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Metastable Solubilities and Thermodynamic Properties of $SrSO_4$ Scale at 278.2 to 323.2 K

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In this paper, the isothermal evaporation method was used to determine the metastable solubilities of strontium sulfate ($SrSO_4$) at (278.2, 283.2, 303.2 and 323.2) K. During the evaporation progress, the concentrations of $SrSO_4$ were measured at a period time and a set of the results were fitted to empirical equations of evaporating times. The metastable solubilities were determined by the maximum concentration and the metastable region of $SrSO_4$ at 278.2 to 323.2 K was determined. By using simplified Pitzer equations and metastable solubilities at the given temperatures, the thermodynamic properties of $SrSO_4$ ($\gamma_\pm$, Φ, G^E) were calculated and all the calculated results were compared with the stable values calculated by the literature solubilities in this work. Then the thermodynamic ion product (Q_{sp}) of $SrSO_4$ were calculated and compared with the thermodynamic solubility product (K_{sp}) of $SrSO_4$ at different temperatures.

Keywords: Strontium sulfate, Metastable solubility, Metastable region, Thermodynamic property.

INTRODUCTION

Scale formation is the precipitation of a solid mineral from brine. Scale formation in oilfield can be divided into two cases: (1) changes of thermodynamic conditions (temperature, pressure, *etc.*) lead to the changes of ion equilibrium in aqueous solution and the solubilities of scale-forming components decline and then precipitate[1]; (2) mixture of waters with incompatible ions leads to precipitate[2,3]. Raju and El-Din[4] found that seawater was not compatible with formation water and the maximum amount of $SrSO_4$ formed at 20 vol % seawater whereas the maximum amount of $CaSO_4$ formed at 70 % seawater in 2004. Most oilfield waters contain a certain number of calcium, strontium, barium and sulfate ions. So the main scales are $SrSO_4$, $CaSO_4 \cdot nH_2O$ and $BaSO_4$.

Scale formation is a major problem in the oil industry and one of the most serious problems is the control of oilfield water's quality. It can occur at all parts of the stratum and wellbore, therefore, some wells and oil layers have to be prematurely abandoned. The existing scales in production tubing and equipment restrict fluid flow and lead to damage of emergency shutdowns, production equipment, increased maintenance cost and overall decrease in production efficiency.

Strontium sulfate ($SrSO_4$) scale is one of the most annoying and costly problems encountered in oilfield operations[5-7]. The problem is far from being solved. Previous researches of $SrSO_4$ scale were at the steady state (*i.e.* the stable equilibrium solubility). The solubility of $SrSO_4$ was measured by Culberson *et al.*[8] in water, synthetic seawater (35 % salinity) and in the single salt solutions (NaCl, KCl, $MgCl_2$, $CaCl_2$) at 25 °C. Reardon and Armstrong[9] measured the celestite ($SrSO_4$) solubility in pure water at temperature range of (283.15 to 363.15) K by achieving the equilibria with respect to crystalline solid phase from both undersaturated and supersaturated solutions and the results showed that solubility reached the maximum value near 298.15 K. Simultaneously, they also measured the solubility of $SrSO_4$ in NaCl solutions up to 5 m concentration and at (283.15 to 313.15) K. Jacques and Bourland[10] did research into the solubilities of $SrSO_4$ in sodium chloride brine and presented a predictive equation that could calculate solubility in water containing (0 to 100) g/L sodium chloride at temperatures from (311.15 to 422.15) K, with pressures from (689 to 20 684) KPa and total ionic strengths of 0 to 3.43. Many researchers[8,11-15] measured the solubility of $SrSO_4$ in pure water at 298.15 K, the values were (0.644, 0.621, 0.762, 0.692, 0.822 and 0.646) mmol/kg H_2O, respectively. In 1935, Gallo[16] measured the solubilities of $SrSO_4$ from (5 to 95) °C and the values decreased after an initial increase, the maximum solubility was obtained when the temperature was 40 °C and was different from the result obtained by Reardon and Armstrong[9]. The tendency obtained by Strbüel[17] was that the solubilities declined from (22 to 100.5) °C and different from the results obtained by Gallo[16]. Kan *et al.*[18] developed a new corrosion-proof, high-temperature, high-pressure flow-through apparatus to measure mineral salt solubilities under relevant oil and gas production conditions. García *et al.*[19] added the pressure parameters to the extended UNIQUAC model presented by Thomsen and Rasmussen[20] and the improved model had been used for correlation and prediction of solid-liquid equilibrium (SLE) of $CaSO_4$, $CaSO_4{\cdot}2H_2O$, $BaSO_4$ and $SrSO_4$ at temperature up to 300 °C and pressures up to 1000 bar. The results obtained by García *et al.*[19] showed that the new model can represent binary, ternary and quaternary solubility data within the experimental accuracy in the temperature range from (-20 to 300) °C and the pressure range from (1 to 1000) bar.

