCl
37	5.1143	2.1269	7.2408	2.00E-4	70.63	0.0055	NaCl+KCl
38	5.1142	2.1273	7.2415	0.00	70.62	0.00	NaCl+KCl

Table 9. Calculated solubility data of the system (NaCl - KCl - Na₂B₄O₇ - K₂B₄O₇ - H₂O) at 298.15 K on the basis of Model I. * N10, Na₂B₄O₇·10H₂O; K4, K₂B₄O₇·4H₂O.

No.	Composition liquid phase molality, / (mol/kgH ₂ O)*						Jänecke index, J/(mol/100mol dry-salt)		Equilibrium solid phases
	Na ⁺	K ⁺	Cl ⁻	B4	B3	B	J(2Na ⁺)	J(B ₄ O ₇ ²⁻)	
1	0.3362	1.4923	0.00	0.7084	0.2058	0.2058	18.38	100.00	N10+K4
2	0.3394	1.5158	0.2000	0.6362	0.1914	0.1914	18.28	89.22	N10+K4
3	0.3431	1.5428	0.3500	0.5868	0.1812	0.1812	18.19	81.44	N10+K4
4	0.3485	1.5771	0.5000	0.5413	0.1715	0.1715	18.10	74.03	N10+K4
5	0.3628	1.6608	0.7800	0.4667	0.1551	0.1551	17.93	61.45	N10+K4
6	0.3777	1.7431	1.0000	0.4165	0.1439	0.1439	17.81	52.85	N10+K4
7	0.4168	1.9432	1.4400	0.3347	0.1253	0.1253	17.66	38.98	N10+K4
8	0.4818	2.2464	2.0000	0.2562	0.1079	0.1079	17.66	26.69	N10+K4
9	0.5519	2.5451	2.5000	0.2018	0.0967	0.0967	17.82	19.28	N10+K4
10	0.6326	2.8591	3.0000	0.1574	0.0884	0.0884	18.12	14.08	N10+K4
11	0.7234	3.1822	3.5000	0.1207	0.0821	0.0821	18.52	10.38	N10+K4
12	0.9355	3.8426	4.5000	0.0654	0.0736	0.0736	19.58	5.82	N10+K4
13,A2	1.0770	4.2295	5.0794	0.04305	0.0705	0.0705	20.30	4.28	N10+K4+KCl
14	0.00	4.9588	4.6844	0.08694	0.0502	0.0502	0.00	5.53	K4+KCl
15	0.1500	4.8452	4.7369	0.07661	0.0525	0.0525	3.00	5.17	K4+KCl
16	0.3000	4.7368	4.7905	0.06822	0.0549	0.0549	5.96	4.89	K4+KCl
17	0.4500	4.6326	4.8449	0.06133	0.0576	0.0576	8.85	4.68	K4+KCl
18	0.6000	4.5320	4.8999	0.05563	0.0604	0.0604	11.69	4.52	K4+KCl
19	0.7500	4.4342	4.9558	0.05089	0.0633	0.0633	14.47	4.41	K4+KCl
20	0.9000	4.3390	5.0122	0.04692	0.0665	0.0665	17.18	4.33	K4+KCl
21	4.8000	2.2665	7.0005	8.237E-4	0.0322	0.0322	67.93	0.93	N10+KCl
22	4.3000	2.4815	6.7150	9.779E-4	0.0323	0.0323	63.41	0.98	N10+KCl
23	3.6000	2.8052	6.3356	0.00141	0.0334	0.0334	56.20	1.09	N10+KCl
24	3.2000	3.0021	6.1289	0.00188	0.0347	0.0347	51.60	1.18	N10+KCl
25	2.8000	3.2078	5.9289	0.00268	0.0368	0.0368	46.61	1.31	N10+KCl
26	2.4000	3.4226	5.7346	0.00415	0.0398	0.0398	41.22	1.51	N10+KCl
27	2.0000	3.6474	5.5442	0.0071	0.0445	0.0445	35.41	1.83	N10+KCl
28	1.6000	3.8845	5.3532	0.0138	0.0519	0.0519	29.17	2.40	N10+KCl
29	5.2316	1.9000	7.0663	9.963E-4	0.0316	0.0316	73.36	0.91	N10+NaCl
30	5.4169	1.5000	6.8530	0.00163	0.0303	0.0303	78.31	0.92	N10+NaCl
31	5.6544	1.0000	6.5902	0.00321	0.0289	0.0289	84.97	0.96	N10+NaCl
32	5.8998	0.5000	6.3310	0.00679	0.0276	0.0276	92.19	1.07	N10+NaCl
33	6.1580	0.00	6.0739	0.0155	0.0266	0.0266	100.00	1.37	N10+NaCl
34,B2	5.1668	2.1309	7.2304	7.463E-4	0.0329	0.0329	70.80	0.92	N10+KCl+NaCl
35	5.1612	2.1307	7.2318	6.00E-4	0.0294	0.0294	70.78	0.82	NaCl+KCl
36	5.1523	2.1303	7.2339	4.00E-4	0.0239	0.0239	70.75	0.67	NaCl+KCl
37	5.1410	2.1296	7.2364	2.00E-4	0.0168	0.0168	70.71	0.47	NaCl+KCl
38	5.1142	2.1273	7.2415	0.00	0.00	0.00	70.62	0.00	NaCl+KCl

