Strontium Sulfate Precipitation from Electrolyte Solutions

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The formation of scale deposits is a serious problem in the operation of oil fields, desalination plants and geothermal wells. Oil field scales are formed mainly from the sparingly soluble sulfates and carbonates of calcium, strontium and barium. All the available scale prediction models are based on thermodynamics and, hence, can predict only the potential to form scale. To understand and predict actual scale formation, it is necessary to study and incorporate into scale prediction models, the kinetics and mechanism of precipitation from solution over wide ranges of temperature, pressure, ionic strength and supersaturation. The kinetic data available in the literature cover a reasonably wide range of supersaturation, but are in a narrow range of temperature around 298 K. There are hardly any discussions on the effects of ionic strength and pressure on spontaneous precipitation.

In this work, the precipitation of strontium sulfate from supersaturated solutions was studied by monitoring the changes in strontium ion concentration during spontaneous precipitation. This work presents the experimental results on the effects of temperature and ionic strength on the rate constant. Kinetic rate expressions, which may be used in the development of models for predicting scale formation, are developed.

Experimental Studies

The kinetics of spontaneous precipitation of strontium sulfate was studied in a batch reactor. The apparatus consisted of a 2-L glass-lined Parr reactor with a heating jacket, temperature controller, attachments for measuring temperature and pressure, liquid sampling, nitrogen purging, and stirring.

Strontium sulfate was precipitated on a U-tube section (316 stainless steel) immersed in a supersaturated solution in the reactor. Before use, the U-tube test section, the thermowell and stirrer shaft were thoroughly polished with silicon carbide grinding paper of 600 grit and cleaned to reduce surface imperfections. The temperature of the test section was maintained constant by recirculating a constant temperature fluid.

At the commencement of an experiment, a supersaturated solution of strontium sulfate was prepared by mixing in the glass liner known concentrations of reagent-grade strontium chloride and sodium sulfate in double distilled water. The concentrations of the two solutions were predetermined so that the initial supersaturation resulted when mixed. Supersaturation ratios (C/C_{eq}) during the experiments were in the range of 1.0 to 4.0, where C is the strontium ion concentration at any time t and C_{eq} is the strontium equilibrium concentration at the solution temperature and ionic strength.

The rate of precipitation was followed by drawing liquid samples through a filter assembly (0.45 micron) at various time intervals over a 10- to 50-h period, until the solution showed little change in strontium concentration with time. The strontium ion concentration of each sample was determined by atomic absorption spectrophotometry. A new test section and filter were used in each experiment. The study was conducted over the temperature range of 303 to 398 K and ionic strength of 0.02 to 4.5 molal. The variation in ionic strength was achieved by adding sodium chloride.

Results and Discussion

The changes in strontium ion concentration as a function of time at temperatures from 303 to 398 K are shown for some of the experiments in Figure 1. The actual conditions of the experiments are given in Tables 1 and 2. In general, the supersaturation ratio (C/C_{eq}) varied from 3–4 at the beginning to 1–2 at the end of each experiment (Table 1). The rates of $SrSO_4$ precipitation obtained from the desupersaturation of solution were fitted to the overall rate equation:

$$-dC/dt = (ks)_c(C - C_{eq})^n \tag{1}$$

where $(ks)_c$ is the rate constant based on concentration driving force, and n is the order of reaction.

Figure 2 shows the plots of $-\log(-dC/dt)$ vs. $-\log(C - C_{eq})$ for experimental results at various temperatures. It was found that over a wide range of the experimental conditions, the order was consistently around two within a period representing approximately 90 percent of the concentration range covered. This is similar to the observation of strontium sulfate seeded

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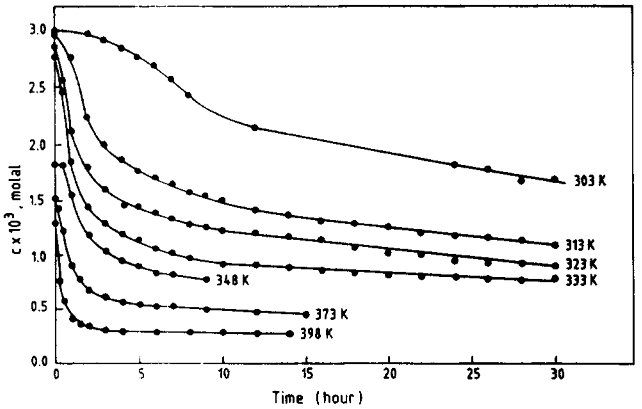