Previous researches also used the stable solubility of $SrSO_4$ to present the prediction models of $SrSO_4$ scale. Yuan *et al.*[21] used the solubility of $SrSO_4$ to present a model for predicting the scaling tendencies of $SrSO_4$ resulting from the mixing of injected and formation waters and from temperature and pressure effects. Todd and Yuan[22] gave the result of laboratory experiments to study the formation of $SrSO_4$ solid solution in multi-pressure-tapped cores. Todd and Yuan[23] also did a laboratory study at 343.15 K to examine (Ba, Sr) SO_4 solid-solution scale formation in porous media and the formation damage resulting from the mixing of two incompatible waters and the results of experiments obtained at the elevated temperatures demonstrate that substantial scale deposition can occur in a rock core and can make the considerable decline of rock permeability as a result of concurrent flowing of two incompatible waters. Monnin[24] obtained a model for barite and celestite solubilities in the Na-K-Ca-Mg-Ba-Sr-Cl-SO_4-H_2O system to 200 °C and to 1 kbar and the pressure corrections were partially validated by comparing model predictions to measured barite and celestite solubilities in pure water to 1 kbar and in NaCl solutions to 500 bars.

However, previous researches have failed to consider the metastable solubility of $SrSO_4$. The phase diagram of solid-liquid binary system for a substance with a positive temperature coefficient of solubility in the given temperature interval is given in Fig. 1[25]. As Fig. 1 shows, it can be divided into three regions: the unsaturated region is under the stable solubility curve; the unstable region is below the supersaturation curve and the region between the stable solubility curve and the supersaturation curve is called the metastable region. In the unstable region, nucleation and growth are spontaneous. Little control can be taken of the behaviour in this region. In the metastable region, growth of crystals will occur even under static conditions when dust or seeds are introduced and nuclei can be generated by agitation. The behaviour in the metastable region is largely more controllable[26]. The knowledge of the solubility curve and the stability of the solution in the vicinity of the equilibrium point, as indicated by metastable zone width, is important to the successful development, optimization and scale-up of a crystallization process[27].

The crystal precipitate and different constructions of $SrSO_4$ are significant to predict the formation of $SrSO_4$ scale. However, no literatures have reported about the metastable solubility and metastable region of $SrSO_4$ before.

With the change of underground temperature, the concentrations of $SrSO_4$ in oilfield water change largely. In order to indicate the changes of the solubility of $SrSO_4$ from low to high temperatures, the metastable solubilities of $SrSO_4$ are determined at (278.2, 283.2, 303.2 and 323.2) K, respectively. In the process of oil production, the solubility of $SrSO_4$ changes largely with time, so it is necessary to study the dynamic change of concentration of $SrSO_4$ with time in pure water.