Table 10. Calculated solubility data of the system (NaCl - KCl - Na₂B₄O₇ - K₂B₄O₇ - H₂O) at 298.15 K on the basis of Model II. * B4, B3, B express for B₄O₅(OH)₄²⁻, B₃O₃(OH)₄⁻, B(OH)₄⁻; N10, Na₂B₄O₇·10H₂O; K4, K₂B₄O₇·4H₂O.

In Figure 9, compared with Models I and II, the calculated values in the boundary points and the cosaturated point of ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{KCl} + \text{NaCl}$) based on model II were in good agreement with the experimental data. However, in the cosaturated point of ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O} + \text{KCl}$), a large difference on the solubility curve still existed. Reversely, the predictive result based on model II closed to the experimental curve. There were two possible reasons: one is that the structure of borate in solution is very complex, and the Pitzer's parameters of borate salts is scarce; the other one is the high saturation degree of borate, the difference between the experimental equilibrium constant and the theoretic calculated equilibrium constant was large enough.

Fig. 9. Comparison of the experimental and calculated phase diagram of the quaternary system ($\text{NaCl} - \text{KCl} - \text{Na}_2\text{B}_4\text{O}_7 - \text{K}_2\text{B}_4\text{O}_7 - \text{H}_2\text{O}$) at 298.15 K. $\bullet$ —, Calculated based on Model I; $\blacktriangle$ —, Calculated based on Model II; $\circ$ —, Experimental.

6. Acknowledgments

Financial support from the State Key Program of NNSFC (Grant.20836009), the NNSFC (Grant. 40773045), the "A Hundred Talents Program" of the Chinese Academy of Sciences (Grant. 0560051057), the Specialized Research Fund for the Doctoral Program of Chinese Higher Education (Grant 20101208110003), The Key Pillar Program in the Tianjin Municipal Science and Technology (11ZCKFGX2800) and Senior Professor Program of Tianjin for TUST (20100405) is acknowledged. Author also hopes to thank all members in my research group and my Ph.D. students Y.H. Liu, S.Q. Wang, Y.F. Guo, X.P. YU, J. Gao, L.Z. Meng, DC Li, Y. Wu, and D.M. Lai for their active contributions on our scientific projects.