Figure 1. Strontium ion concentration in solution vs. time for $SrSO_4$ precipitation in Experiments 2(303 K), 3(313 K), 6(323 K), 5(333 K), 35(348 K), 39(373 K), and 38(398 K).

crystal growth at 298 K by Campbell and Nancollas (1969). After the second-order growth period, the first-order precipitation rate was evident in some experiments (Experiment 6 at 323 K in Figure 2). The circumstances leading to first-order dependence may be due to a diffusion-controlled step when the crystals were larger and supersaturations were very low (Chiang and Donohue, 1988; Lee et al., 1988).

To obtain more accurate rate constants from the precipitation data, the integrated form of Eq. 1, with $n=2$, was used to fit the data:

$$1/(C-C_{eq})-1/(C-C_{eq})_{t=0}=(ks)_c t \tag{2}$$

where C_{eq} was calculated from the thermodynamic solubility product (K^o_{sp}) and mean activity coefficient ($\gamma_\pm$):

$$C_{eq}=(K^o_{sp})^{1/2}/\gamma_\pm \tag{3}$$

The large experimental solubility database of Vetter et al. (1983) was used to determine $\gamma_\pm$.

Temperature Effect

For the spontaneous precipitation of $SrSO_4$, the apparent activation energy obtained by the Arrhenius plot of the concentration rate constants over the temperature range 303 to 398 K (Figure 3) was 59 kJ/mol. The value reported by Lee et al. (1988) over the temperature range of 303-333 K was 85 kJ/mol. The discrepancy in the activation energies of the two studies is believed to be due mainly to the different sets of strontium sulfate solubility data used in the analysis of the data. The limited solubility data of Jacques et al. (1979) used by Lee et al. (1988) were higher in value at higher temperatures than the comprehensive data of Vetter et al. (1983) used in this study. For the same precipitation rate, the rate constants obtained in the previous study were higher than those obtained in this study, since the relative supersaturation is lower when a higher solubility value is used.

Table 2. Rate constants of $SrSO_4$ Precipitation and Activity Coefficients at 333 K and Atmospheric Pressure at Various Ionic Strengths

Expt. No.	*Ionic strength* Initial (molal)	Final (molal)	$(ks)_c$ ($\text{molal}^{-1}\cdot\text{h}^{-1}$)	$(ks)_a$	$\gamma_\pm$
5	0.0171	0.0088	380	710	0.732
43	0.080	0.073	127	567	0.473
32	0.915	0.905	17.4	518	0.183
33	2.166	2.156	10.2	560	0.135
34	4.502	4.492	9.6	580	0.129

The temperature dependence of rate constant for second-order $SrSO_4$ precipitation in $\text{molal}^{-1}\cdot\text{h}^{-1}$, based on the results of this study, may be represented by the Arrhenius equation as:

$$(ks)_c=4.06\times10^{11}\exp(-7{,}050/T) \tag{4}$$

where T is absolute temperature. The preexponential factor for $SrSO_4$ precipitation in the above equation is small compared to the value of about 3.6×10^{15} $\text{molal}^{-1}\cdot\text{h}^{-1}$ for the standard collision frequency of a bimolecular reaction, indicating that $SrSO_4$ precipitation is a slow reaction. The second-order dependence of the rate and the activation energy of this study suggest that the spontaneous precipitation of $SrSO_4$ is surface-reaction-controlled. The absence of any appreciable effect of mixing observed during this study supports the surface control mechanism.

Influence of Ionic Strength

The rates of precipitation over the range 0.02 to 4.5 molal

Table 1. Experimental Conditions and Rate Constants of $SrSO_4$ Precipitation at Atmospheric Pressure