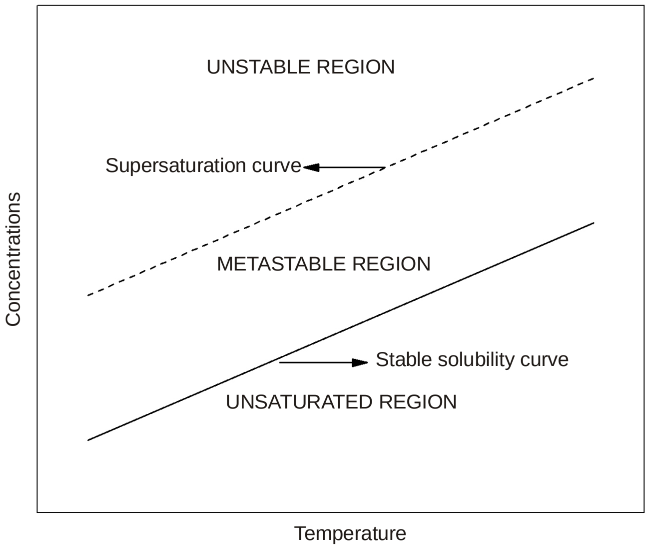

Fig. 1. Part of the phase diagram for a solid-liquid binary system

The research results reported in this article are in three parts: (1) the concentrations of $SrSO_4$ with the isothermal evaporation of $SrSO_4$ solutions are measured and the metastable solubilities and metastable region of $SrSO_4$ from (278.2 to 323.2) K are determined. (2) The concentrations of $SrSO_4$ are fitted as equations of evaporating time. (3) The thermodynamic properties ($\gamma_\pm$, Φ, G^E, Q_{sp}, K_{sp}) of metastable and equilibrium $SrSO_4$ are calculated at multi-temperature.

EXPERIMENTAL

A SHH-250 type thermostatic evaporator with a precision of ± 0.1 K and made by the Chongqing INBORN Instrument Corporation, China, was used for the experiments in this study.

The chemical used in this work was of analytical purity grade obtained from Tianjin Kermel Reagent Plant. It was strontium sulfate [$SrSO_4$, 98 % (by mass)]. A TKA GenPure made by TKA Wasseraufbereitungssysteme GMBH, German, was used to obtain the ultrapure water with an electrical conductivity less than 1×10^{-5} S m^{-1} and the salinity less than 0.1 mg/L. For each experiment, the required amounts of reagents were dissolved in enough ultrapure water to produce the experimental solutions.

The strontium ion concentration was determined by inductively coupled plasma optical emission spectrometry [precision: less than 0.0008 mmol/kg H_2O (by molality), type ICP-OES 5300 V], made by PerkinElmer, German.

The isothermal evaporation method[28] was employed in this study. According to the stable equilibrium solubility of $SrSO_4$ in pure water at (278.2, 283.2, 303.2 and 323.2) K, the appropriate quantity $SrSO_4$ were dissolved into about 250 mL of ultrapure water and loaded into clean opened polyethylene containers (15 cm long, 10.5 cm wide, 5 cm high). The containers were placed in a thermostatic evaporator (SHH-250 type). The temperatures of the solution inside the evaporator were controlled to (278.2, 283.2, 303.2 and 323.2) K and measured by a Joule thermocouple with an operating range of (258.2 to 333.2) K and a system precision of ± 0.1 K.

After the solution in the polyethylene container evaporating for a certain time, a 5 mL sample of the clear liquid phase solution was taken out periodically from the liquid phase of the polyethylene container through a pipette and then diluted to 50 mL in a volumetric flask with ultrapure water for quantitative analysis. The sampling periods were, respectively (0.5, 1, 1.5, 2 and 4) h. During evaporation progress of the solutions, the course of crystallization of $SrSO_4$ was observed by naked eye. When the crystal of $SrSO_4$ was found in the solution for the first time, we recorded the corresponding evaporation time. The same procedure was repeated until the solution was fully evaporated.

In order to testify the reproducibility and uncertainty of the measurements in this study, the parallel experiments were done for five times at each temperature and the order numbers of the experiments are I, II, III, IV and V were shown in Table-3, respectively.

