Solubility Prediction of CsCl-Cs₂SO₄–H₂O System at 298.15K Using the Ion-Interaction Model

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Abstract: The component solubilities of CsCl-Cs₂SO₄-H₂O system at 298.15K were calculated by using Pitzer ion interaction model and its extended HW models. Excellent agreement with experimental solubilities indicated that the models can be successfully used to calculate the component solubilities. This study affords the necessary parameters for solubility predictions of complicated systems and establishes a theoretical basis for the separation of these valuable metals from salt lake brine.

Keywords: Pitzer ion-interaction model, solubility calculation, salt lake brine.

INTRODUCTION

The international demand of cesium and its compounds has increased dramatically, since the discoveries that these compounds are widely applied in the electronics, medication and defense industries [1]. Therefore, the researches of separating and extracting of cesium and its compounds from various sources attracted much interest of industrials and research institutes worldwide. Usually, cesium and its compounds were extracted from solid ore, however, the scarcity of useful ore and the environmental impact hampered the activities of producing cesium and its compounds from the ores, thus, it is essential to find the other sources of these compounds.

Concentration of cesium in salt lake brines of the Qinghai-Tibet plateau has been found to be high [2]. The ion concentration of cesium in the brine of Zabuye Salt Lake in Tibet has been determined as 12-21 mg/L, which is much higher than the international exploration standard. Therefore, the salt lake brine provides a rich source of cesium. In the brine, cesium was coexisted with other minerals such as lithium, sodium, potassium, chloride and sulfate [3], and extraction of cesium from these salt lakes requires the solubility data of the phase systems constituted by cesium, lithium, sodium, potassium, chloride and sulfate, therefore, studies of the component solubilities of the phase systems, in which cesium is involved is very important and essential. However, the determination of the component solubilities of the very complicated system at different temperature is very toilsome and laborious. Fortunately, the Pitzer ion-interaction model [4, 5] and its extended HW model [6-8] have been proved as the valuable tools to predict the mineral solubilities in natural water and complex brines [9-12].

In the prior publications, we calculated the component solubilities in the ternary systems of NaCl-RbCl-H₂O, KCl-CsCl-H₂O and KBr-CsBr-H₂O at 25°C [13]. In this article,

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we present the solubility calculation of CsCl-Cs₂SO₄-H₂O at 298.15K by using the Pitzer ion-interaction model. Some mixing ternary parameters derived from this calculation can be used in solubility prediction of more complicated quaternary or quinary systems constituted by Cs^+, Cl^-, SO_4^{2-} and other species.

THEORETICAL BACKGROUND

Pitzer's ion-interaction model and its extended Harvie and Weare model can be expressed by following equations:

$$\Sigma m_i(\varphi-1)=2[-A^\varphi I^{3/2}/(1+1.2I^{1/2})$$
$$+\Sigma\Sigma m_c m_a(B_{ca}^\varphi+ZC_{ca})$$
$$+\Sigma\Sigma m_c m_{c'}(\Phi_{cc'}^\varphi+\Sigma m_a\psi_{cc'a})$$
$$+\Sigma\Sigma m_a m_{a'}(\Phi_{aa'}^\varphi+\Sigma m_c\psi_{aa'c})] \tag{1}$$

$$\ln\gamma_M=z_M^2F+\Sigma m_a(2B_{Ma}+ZC_{Ma})$$
$$+\Sigma m_c(2\Phi_{Mc}+\Sigma m_a\psi_{Mca})$$
$$+\Sigma\Sigma m_a m_{a'}\psi_{aa'M}$$
$$+\left|z_M\right|\Sigma\Sigma m_c m_a C_{ca} \tag{2}$$

$$\ln\gamma_X=z_x^2F+\Sigma m_c(2B_{cX}+ZC_{cX})$$
$$+\Sigma m_a(2\Phi_{Xa}+\Sigma m_c\psi_{Xac})$$
$$+\Sigma\Sigma m_c m_{c'}\psi_{cc'X}$$
$$+\left|z_X\right|\Sigma\Sigma m_c m_a C_{ca} \tag{3}$$

