Solubility Predication in the Systems of NaCl-$SrCl_2$-H_2O and KCl-$SrCl_2$-H_2O at 25 ℃ Using Pitzer Ion-interaction Model

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Abstract: Components solubilities in NaCl-$SrCl_2$-H_2O and KCl-$SrCl_2$-H_2O system at 25 ℃ were calculated by using Pitzer ion-interaction model and phase diagrams had been plotted. Agreement with experimental solubility indicated that the models can be successfully used to calculate the components solubility in the system containing strontium.

Key words: Pitzer ion-interaction model; Solubility; Strontium
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Concentration of Strontium in oil field brines of Qaidam basin has found to be high[1]. The strontium ion coexists with other ions such as sodium, potassium, chloride and sulfate. Extraction of the strontium from oil field brines requires the solubility data for phase systems encompassed in the natural brine. Pitzer ion-interaction model has been successfully applied in many calculations of solubilities and thermodynamic properties in natural water and complex brines[2-3]. In this paper, Pitzer model is adopted to calculate the solubility of NaCl-SrCl-H_2O and KCl-$SrCl_2$-H_2O system at 25 ℃.

1 THEORETICAL CONSIDERATION

Solubility products are used to calculate solubility, i.e. a salt solution is saturated at a given temperature and pressure when the ion activity product is equal to the solubility product. For a hydrated salt $M_{\nu_M}X_{\nu_X}\cdot\nu_0H_2O$, the solubility product K_{sp}, at a definite temperature for the dissolution reaction

$$M_{\nu_M}X_{\nu_X}\cdot\nu_0H_2O = \nu_M M^{+Z_M} + \nu_X X^{-Z_X} + \nu_0 H_2O \quad (1)$$

is expressed by

$$\ln K_{sp} = \nu_M \ln(m_M\gamma_M) + \nu_X \ln(m_X\gamma_X) + \nu_0 \ln a_w \quad (2)$$

where m_i and γ_i represent the concentration ($mol\cdot kg^{-1}$) and activity coefficient of the ions respectively.

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

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

where M_w is the molar mass of water and the sum covers all solute species. The activity coefficients γ and osmotic coefficient ϕ can be calculatd using the extended Pitzer ion-interaction model derived by Harvie C E and Weare S H[3].

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2 PITZER PARAMETERS AND SOLUBILITY PRODUCTS

The Pitzer single electrolyte parameters for NaCl, KCl and SrCl$_2$ are available in the literatures. These parameters are fitted from osmotic or activity coefficients by least-square method. And the values are listed in Table 1.

Table 1 Pitzer's binary parameters for single electrolyte at 25 ℃

	$\beta^{(0)}$	$\beta^{(1)}$	C^{Φ}	m_{max}/(mol·kg^{-1})	σ	Reference
NaCl	0.076 5	0.266 4	0.001 27	6	0.001	[4]
KCl	0.048 35	0.212 2	−0.000 84	4.8	0.000 5	[4]
SrCl$_2$	0.286	1.667	−0.000 652	4	0.003	[4]

For Pitzer's mixing parameters $\theta_{cc'}$, and $\psi_{cc'a}$, the authors use the values calculated by Clegg S L and Kim H T from osmotic coefficients. The parameters used for calculating the solubilities of the investigated systems are listed in Table 2.

Table 2 Pitzer mixing parameters for investigated systems at 25 ℃

system	$\theta_{cc'}$	$\psi_{cc'a}$	Reference
NaCl-SrCl$_2$-H$_2$O	0.056 2	−0.007 05	[5]
KCl-SrCl$_2$-H$_2$O	0.014 9	−0.020 1	[6]

The logarithm of the solubility products for NaCl, KCl and SrCl$_2$·6H$_2$O are also taken from reference. They are listed in Table 3.

Table 3 Values of $\ln K_{sp}$ of solid phase

Solid Phase	$\ln K_{sp}$	Reference
NaCl	3.63	[7]
KCl	2.058	[7]
SrCl$_2$·6H$_2$O	4.35	[8]

3 RESULTS AND DISCUSSION

To determine the applicability of the parameters and the solubility products, the component solubilities for NaCl-SrCl$_2$-H$_2$O and KCl-SrCl$_2$-H$_2$O systems at 25 ℃ are calculated on the basis of equation 2—3 and the Pitzer model. The calculated solubility data are listed in Table 4—5. It should be noted that solutes below their saturated solution molalities were fixed at 0, 0.5, 1, ... and the saturated solutes are calculated.