7. References

Analytical Laboratory of Institute of Salt Lakes at CAS. (1988). *The analytical methods of brines and salts*, 2nd ed., Chin. Sci. Press, ISBN 7-03-000637-2, pp. 35-41 & 64-66, Beijing

- Deng, T.L. (2004). Phase equilibrium on the aqueous five-component system of lithium, sodium, potassium, chloride, borate at 298.15 K, *J. Chem. Eng. Data*, Vol. 47, No. 9, pp. 1295-1299, ISSN 0021-9568
- Deng, T.L.; Li, D. (2008a). Solid-liquid metastable equilibria in the quaternary system (NaCl + LiCl + CaCl₂ + H₂O) at 288.15 K, *J. Chem. Eng. Data*, Vol. 53, No. 11, pp. 2488-2492, ISSN 0021-9568
- Deng, T.L.; Li, D.C. (2008b). Solid-liquid metastable equilibria in the quaternary system (NaCl + KCl + CaCl₂ + H₂O) at 288.15 K, *Fluid Phase Equilibria*, Vol. 269, No. 1-2, pp. 98-103, ISSN 0378-3812
- Deng, T.L.; Li, D.C.; Wang, S.Q. (2008c). Metastable phase equilibrium on the aqueous quaternary system (KCl - CaCl₂ - H₂O) at (288.15 and 308.15) K, *J. Chem. Eng. Data*, Vol. 53, No. 4, pp. 1007-1011, ISSN 0021-9568
- Deng, T.L.; Meng, L.Z.; Sun, B. (2008d). Metastable phase equilibria of the reciprocal quaternary system containing sodium, potassium, chloride and borate ions at 308.15 K, *J. Chem. Eng. Data*, Vol. 53, No. 3, pp. 704-709, ISSN 0021-9568
- Deng, T.L.; Wang, S.Q. (2008e). Metastable phase equilibrium in the reciprocal quaternary system (NaCl + MgCl₂ + Na₂SO₄ + MgSO₄ + H₂O) at 273.15 K, *J. Chem. Eng. Data*, Vol. 53, No. 12, pp. 2723-2727, ISSN 0021-9568
- Deng, T.L.; Wang, S.Q.; Sun, B. (2008f). Metastable phase equilibrium on the aqueous quaternary system (KCl + K₂SO₄ + K₂B₄O₇ + H₂O) at 308.15 K, *J. Chem. Eng. Data*, Vol. 53, No. 2, pp. 411-414, ISSN 0021-9568
- Deng, T.L.; Yin, H.A.; Tang, M.L. (2002). Experimental and predictive phase equilibrium of the quarry System at 298K, *J. Chem. Eng. Data*, Vol. 47, pp. 26-29, ISSN 0021-9568
- Deng, T.L.; Yin, H.J.; Guo, Y.F. (2011). Metastable phase equilibrium in the aqueous ternary system (Li₂SO₄ + MgSO₄ + H₂O) at 323.15 K, *J. Chem. Eng. Data*, Vol. 56, No. 9, pp. 3585-3588, ISSN 0021-9568
- Deng, T.L.; Yin, H.J.; Li, D.C. (2009a). Metastable phase equilibrium on the aqueous ternary system (K₂SO₄ - MgSO₄ - H₂O) at 348.15 K, *J. Chem. Eng. Data*, Vol. 54, No. 2, pp. 498-501, ISSN 0021-9568
- Deng, T.L.; Yu, X.; Li, D.C. (2009b). Metastable phase equilibrium on the aqueous ternary system (K₂SO₄ - MgSO₄ - H₂O) at (288.15 and 308.15) K, *J. Solution Chem*, Vol. 38, No. 1, pp. 27-34, ISSN 0095-9782
- Deng, T.L.; Yu, X.; Sun, B. (2008g). Metastable phase equilibrium in the aqueous quaternary system (Li₂SO₄ - K₂SO₄ - MgSO₄ - H₂O) at 288.15 K, *J. Chem. Eng. Data*, Vol. 53, No. 11, pp. 2496-2500, ISSN 0021-9568
- Deng, T.L.; Zhang, B.J.; Li, D.C.; Guo, Y.F. (2009c). Simulation studies on the metastable phase equilibria in the aqueous ternary systems (NaCl - MgCl₂ - H₂O) and (KCl - MgCl₂ - H₂O) at 308.15 K, *Front. J. Chem. Eng.*, Vol. 3, No. 2, pp. 172-175, ISSN 2095-0179
- Donad, S.P.; Kean, H.K. (1985). The application of the Pitzer equations to 1-1 electrolytes in mixed solvents, *J. Solution Chem*, Vol. 14, No. 4, pp. 635-651, ISSN 0095-9782
- Fang, C.H.; Song, P.S.; Chen, J.Q. (1993). Theoretical calculation of the metastable phase diagram of the quinary system (Na + K + Cl + SO₄ + CO₃ + H₂O) at 25°C, *J. Salt Lakes Res.*, Vol. 1, No. 2, pp. 16-22, ISSN1008-858X