To indicate the scaling mechanism of $SrSO_4$ on the basis of thermodynamic properties, it is necessary to calculate the thermodynamic properties of $SrSO_4$.

The solid-liquid equilibrium for $SrSO_4(s)$ is

$$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}(aq)$$

The thermodynamic solubility product (K_{sp}) of $SrSO_4$ at the stable state is given by

$$K_{sp} = a_{Sr^{2+}(aq)} \times a_{SO_4^{2-}(aq)} \qquad (1)$$

and for pure $SrSO_4$ dissolving

$$K_{sp} = s^2 \times \gamma_\pm^2 \qquad (2)$$

and for the pure $SrSO_4$ dissolving at metastable state, the thermodynamic ion product (Q_{sp}) of $SrSO_4$ at the metastable state is given by

$$Q_{sp} = s^2 \times \gamma_\pm^2 \qquad (3)$$

where s is the solubility of $SrSO_4$, g/100g H_2O and s = 10 M_{SrSO_4} m, m is the molality of $SrSO_4$ solution, mol/kg (the values of m is using the average values in this study), M_{SrSO_4} is the molar mass of water, 183.6826 g/mol and $\gamma_\pm$ is the mean activity coefficient of $SrSO_4$. From eqn. 2 and 3, we derived the logarithmic relationship between s and $\gamma_\pm$

$$-\ln s = -\frac{1}{2}\ln K_{sp} + \ln \gamma_\pm \text{ or } -\ln s = -\frac{1}{2}\ln Q_{sp} + \ln \gamma_\pm \qquad (4)$$

Based on the Pitzer equations, we present the final equations for the mean activity coefficients ($\gamma_\pm$) and osmotic coefficient (ϕ) of $SrSO_4$ in pure water as

$$\ln \gamma_\pm = 4 \times f^\gamma + 2 \times m \times B_{MX}^\gamma \qquad (5)$$

$$\phi - 1 = 4 \times f^\phi + 2 \times m \times B_{MX}^\phi \qquad (6)$$

where the subscripts M and X refer to Sr^{2+} and SO_4^{2-} ions, m is the molality of the $SrSO_4$ solution. f^γ, f^ϕ, B_{MX}^γ and B_{MX}^ϕ are the functions of ionic strength. They are defined as follows:

$$f^\gamma = -A^\phi[I^{1/2}/(1+bI^{1/2}) + \frac{2}{b}\ln(1+bI^{1/2})] \qquad (7)$$

$$B_{MX}^\gamma = 2\beta_{MX}^{(0)} + 2\beta_{MX}^{(1)} \cdot \{1-[1+\alpha_1 \cdot I^{1/2} - \frac{1}{2}(\alpha_1 \cdot I^{1/2})^2]\cdot e^{-\alpha_1 \cdot I^{1/2}}\}/(\alpha_1 \cdot I^{1/2})^2 + 2\beta_{MX}^{(1)} \cdot \{1-[1+\alpha_2 \cdot I^{1/2} - \frac{1}{2}(\alpha_2 \cdot I^{1/2})^2]\cdot e^{-\alpha_2 \cdot I^{1/2}}\}/(\alpha_2 \cdot I^{1/2})^2 \qquad (8)$$

$$f^\phi = -A^\phi[I^{1/2}/(1+bI^{1/2})] \qquad (9)$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \cdot e^{-\alpha_1} \cdot I^{1/2} + \beta_{MX}^{(2)} \cdot e^{-\alpha_2} \cdot I^{1/2} \qquad (10)$$

where I is the ionic strength of the solution, $I = \frac{1}{2}\sum mZ_i^2$, m is the molality of $SrSO_4$ solution and Z_i is the valence number of each ion; b is the empirical constant, 1.2. A^ϕ is the Debye-Hükel coefficient of osmotic coefficients[30]. For the 2-2 type electrolyte, $\alpha_1 = 2$, $\alpha_2 = 1.4$.

