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NOTE

Thermodynamic Simulation on Rb_2SO_4-Cs_2SO_4-$MgSO_4$-H_2O System at 25 ºC

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The Pitzer ion-interaction was applied to calculate the solubility isotherms of quaternary system Rb_2SO_4-Cs_2SO_4-$MgSO_4$-H_2O at 25 ºC in which the mixing crystals were formed. Theoretical phase equilibrium of Rb_2SO_4-Cs_2SO_4-$MgSO_4$-H_2O has been obtained assuming that no new solid phases crystallize in them. The calculated phase diagram consists of five crystallization fields, three invariant points and seven univariant curves. The five crystallization fields correspond to Rb_2SO_4, Cs_2SO_4, $MgSO_4·7H_2O$, $Cs_2SO_4·MgSO_4·6H_2O$ and $Rb_2SO_4·MgSO_4·6H_2O$. The results of calculation can be used to model salt crystallization during the concentration of brines.

Key Words: Phase diagrams, Solubility, Ion-interaction model, Salt lake brine.

High concentrations of rubidium and cesium have been found in the salt lake brines of western China. These rare alkali metal ions coexist with sodium, potassium, magnesium and sulfate in salt lake brines. Phase equilibrium researches on the salt lake systems will provide the theoretical basis for the extraction of rubidium and cesium from above-mentioned salt lakes. However, there is relatively small number of solubility data on the systems containing rubidium and cesium. Measurements of solubilities for the multicomponent salt-water system are time-consuming and laborious. Therefore, the determination of the component solubilities of such system by using theoretical model is of great significance to the phase equilibrium studies.

Among the models used for solubility prediction, Pitzer's ion-interaction model and its extended HW model[1-3] have been most used and successfully predicted the solubility isotherms in multi-component water salt systems[4,5]. In previous study, the ion-interaction model was used for the simulation of ternary aqueous solution containing rubidium[6]. The purpose of the present work is the phase equilibrium calculation of quaternary system Rb_2SO_4-Cs_2SO_4-$MgSO_4$-H_2O by means of Pitzer ion-interaction model.

The method of solubility equilibrium constant is used to calculate solubility. At a definite temperature and pressure, when ion activity product of a salt in the electrolyte solution is equal to its solubility equilibrium constant, this salt is saturated and its saturation concentration is its solubility. For a hydrated salt $M_{\nu M}X_{\nu X}·\nu_0H_2O$, the solubility equilibrium constant at a definite temperature for the dissolution reaction

$$M_{\nu M}X_{\nu X}·\nu_0H_2O = \nu MM^{+ZM} + \nu_X X^{-ZX} + \nu_0H_2O \quad (1)$$

is expressed by

$$K_{sp} = a_M{}^{\nu M}·a_X{}^{\nu X}·a_w{}^{\nu_0} \quad (2)$$

The activity of water is related to the osmotic coefficient ϕ, by the equation

$$\ln a_w = -\phi(M_w/1000)\Sigma m_i \quad (3)$$

where M_w is the molar mass of water and the sum cover all solute species. These activity and osmotic coefficient were calculated from the ion-interaction model of Pitzer. In this study, the extended ion-interaction model by Harvie and Weare was used. The details of this model have been discussed in Harvie and Weare's publications.

No phase equilibrium data for Rb_2SO_4-Cs_2SO_4-$MgSO_4$-H_2O at 25 ºC were found in literature. Experimental results[7] show the solubility isotherm of Rb_2SO_4-$MgSO_4$-H_2O at 25 ºC consists of three branches, corresponding to the crystallization of $Mg_2SO_4·7H_2O$, Rb_2SO_4 and the compound $Rb_2SO_4·MgSO_4·6H_2O$. The solubility isotherm of $MgSO_4$-Cs_2SO_4-H_2O at 25 ºC consists of three branches, which correspond to the crystallization of $Mg_2SO_4·7H_2O$, Cs_2SO_4 and the compound $Cs_2SO_4·MgSO_4·6H_2O$. The experimental results[8] on the systems Rb_2SO_4-Cs_2SO_4-H_2O at 25 ºC indicate the formation of mixed crystals. By assuming that only simple salt components of the system crystallize in them, the solubility isotherms of Rb_2SO_4-Cs_2SO_4-H_2O at 25 ºC were calculated in this paper. The results obtained from the thermodynamic simulation of the systems show that the composition of the mixed

TABLE-1
PITZER BINARY PARAMETERS FOR THE SINGLE SALT AT 25 ºC

	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	σ	Ref.
$MgSO_4$	0.221	3.343	-37.23	0.025	0.04	3
Rb_2SO_4	0.06518	0.7407	-	-0.0006339	0.02	9
Cs_2SO_4	0.09484	0.6026	-	-0.0002549	0.00105	9

crystals is very close to that of the pure salts. Fig. 1 shows the calculated and experimentally obtained solubility isotherms of Rb_2SO_4-Cs_2SO_4-H_2O. The experimental data are in good agreement with the calculated ones.