- Felmy, A.R.; Weare, J.H. (1986). The prediction of borate mineral equilibria in nature waters: Application to Searles Lake, California, *Geochim. Cosmochim. Acta*, Vol. 50, No. 10, pp. 2771-2783, ISSN 0016-7037
- Gao, J.; Deng, T.L. (2011a). Metastable phase equilibrium in the aqueous quaternary system ($\text{LiCl} + \text{MgCl}_2 + \text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$) at 308.15 K, *J. Chem. Eng. Data*, Vol. 56, No. 4, pp. 1452-1458, ISSN 0021-9568
- Gao, J.; Deng, T.L. (2011b). Metastable phase equilibrium in the aqueous quaternary system ($\text{MgCl}_2 + \text{MgSO}_4 + \text{H}_2\text{O}$) at 308.15 K, *J. Chem. Eng. Data*, Vol. 56, No. 5, pp. 1847-1851, ISSN 0021-9568
- Gao, S.Y.; Song, P.S.; Xia, S.P.; Zheng, M.P. (2007). *Salt Lake Chemistry – A new type of lithium and boron salt lake*, Chinese Science Press, ISBN 978-7-03-016972-3, Beijing
- Greenberg, J.P.; Moller, N. (1989). The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl- SO_4 - H_2O system to high concentration from 0°C to 250°C, *Geochim. Cosmochim. Acta*, Vol. 53, No. 9, pp. 2503-2518, ISSN 0016-7037
- Guo, Y.F.; Yin, H.J.; Wu, X.H.; Deng, T.L. (2010). Metastable phase equilibrium in the aqueous quaternary system ($\text{NaCl} + \text{MgCl}_2 + \text{Na}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$) at 323.15 K, *J. Chem. Eng. Data*, Vol. 55, No. 10, pp. 4215-4220, ISSN 0021-9568
- Harvie, C.E.; Moller, N.; Weare, J.H. (1984). 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 strength at 25°C, *Geochim. Cosmochim. Acta*, Vol. 48, No. 4, pp. 723-751, ISSN 0016-7037
- Harvie, C.E.; Weare, J.H. (1980). The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl- SO_4 - H_2O system from zero to high concentration at 25°C, *Geochim. Cosmochim. Acta*, Vol. 44, No. 7, pp. 981-997, ISSN 0016-7037
- Jin, Z. M.; Xiao, X. Z.; Liang, S. M. (1980). Study of the metastable equilibrium for pentanary system of (Na^+ , K^+ , Mg^{2+}), (Cl^- , SO_4^{2-}), H_2O . *Acta Chim. Sinica*, Vol. 38, No. 2, pp. 313-321, ISSN 0567-7351
- Jin, Z. M.; Zhou, H. N.; Wang, L. S. (2001). Study on the metastable phase equilibrium of Na^+ , K^+ , Mg^{2+} // Cl^- , SO_4^{2-} - H_2O quinary system at 35°C. *Chem. J. Chin. Univ.* Vol. 22, No. 3, pp. 634-638, ISSN 0251-0790
- Jin, Z. M.; Zhou, H. N.; Wang, L. S. (2002). Studies on the metastable phase equilibrium of Na^+ , K^+ , Mg^{2+} // Cl^- , SO_4^{2-} - H_2O quinary system at 15°C. *Chem. J. Chin. Univ.* Vol. 23, No. 3, pp. 690-694, ISSN 0251-0790
- Kim, H-T.; Frederick, W.J. (1988a). Evaluation of Pitzer ion interaction parameters of aqueous electrolytes at 25 °C.1.Single salt parameters, *J. Chem. Eng. Data*, Vol. 33, No. 2, pp. 177-184, ISSN 0021-9568
- Kim, H-T.; Frederick, W.J. (1988b). Evaluation of Pitzer ion interaction parameters of aqueous electrolytes at 25°C.2.Ternary mixing parameters, *J. Chem. Eng. Data*, Vol. 33, No. 3, pp. 278-283, ISSN 0021-9568
- Kurnakov, N. S. (1938). Solar phase diagram in the regions of potassium salts for the five-component system of ($\text{NaCl} - \text{MgSO}_4 - \text{MgCl}_2 - \text{KCl} - \text{H}_2\text{O}$ at (288.15, 298.15, and 308.15) K, *Ehvo. Fieh. Khim. Analieha*, Vol.10, No. 5, pp. 333-366.
- Li, D.C.; Deng, T.L. (2009). Solid-liquid metastable equilibria in the quaternary system ($\text{NaCl} + \text{KCl} + \text{CaCl}_2 + \text{H}_2\text{O}$) at 308.15 K, *J. Therm. Anal. Calorim.* Vol. 95, No. 2, pp. 361-367, ISSN 0021-9568