The Pitzer coefficients $\beta^{(0)}$, $\beta^{(1)}$ and $\beta^{(2)}$ for $SrSO_4$ at temperatures other than 298.15 K can be calculated by using the equation[29].

$$\beta^{(i)} = a + b\,(T\text{-}Tr) + c(T^2\text{-}Tr^2) \qquad (11)$$

where T_r is the reference temperature, 298.2 K.

The excess Gibbs free energy (G^E) and activity of water (a_w) are calculated by the following equations:

$$G^E = 4mRT(1-\phi+\ln\gamma_\pm) \qquad (12)$$

$$a_w = \exp(-4 \cdot M_A \cdot \phi / 1000) \qquad (13)$$

where M_A is the molar mass of water, 18.016 g/mol; R is the molar gas constant, 8.3145 J mol^{-1} K^{-1}; ϕ is the calculated osmotic coefficient of $SrSO_4$; $\gamma_\pm$ is the calculated mean activity coefficient of $SrSO_4$.

RESULTS AND DISCUSSION

According to the parallel experiments, the initial concentration of $SrSO_4$ solution and the metastable solubilities are basically the same at each temperature, we choose a set of the parallel experiments to show the change of concentration of $SrSO_4$ solution during the evaporating process and the results at (278.2, 283.2, 303.2 and 323.2) K are listed in Table-1.

And then, the data at each temperature are plotted and fitted with the evaporating time into curve equations in Fig. 2. The parameters of the fitted equations are listed in Table-2 and concentration = $a \cdot t^3 + b \cdot t^2 + c \cdot t + d$. We just present the metastable solubilities in Table-3 and the results of the parallel experiments are basically the same, so the metastable method is feasible. Simultaneously, we average the metastable solubilities of the parallel experiments at each temperature.

As shown in Fig. 2, the concentrations of $SrSO_4$ increase by the evaporating times. The maximum concentration is the metastable solubility of $SrSO_4$ at the corresponding temperature. Notice that the tendencies of the curves are not parabolic as usual, but the samples were continuously and periodically taken out from the containers until the solutions were fully evaporated.

Table-3 shows the results of parallel experiments, the reproducibility (RSD) and uncertainty (U) of measurements comparisons. It also shows the difference between metastable

TABLE-1
A SET OF EXPERIMENTAL CONCENTRATIONS OF STRONTIUM SULFATE WITH EVAPORATING TIMES

Time (h)	Concentration (mmol/kg H_2O)	Time (h)	Concentration (mmol/kg H_2O)	Time (h)	Concentration (mmol/kg H_2O)	Time (h)	Concentration (mmol/kg H_2O)
278.2 K		283.2 K		303.2 K		323.2 K	
19.00	0.3857	22.08	0.6409	23.92	0.6932	13.50	0.7688
24.00	0.4092	24.00	0.7482	24.92	0.8405	14.50	0.7843
28.00	0.4555	25.50	0.8190	25.92	0.9553	15.50	0.8799
43.00	0.5632	27.00	0.8751	26.92	1.0392	16.75	0.9473
45.00	0.6014	28.50	1.0744	27.92	1.2127	17.50	1.0365
47.00	0.6023	30.00	1.1681	28.92	1.3862	17.75	1.1293
49.00	0.5988	31.00	1.3805	29.92	1.3827	18.25	1.2637
51.00	0.6895	-	-	30.92	1.5521	19.75	1.6304
53.00	0.7414	-	-	-	-	20.50	1.7970
64.00	1.2566	-	-	-	-	-	-
66.00	1.4204	-	-	-	-	-	-