Expt. No.	Temp. T (K)	Time t (h)	*Ionic Strength* Initial ($I\times10^3$	Final molal)	*Solution Conc.* Initial ($C\times10^3$	Final molal)	*Equil. Conc.* Initial ($C_{eq}\times10^3$	Final molal)	*Rate Constants* $(ks)_a$	$(ks)_c$ ($\text{molal}^{-1}\cdot\text{h}^{-1}$)
2	303	120	17.54	10.85	2.92	1.250	0.858	0.817	55.7	25.5
3	313	30	17.79	10.23	2.98	1.093	0.842	0.796	170.2	82.8
4*	313	30	17.50	11.84	2.92	1.503	0.841	0.807	71.7	34.4
7**	313	50	17.08	10.60	2.80	1.183	0.839	0.799	103.6	50.6
9†	313	8	18.09	13.43	2.58	1.413	0.858	0.831	326	148
6	323	50	16.63	8.89	2.77	0.837	0.794	0.746	296	147
8	323	30	17.29	9.97	2.88	1.050	0.799	0.755	310	155
5	333	30	17.15	8.89	2.86	0.791	0.746	0.697	710	380
35	348	9	11.16	6.93	1.83	0.770	0.618	0.529	1,005	565
39	373	15	9.01	4.72	1.52	0.476	0.456	0.450	4,700	2,300
38	398	13	5.57	3.53	1.29	0.277	0.383	0.370		

*No stirring and no metal surface
**No stirring and all metal surface
†Seeded metal surface

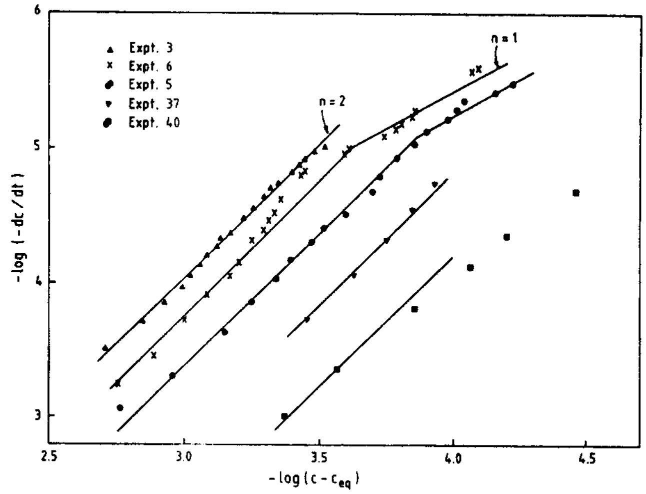

Figure 2. Plots of $-\log(-dC/dt)$ vs. $-\log(C-C_{eq})$ showing regions of second-order ($n=2$) and first-order ($n=1$) dependence of the rate of $SrSO_4$ precipitation in experiments 3(313 K), 6(323 K), 5(333 K), 37(373 K), and 40(398 K).

ionic strength (I) at 333 K obeyed second-order kinetics as seen from the linear nature of the plots in Figure 4. The concentration rate constants, $(ks)_c$, and the calculated $\gamma_\pm$ at different ionic strengths are given in Table 2 and plotted as Figure 5. Also shown in Table 2 are the activity rate constants, $(ks)_a$, which are related to the concentration rate constants, $(ks)_c$, by the relation:

$$(ks)_c = (ks)_a\, \gamma_\pm^{\,2} \qquad (5)$$

Figure 5 shows that $(ks)_c$ is a strong function of ionic strength at low ionic strengths and a weak function at high ionic strengths ($I > 1$ molal) and $(ks)_a$ to be fairly constant for $I > 0.1$ molal. The rate constants were adequately described as a function of ionic strength by the relation:

$$\log(ks)_c = 2.8550 - 2.9186\, I^{1/2} + 1.5071 I - 2.571\, I^{3/2} \qquad (6)$$

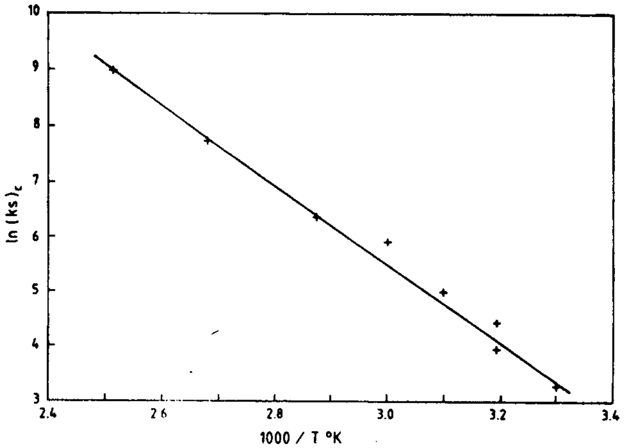

Figure 3. Arrhenius plot of concentration rate constants at various temperatures.