- Li, Y.H.; Song, P.S.; Xia, S.P. (2006). Solubility prediction for the HCl-MgCl₂-H₂O system at 40°C and solubility equilibrium constant calculation for HCl·MgCl₂·7H₂O at 40°C, *CALPHAD*, Vol. 30, No. 1, pp. 61-64, ISSN 0364-5916
- Li, Z.Y.; Deng, T.L.; Liao, M.X. (2010). Solid-liquid metastable equilibria in the quaternary system Li₂SO₄ + MgSO₄ + Na₂SO₄ + H₂O at T = 263.15 K, *Fluid Phase Equilibria*, Vol. 293, No.1, pp. 42-46, ISSN 0378-3812
- Liu, Y.H.; Deng, T.L.; Song, P.S. (2011). Metastable phase equilibrium of the reciprocal quaternary system LiCl + KCl + Li₂SO₄ + K₂SO₄ + H₂O at 308.15 K, *J. Chem. Eng. Data*, Vol. 56, No. 4, pp. 1139-1147, ISSN 0021-9568
- Meng, L.Z.; Deng, T.L. (2011). Solubility prediction for the system of (MgCl₂-MgSO₄-MgB₄O₇-H₂O) at 298.15 K using the ion-interaction model, *Russ. J. Inorg. Chem*, Vol. 56, No. 8, pp. 1-4, ISSN 0036-0236
- Pabalan, R.T.; Pitzer, K.S. (1987). Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Mg-Cl-SO₄-OH-H₂O, *Geochim. Cosmochim. Acta*, Vol. 51, No. 9, pp. 2429-2443, ISSN 0016-7037
- Pitzer, K.S. (1973a). Thermodynamics of electrolytes I: theoretical basis and general equation. *J. Phys. Chem*, Vol. 77, No. 2, pp. 268-277, ISSN 1932-7447
- Pitzer, K.S. (1973b). Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent, *J. Phys. Chem*, Vol. 77, No. 19, pp. 2300-2308, ISSN 1932-7447
- Pitzer, K.S. (1974a). Thermodynamics of electrolytes. III. Activity and osmotic coefficients for 2-2 electrolytes, *J. Solution Chem*, Vol. 3, No. 7, pp. 539-546, ISSN 0095-9782
- Pitzer, K.S. (1974b). Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes, *J. Am. Chem. Soc*, Vol. 96, No. 18, pp. 5701-5707, ISSN 0002-7863
- Pitzer, K.S. (1975). Thermodynamics of electrolytes. V. Effects of higher-order electrostatic terms, *J. Solution Chem*, Vol. 4, No. 3, pp. 249-265, ISSN 0095-9782
- Pitzer, K.S. (1977). Electrolytes theory-improvements since Debye-Hückel, *Account Chem. Res*, Vol. 10, No. 10, pp. 371-377, ISSN 0013-4686
- Pitzer, K.S. (1995). *Semiempirical equations for pure and mixed electrolytes. Thermodynamics*, 3rd ed.; McGraw-Hill Press, ISBN 0-07-050221-8, New York, Sydney, Tokyo, Toronto
- Pitzer, K.S. (2000). *Activity coefficients in electrolyte solutions*, 2nd ed.; CRC Press, ISBN 0-8493-5415-3, Boca Raton, Ann Arbor, Boston, London
- Song, P.S. (1998). Calculation of the metastable phase diagram for sea water system, *J. Salt Lakes Res.*, Vol. 6, No. 2-3, pp. 17-26, ISSN1008-858X
- Song, P.S. (2000). Salt lakes and their exploiting progresses on the relatively resources. *J. Salt Lakes Res.* Vol. 8, No. 1, pp. 1-16, ISSN1008-858X
- Song, P.S.; Du, X.H. (1986). Phase equilibrium and properties of the saturated solution in the quaternary system Li₂B₄O₇-Li₂SO₄-LiCl-H₂O at 25°C, *Chinese Science Bulletin*, Vol. 31, No. 19, pp. 1338-1343, ISSN 0567-7351
- Song, P.S.; Yao, Y. (2001). Thermodynamics and phase diagram of the salt lake brine system at 25°C I. Li⁺, K⁺, Mg²⁺//Cl⁻, SO₄²⁻-H₂O system, *CALPHAD*, Vol. 25, No. 3, pp. 329-341, ISSN 0364-5916