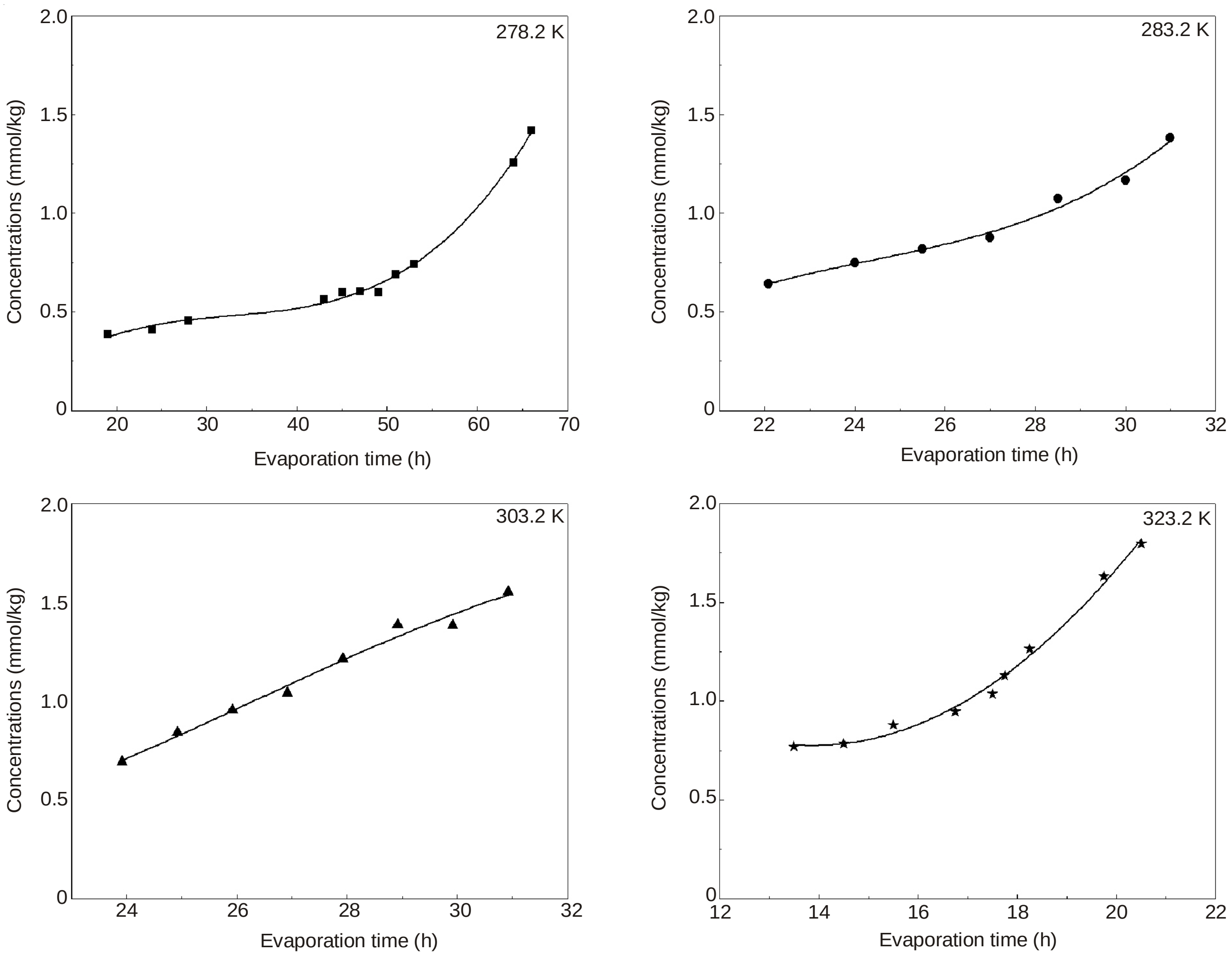

Fig. 2. Concentrations of $SrSO_4$ with evaporating time at (278.2, 283.2, 303.2 and 323.2) K; In this study, ■ is the concentration of $SrSO_4$ at 278.2 K; ● is the concentration of $SrSO_4$ 283.2 K; ▲ is the concentration of $SrSO_4$ at 303.2 K; ✶ is the concentration of $SrSO_4$ at 323.2 K