$$F=-A^\varphi[I^{1/2}/(1+1.2I^{1/2})+2/1.2\ln(1+1.2I^{1/2})]$$
$$+\Sigma\Sigma B'_{ca}+\Sigma\Sigma m_c m_{c'}\Phi'_{cc'}$$
$$+\Sigma\Sigma m_a m_{a'}\Phi'_{aa'} \tag{4}$$

$$C_{MX}=C_{MX}^\varphi/2\left|z_M z_X\right|^{1/2} \tag{5}$$

$$Z=\Sigma\left|z_i\right|m_i \tag{6}$$

$$B_{MX}^\varphi=\beta_{MX}^{(0)}+\beta_{MX}^{(1)}e^{-\alpha MX\sqrt{I}}+\beta_{MX}^{(2)}e^{-12\sqrt{I}} \tag{7}$$

$$B_{MX}=\beta_{MX}^{(0)}+\beta_{MX}^{(1)}g(\alpha_{MX}\sqrt{I})+\beta_{MX}^{(2)}g(12\sqrt{I}) \tag{8}$$

$$B'_{MX}=\beta_{MX}^{(1)}g'(\alpha\sqrt{I})/I+\beta_{MX}^{(2)}g'(12\sqrt{I})/I \tag{9}$$

$$g(x)=2[1-(1+x)e^{-x}]/x^2 \tag{10}$$

$$g'(x)=-2[1-(1+x+x^2/2)e^{-x}]/x^2 \tag{11}$$

$$x=\alpha_{MX}\sqrt{I} \text{ or } 12\sqrt{I} \tag{12}$$

$$\Phi_{ij}^\varphi=\theta_{ij}+{}^E\theta_{ij}(I)+I^E\theta'_{ij}(I) \tag{13}$$

$$\Phi_{ij}=\theta_{ij}+{}^E\theta_{ij}(I) \tag{14}$$

$$\Phi'_{ij} = {}^{E}\theta'_{ij}(I) \tag{15}$$

In the above equations of (1) - (15), $\ln\gamma_i$ and ϕ represent the activity coefficient and osmotic coefficient. According to the Pitzer and HW models, the activity and osmotic coefficients are parametric functions of $\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ}, θ_{ij}, ψ_{Mca}. $\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ} are single parameters of a pure electrolyte. θ_{ij} represents the interaction of the two ions with the same sign and ψ_{Mca} represents the interactions among the three ions, in which the sign of the third one is different from the first two ions.

For a hydrated salt of $M_{vm}X_{vx}\cdot v_0H_2O$, its equilibrium constant, mean activity coefficient and activity of water could be expressed by:

$$M_{vm}X_{vx}\cdot v_0H_2O = v_M M^{+zm} + v_x X^{-zx} + v_0H_2O \tag{16}$$

$$\ln K = v_M \ln(m_M\gamma_M) + v_x\ln(m_X\gamma_X) + v_0 \ln a_{H2O} \tag{17}$$

$$\ln\gamma_{\pm} = (v_M \ln\gamma_M + v_x \ln\gamma_x)/v \tag{18}$$

$$\ln a_w = -\varphi(M_w/1000)\Sigma m_i \tag{19}$$

In the system of CsCl-Cs$_2$SO$_4$-H$_2$O, when the parameters of $\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ}, θ_{ij}, ψ_{Mca} of CsCl and Cs$_2$SO$_4$, and the concentration of CsCl are all known, the solubility of Cs$_2$SO$_4$ could be calculated from equations 1, 2, 3, 16, 17, 18 and 19.

PARAMETERIZATION

Pitzer's binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ}) for the pure electrolytes of CsCl-Cs$_2$SO$_4$-H$_2$O at 298.15K were available in the literature. These parameters are listed in Table **1**.