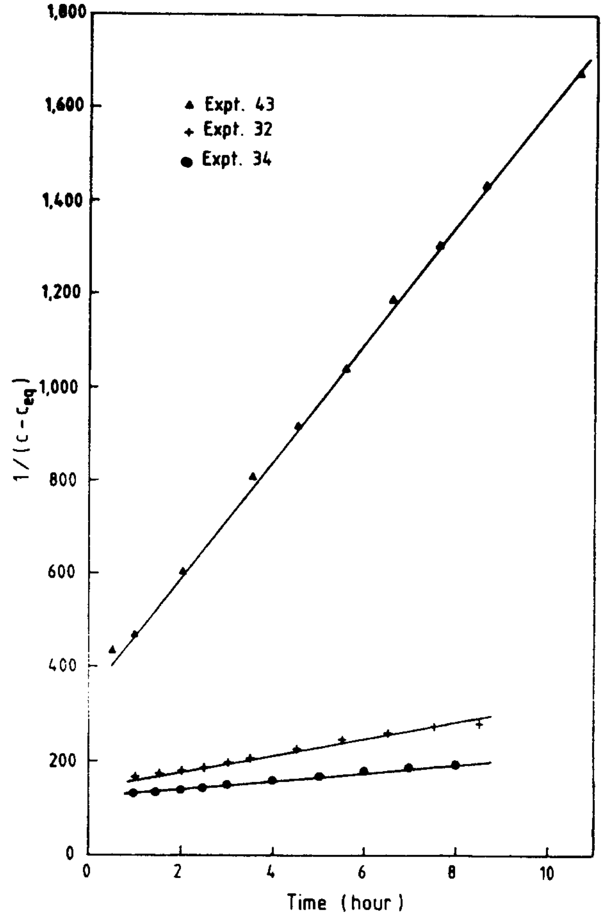

Figure 4. Integrated form of the second-order rate equation for experiments at various initial ionic strengths.

Expt. 43 $I = 0.08$ molal, Expt. 32 $I = 0.915$ molal, and Expt. 34 $I = 4.50$ molal.

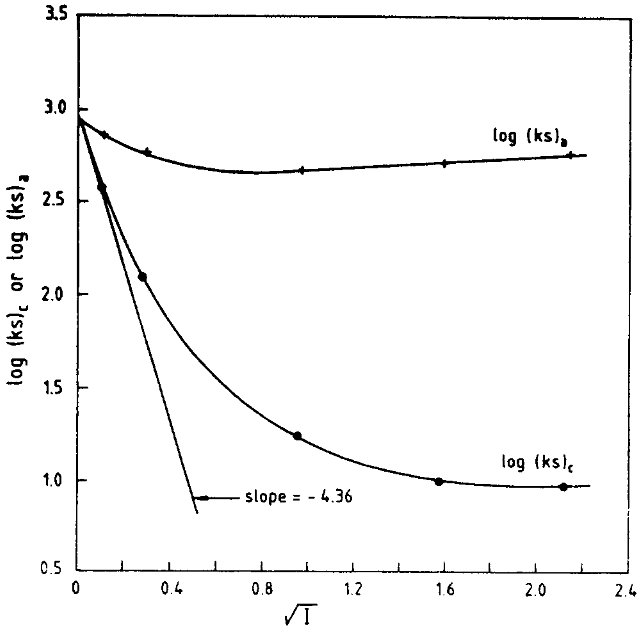

Figure 5. $\log(ks)_c$ and $\log(ks)_a$ vs. $I^{1/2}$.

Conclusions

Strontium sulfate precipitates by a second-order rate law in the supersaturation range of 1.0 to 4.0. At low supersaturations, however, the precipitation rate may follow a first-order dependence. The rate of spontaneous precipitation of $SrSO_4$ increased with increasing temperature, since both the rate constant and the relative supersaturation increase with increasing temperature. The increase in relative supersaturation is caused by the decrease in the thermodynamic solubility product of $SrSO_4$ when the temperature increases. From the data, an apparent activation energy of about 59 kJ/mol and a preexponential factor of about 4.06×10^{11} $\text{molal}^{-1} \cdot \text{h}^{-1}$ were obtained.

An increase in ionic strength was found to decrease the rate of $SrSO_4$ precipitation from solution, since both $(ks)_c$ and $\gamma_{\pm}$ in the rate equation decrease with an increase in ionic strength. The concentration rate constant decreased rapidly with an increase in ionic strength at low ionic strengths, but decreased very slowly at ionic strengths greater than 2 molal.

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