TABLE-2
PARAMETERS OF FITTED CURVES AT EACH TEMPERATURE

Temperature (K)	a	b	c	d
278.2	2.1311×10^{-5}	-0.00208	0.07196	-0.3901
283.2	1.0100×10^{-3}	-0.07347	1.8375	-14.9227
303.2	-5.9470×10^{-4}	0.04687	-1.1024	8.3885
323.2	3.8207×10^{-5}	0.02187	-0.6279	5.1754

solubilities and stable solubilities of $SrSO_4$ at (278.2, 283.2, 303.2 and 323.2) K[16]. Simultaneously, as shown in Table-3, the metastable solubilities are obviously larger than the stable solubilities. And the stable solubility curve and the supersaturation curve of $SrSO_4$ from (278.2 to 323.2) K are shown in Fig. 3. As shown in Fig. 3, the region between the stable solubility curve and the supersaturation curve is the metastable region of $SrSO_4$ at the given temperature interval in this paper. At a constant temperature, evaporating the $SrSO_4$ solution from initial A' leads to point A on the stable solubility curve. At this point, the solution is just saturated and in equilibrium with the solid phase. Further isothermal evaporation follows section AB in the metastable region up to the metastable boundary (*i.e.* the supersaturation curve)-point B. After passing this limit, the strontium sulfate solution is in a labile state and the solid phase is immediately and spontaneously precipitated.

When the $SrSO_4$ solution is evaporated to a certain time, the crystal of $SrSO_4$ begins to occur and then the solution is supersaturated. The evaporation times of $SrSO_4$ solution that the crystal occurred at the first time are (43, 25.5, 25 and 16.75) h, respectively, at (278.2, 283.2, 303.2 and 323.2) K.

The thermodynamic properties ($\gamma_\pm$, Φ, G^E, Q_{sp}, K_{sp}) of $SrSO_4$ were calculated by simplified Pitzer equations. All the calculations can provide theoretical foundations for the prediction of $SrSO_4$ scale in oil water.

According to eqns. 2 to 5,7,8 and 11, we calculated the mean activity coefficients ($\gamma_\pm$) and thermodynamic ion product (Q_{sp}) of $SrSO_4$ by using the experimental metastable solubilities (the average values). The thermodynamic solubility product (K_{sp}) and mean activity coefficients of $SrSO_4$ at the same temperatures were calculated by the literature data and then compared with the metastable results.

Table-4 shows the calculated results of mean activity coefficients of aqueous strontium sulfate in pure water, the ion product and solubility product of $SrSO_4$. As Table-4 shows, the ion product of $SrSO_4$ at metastable state is larger than the stable solubility product.

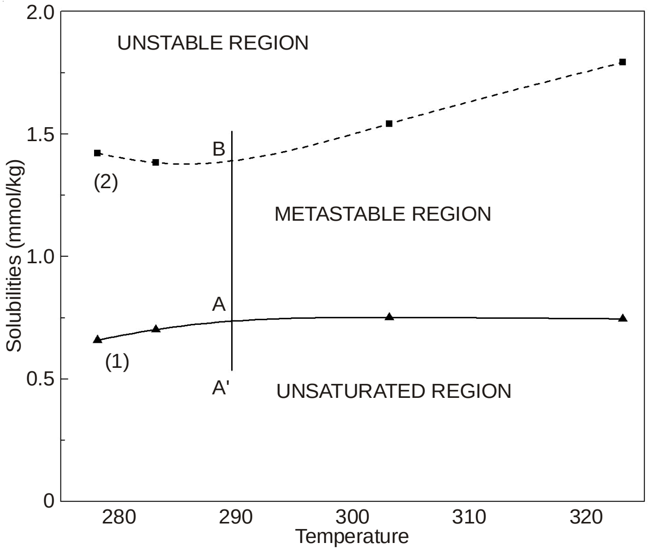

Fig. 3. Stable solubility curve of $SrSO_4$ (1) and the supersaturation curve (2) of $SrSO_4$; The solid curve (1) is the stable solubility line of $SrSO_4$; The dotted curve (2) is the supersaturation line; ■, in this study, is the metastable solubility of $SrSO_4$; ▲, in this study, is the stable solubility of $SrSO_4$

Combining eqns. 6 and 9 to 11 can calculate the osmotic coefficients (ϕ) of $SrSO_4$ in pure water by using the experimental metastable solubility and stable solubilities. Then the values are shown in Table-4. And the metastable osmotic coefficients of $SrSO_4$ are smaller than the stable state ones as shown in Table-4.