Table 1.   Pitzer's Binary Parameters for Single Electrolytes at 298.15 K

	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}	m_{max}	σ	Ref.
CsCl	0.0390	-0.0374	-0.0012	11.3	0.0030	[14]
Cs$_2$SO$_4$	0.0948	0.6026	-0.00025	3.11	0.00105	[15]

For Pitzer's binary mixing parameter θ_{ClSO4}, we adopted the data of Harvie (θ_{ClSO4}=0.02) [8]. The Pitzer ternary mixing parameters $\psi_{CsClSO4}$ is not available in the literature, and the measurements of the activity of the investigated system was not been found. Hence the evaluation of the mixing parameter relied on solubility data. $\psi_{CsClSO4}$ and the equilibrium constant were acquired by fitting the solubility data of the literature [16]. The obtained $\psi_{CsClSO4}$ is 0.007016. The solubility equilibrium constant $\ln K^{o}_{sp}$ of Cs$_2$SO$_4$ and CsCl are 1.9323 and 3.431. They are in good agreement with those in the literature (1.958 and 3.49). The deviations are due to the different concentration ranges for which the solubility equilibrium constants were calculated.

RESULTS AND DISCUSSION

To determine the accuracy of the parameters and the solubility equilibrium constants, the component solubilities for CsCl-Cs$_2$SO$_4$-H$_2$O system at 298.15K were calculated. The experimental and calculated solubility data are listed in Table **2**. The eutonic point was calculated with the obtained parameters. The solubility curves based on the experimental results and the calculated results are shown in Fig. (**1**). The letter 'm' in the axis labels means molality.

Table 2.   Solubility in the CsCl-Cs$_2$SO$_4$-H$_2$O System at 298.15K (in Molality)

Experimental		Calculated		Solid Phase
CsCl	Cs$_2$SO$_4$	CsCl	Cs$_2$SO$_4$	
0	5.1050	0	4.9608	Cs$_2$SO$_4$
1.5336	4.2702	1.5336	4.1938	Cs$_2$SO$_4$
2.9792	3.0695	2.9792	3.5318	Cs$_2$SO$_4$
4.8525	2.6085	4.8525	2.7617	Cs$_2$SO$_4$
5.8261	2.4125	5.8261	2.4007	Cs$_2$SO$_4$
7.7204	1.8716	7.7204	1.7746	Cs$_2$SO$_4$
8.4170	1.3468	8.0416	1.6785	Cs$_2$SO$_4$+ CsCl
10.5186	0.3667	10.3288	0.3667	CsCl
11.4127	0	11.0459	0	CsCl
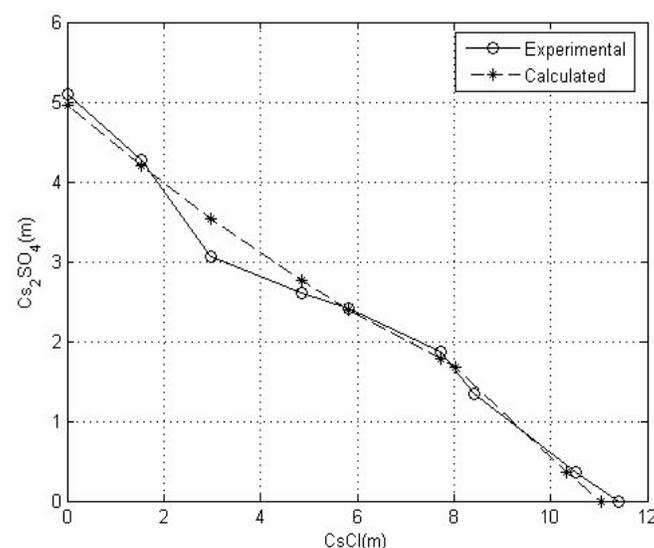
Fig. (1). Calculated and experimental solubility of CsCl-Cs$_2$SO$_4$-H$_2$O system at 298.15K.

The comparison between experimental and calculated results shows that the calculated results are consistent with the experimental data, although there is deviation on the third point in Fig. (**1**). This study indicated that the obtained mixing parameters and equilibrium constants are reliable and can be used in solubility calculation on more complicated system.

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