- Song, P.S.; Yao, Y. (2003). Thermodynamic model for the salt lake brine system and its applications-I. Applications in physical chemistry for the system Li^+ , Na^+ , K^+ , $\text{Mg}^{2+}/\text{Cl}^-$, $\text{SO}_4^{2-} - \text{H}_2\text{O}$, *J. Salt Lakes Res.*, Vol. 11, No. 3, pp. 1-8, ISSN1008-858X
- Spencer, R.J.; Moller, N.; Weare, J. (1990). The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Mg-Cl- SO_4 - H_2O system at temperatures below 25°C, *Geochim. Cosmochim. Acta*, Vol. 54, No. 4, pp. 575-590, ISSN 0016-7037
- Su, Y. G.; Li, J.; Jiang, C. F. (1992). Metastable phase equilibrium of K^+ , Na^+ , $\text{Mg}^{2+}/\text{Cl}^-$, $\text{SO}_4^{2-} - \text{H}_2\text{O}$ quinary system at 15°C. *J. Chem. Ind. Eng.* Vol. 43, No. 3, pp. 549-555, ISSN 0438-1157
- Teeple, J.E. (1929). *The development of Searles Lake brines: with equilibrium data*, American Chemical Society Monograph Series, Chemical Catalog Company Press, ISBN 0-07-571934-6, New York.
- Vant'hoff, J.H. (1912). Solubilities of the five-component system of ($\text{NaCl} - \text{MgSO}_4 - \text{MgCl}_2 - \text{KCl} - \text{H}_2\text{O}$ at 298.15 K, in: Howard L. Silcock. (1979). Solubilities of inorganic and organic compounds, Vol.3 Part 2: Ternary and multi-component systems of inorganic substances, Pergamon Press, ISBN 0-08-023570-0, Oxford, New York, Toronto, Sydney, Paris, Frankfurt.
- Wang, S.Q.; Deng, T.L. (2008). Solid-liquid isothermal evaporation phase equilibria in the aqueous ternary system ($\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$) at $T = 308.15$ K, *Journal of Chemistry Thermodynamics*, Vol. 40, No. 6, pp. 1007-1011, ISSN 0021-9614
- Wang, S.Q.; Deng, T.L. (2010). Metastable phase equilibria of the reciprocal quaternary system containing lithium, sodium, chloride, and sulfate ions at 273.15 K, *J. Chem. Eng. Data*, Vol. 55, No. 10, pp. 4211-4215, ISSN 0021-9568
- Wang, S.Q.; Guo, Y.F.; Deng, T.L. (2011a). Solid-liquid metastable equilibria in the aqueous ternary system containing lithium, magnesium, and sulfate ions at 273.15 K, *Proceedings of CECNet*, Vol. 6, pp. 5243-5246, XianNing, China, ISBN 978-1-61284-470-1, April 16-18, 2011
- Wang, S.Q.; Guo, Y.F.; Deng, T.L. (2011b). Solubility predictions for the reciprocal quaternary system ($\text{NaCl} + \text{MgCl}_2 + \text{Na}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$) at 283.15 K using Pitzer ion-interaction model, *Proceedings of CECNet*, Vol. 2, pp. 1661-1664, XianNing, China, ISBN 978-1-61284-470-1, April 16-18, 2011
- Yang, J.Z. (1988). Thermodynamics of electrolyte mixtures. Activity and osmotic coefficient with higher-order limiting law for symmetrical mixing, *J. Solution Chem*, Vol., No. 7, pp. 909-924, ISSN 0095-9782
- Yang, J.Z. (1989). The application of the ion-interaction model to multi-component 1-1 type electrolytes in mixed solvents, *J. Solution Chem*, Vol. 3, No. 2, pp. 201-210, ISSN 0095-9782
- Yang, J.Z. (1992). Thermodynamics of amino acid dissociation in mixed solvents. 3: Glycine in aqueous glucose solutions from 5 to 45°C, *J. Solution Chem*, Vol. 11, No. 9, pp. 1131-1143, ISSN 0095-9782
- Yang, J.Z. (2005). Medium effect of an organic solvent on the activity coefficients of HCl consistent with Pitzer's electrolyte solution theory, *J. Solution Chem*, Vol. 1, No. 1, pp. 71-76, ISSN 0095-9782
- Zhao, Y.Y. (2003). Chinese salt lake resources and the exploiting progresses. *Mineral Deposits*, Vol. 22, No. 1, pp. 99-106, ISSN 0258-7106