By using the mean activity and osmotic coefficients calculated before in this study, we have calculated the values of G^E and a_w easily and the results are shown in Table-4. As is shown in Table-4, the values of G^E at metastable state are smaller than the stable state and the values of a_w at metastable state are bigger than the stable state.

Conclusion

The concentration values of $SrSO_4$ in the process of evaporation were measured and a set of the results were fitted

TABLE-3
METASTABLE EQUILIBRIUM SOLUBILITIES AND COMPARISONS BETWEEN METASTABLE AND STABLE EQUILIBRIUM SOLUBILITIES AT EACH TEMPERATURE

Temperature (K)	Stable	Metastable							
	Solubility (mmol/kg H_2O)	Solubility (mmol/kg H_2O)						RSD (%)	U (mmol/kg H_2O)
		I	II	III	IV	V	Average		
278.2	0.6590	1.4140	1.4266	1.4197	1.4232	1.4204	1.4208	0.3288	0.0021
283.2	0.7020	1.3994	1.3845	1.3708	1.3814	1.3805	1.3833	0.7492	0.0046
303.2	0.7510	1.5045	1.5310	1.5612	1.5589	1.5521	1.5415	1.5494	0.0107
323.2	0.7460	1.7664	1.8161	1.7865	1.8052	1.7970	1.7924	1.0580	0.0085

TABLE-4
CALCULATED THERMODYNAMIC PROPERTIES (ln $\gamma_\pm$, Q_{sp}, K_{sp}, ϕ and G^E) OF $SrSO_4$ AND ACTIVITY OF WATER (a_w)

Temperature (K)	Metastable							Stable						
	Molality (mmol/kg H_2O)	ln s	ln $\gamma_\pm$	$Q_{sp} \times 10^4$	ϕ	G^E (kJ/mol)	a_w	Molality (mmol/kg H_2O)	ln s	ln $\gamma_\pm$	$K_{sp} \times 10^4$	ϕ	G^E (kJ/mol)	a_w
278.2	1.4208	-3.6462	-0.3846	3.1546	0.8931	-3.6484	0.9377	0.6590	-4.4146	-0.2682	0.8562	0.9236	-1.1695	0.9356
283.2	1.3833	-3.6747	-0.3829	2.9897	0.8937	-3.5916	0.9376	0.7020	-4.3505	-0.2777	0.9549	0.9212	-1.3154	0.9358
303.2	1.5415	-3.5644	-0.4208	3.4559	0.8841	-4.7382	0.9383	0.7510	-4.2831	-0.2826	1.0642	0.9185	-1.5867	0.9359
323.2	1.7924	-3.4136	-0.4758	4.1850	0.8702	-6.6665	0.9392	0.7460	-4.2902	-0.2910	1.0416	0.9187	-1.7105	0.9359

to equations of evaporating times. Then the metastable solubilities of $SrSO_4$ at (278.2, 283.2, 303.2 and 323.2) K were determined in this work. In this study, the metastable solubilities of $SrSO_4$ were compared with the stable solubilities measured by the previous studies. The metastable region of $SrSO_4$ from (278.2 to 323.2) K was also determined simultaneously and can be used to predict the formation of $SrSO_4$ scale.

The thermodynamic properties ($\gamma_{\pm}$, Φ, G^E, Q_{sp}) of $SrSO_4$ and a_w were calculated by the metastable solubilities and simplified Pitzer equations. All these thermodynamic properties were compared with the stable values.

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