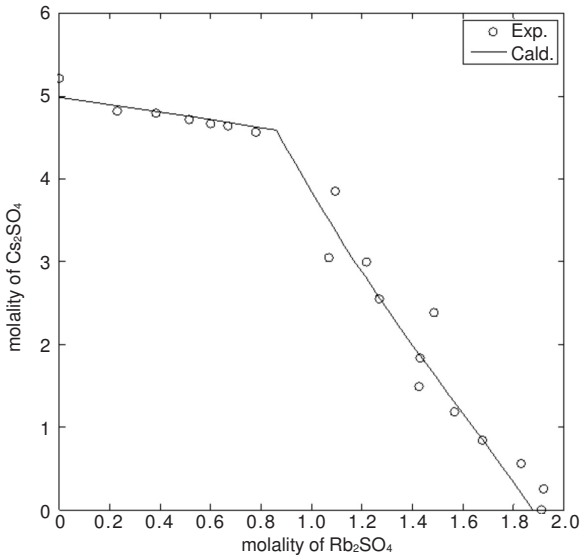

Fig. 1. Solubility isotherms of Rb_2SO_4-Cs_2SO_4-H_2O system at 25 ºC

On the basis of data concerning the binary and ternary subsystems, the solubility isotherms of the quaternary reciprocal system Rb_2SO_4-Cs_2SO_4-$MgSO_4$-H_2O at 25 ºC have been calculated using Pitzer model. Fig. 2 shows calculated solubility isotherms of the system investigated.

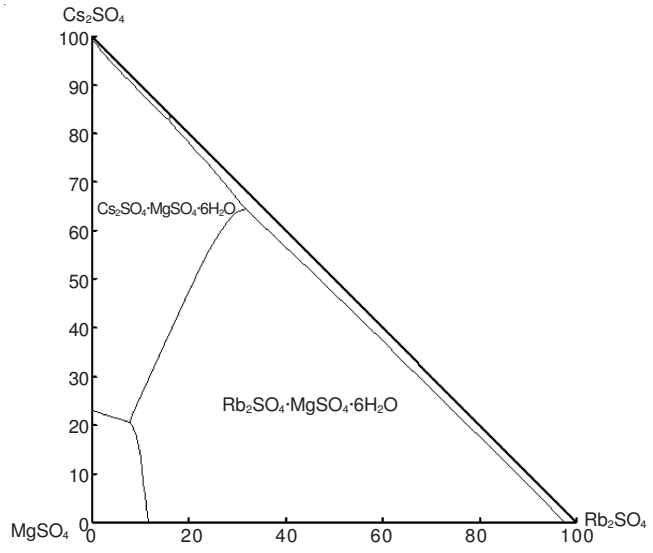

Fig. 2. Theoretical solubility isotherms in the system Rb_2SO_4-Cs_2SO_4-$MgSO_4$-H_2O at 25 ºC

The calculated phase diagram consists of five crystallization fields, three invariant points and seven univariant curves. The five crystallization fields correspond to Rb_2SO_4, Cs_2SO_4, $MgSO_4{\cdot}7H_2O$, $Cs_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$ and $Rb_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$.

All binary Pitzer parameters for single salts were taken from the literature and listed in Table-1. These parameters were evaluated using the experimental data concerning the dependence of the osmotic coefficient or the water activity on the solution concentration. The parameters' applicabilities have been proved by simulation of ternary systems.

The mixing parameters θ_{RbMg}, θ_{RbCs}, θ_{CsMg} and ψ_{MgCsSO_4} were given in the literature[10]. The mixing parameter ψ_{RbCsSO_4} is not reported in the literature and taken to be zero in the calculation. This approach has been proposed by Pitzer and Kim for a series of systems[11]. Experimental results in the literature indicate that double salt $Rb_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$ crystallizes in the Rb_2SO_4-$MgSO_4$-H_2O system. The mixing parameter ψ_{MgRbSO_4} and solubility product for $Rb_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$ were calculated with the solubility data[7]. The mixing parameters θ and ψ for the subsystems are listed in the Table-2. The values found for logarithm of the solubility products ln K^{o}_{sp} are given in Table-3.

TABLE-2
PITZER MIXING PARAMETERS FOR TERNARY SOLUTIONS AT 25 ºC

	θ	ψ
$MgSO_4$-Rb_2SO_4-H_2O	-0.104	-0.0178
$MgSO_4$-Cs_2SO_4-H_2O	-0.126	-0.0274
Cs_2SO_4-Rb_2SO_4-H_2O	0.00025	0

TABLE-3
VALUES OF THE THERMODYNAMIC SOLUBILITY PRODUCTS K^{o}_{sp} AT 25 ºC

	ln K^{o}_{sp}	Reference
$Rb_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$	-11.486	This paper
$Cs_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$	-9.684	12
Rb_2SO_4	-1.92	13
Cs_2SO_4	1.958	13
$MgSO_4{\cdot}7H_2O$	-4.29	13

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