Table 4 The calculated solubility for NaCl-SrCl$_2$-H$_2$O at 25 ℃ (mol·kg^{-1})

NaCl	SrCl$_2$	Solid Phase
0	3.477	SrCl$_2$·6H$_2$O
0.5	3.324	ditto
1	3.173	ditto
1.5	3.023	ditto
2	2.876	ditto
2.015	2.871	SrCl$_2$·6H$_2$O+NaCl
2.442	2.5	NaCl
3.082	2	ditto
3.784	1.5	ditto
4.535	1	ditto
5.319	0.5	ditto
6.120	0	ditto

Table 5 The calculated solubility for KCl-SrCl$_2$-H$_2$O at 25 ℃ (mol·kg^{-1})

KCl	SrCl$_2$	Solid Phase
0	3.477	SrCl$_2$·6H$_2$O
0.5	3.413	ditto
1	3.355	ditto
1.377	3.316	SrCl$_2$·6H$_2$O+KCl
1.570	3	KCl
1.934	2.5	ditto
2.374	2	ditto
2.888	1.5	ditto
3.470	1	ditto
4.103	0.5	ditto
4.762	0	ditto

The solubility curves comparing the experimental results and the calculated results are shown in Fig. 1—2.

For the NaCl-SrCl$_2$-H$_2$O system, the solid phases determined by Kydynov K[9] are SrCl$_2$·6H$_2$O,

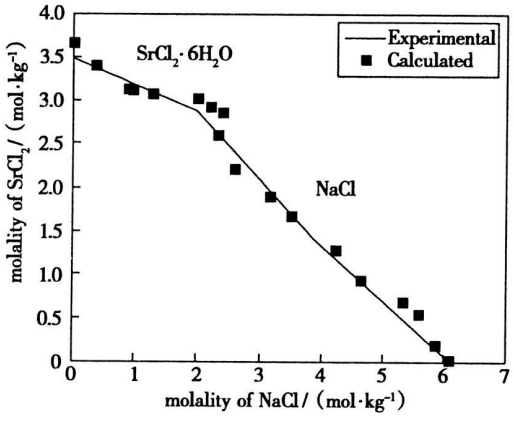

Fig. 1 Phase diagram of NaCl-$SrCl_2$-H_2O system at 25 ℃ from experiment and calculation

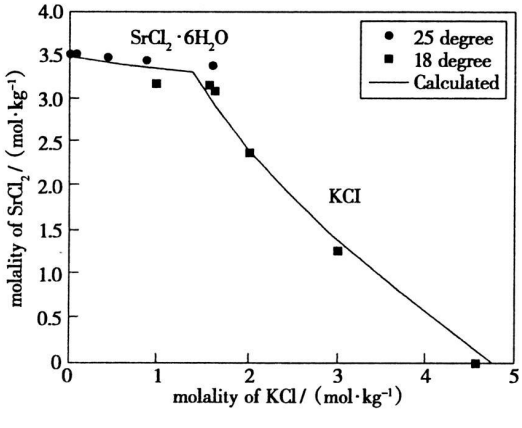

Fig. 2 Phase diagram of KCl-$SrCl_2$-H_2O system at 25 ℃ from experiment and calculation

$SrCl_2 \cdot 2H_2O$ and NaCl. The authors calculate two eutonic points and the results deviated from experimental data seriously. Assarsson G O reported that the transition temperature hexahydrate-dihydrate in binary $SrCl_2$-H_2O system is 61.3 ℃[11]. According to the literature[8], there is only one invariant point composed of $SrCl_2 \cdot 6H_2O$ and NaCl in the system at 25 ℃. The calculated eutonic point concentration for NaCl and $SrCl_2$ are 2.015 mol·kg^{-1} and 2.871 mol·kg^{-1}. The relative errors are 10% and 2% respectively. The deviation may be caused by incorrect determination of solid phase in the literature[9]. As being shown in Fig. 1, the experimental determined solubility of pure $SrCl_2$ is 3.672 mol·kg^{-1}. The calculated value is 3.477 mol·kg^{-1} and the result is consistent with the experimental values determined by Harkins W D (3.517 mol·kg^{-1})[10] and Milikan J (3.487 mol·kg^{-1})[9]. In Fig. 2, only four experimental points are determined by Harkins W D[10] and the eutonic point of the system is not determined. The calculated eutonic point concentrations for KCl and $SrCl_2$ are 1.377 mol·kg^{-1} and 3.316 mol·kg^{-1} respectively. The solubility isotherm at 18 ℃ determined by Assarsson G O[11] was plotted. As being shown, the solubility of the KCl at the equilibria increases appreciably.

The calculated component solubilities in investigated systems are consistent with the experimental data. The results indicate that the Pitzer model can be successfully applied to calculate the component solubilities of the systems constituted by Strontium.

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基于 Pitzer模型的 25℃时 NaCl-SrCl$_2$-H$_2$O和 KCl-SrCl$_2$-H$_2$O体系溶解度计算

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摘　要:用 Pitzer离子相互作用模型计算了 25℃时 NaCl-SrCl$_2$-H$_2$O体系和 KCl-SrCl$_2$-H$_2$O体系的溶解度并绘制了相图,计算值与实验值相符合。结果表明,Pitzer模型能够用于含锶水盐体系的溶解度计算。

关键词:Pitzer离子相互作用模型;溶解度;锶