- Zheng, M.P.; Xiang, J.; Wei, X.J.; Zheng, Y. (1989). *Saline lakes on the Qinghai-Xizang (Tibet) Plateau*, Beijing Science and Technology Press, ISBN 7-5304-0519-5, Beijing
- Zheng, X. Y.; Tang, Y.; Xu, C.; Li, B.X.; Zhang, B.Z.; Yu, S.S. (1988). *Tibet saline lake*; Chinese Science Press, ISBN 7-03-000333-0, Beijing

Advances in Crystallization Processes

Edited by Dr. Yitzhak Mastai

ISBN 978-953-51-0581-7

Hard cover, 648 pages

Publisher InTech

Published online 27, April, 2012

Published in print edition April, 2012

Crystallization is used at some stage in nearly all process industries as a method of production, purification or recovery of solid materials. In recent years, a number of new applications have also come to rely on crystallization processes such as the crystallization of nano and amorphous materials. The articles for this book have been contributed by the most respected researchers in this area and cover the frontier areas of research and developments in crystallization processes. Divided into five parts this book provides the latest research developments in many aspects of crystallization including: chiral crystallization, crystallization of nanomaterials and the crystallization of amorphous and glassy materials. This book is of interest to both fundamental research and also to practicing scientists and will prove invaluable to all chemical engineers and industrial chemists in the process industries as well as crystallization workers and students in industry and academia.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Tianlong Deng (2012). Stable and Metastable Phase Equilibria in the Salt-Water Systems, *Advances in Crystallization Processes*, Dr. Yitzhak Mastai (Ed.), ISBN: 978-953-51-0581-7, InTech, Available from: <http://www.intechopen.com/books/advances-in-crystallization-processes/stable-and-metastable-phase-equilibria-of-the-salt-water-system>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](#), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.