Solubility of Barium Sulfate in Sodium Chloride Solutions from 25° to 95° C.

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APPARENTLY, no study has previously been made of the solubility of barium sulfate in aqueous sodium chloride solutions of high ionic strength. Neuman (*6*) made measurements of the solubility of barium sulfate in aqueous solutions of several strong electrolytes, but investigated no ionic strength above 0.04 molal. The deposition of barium sulfate as scale from highly concentrated brines produced from oil wells is a fairly common occurrence. As part of a study of this scale formation problem, the concentration solubility product of barium sulfate in the $BaSO_4$-$NaCl$-H_2O system has been determined at several temperatures between 25° C. and 95° C. for sodium chloride molalities between about 0.1 and 5.0.

EXPERIMENTAL

Analytical Methods. Barium was determined by a spectrographic method (*1*). The coefficient of variation was 5% when the barium content exceeded 3.0 mg. per liter; the limit of detection was 0.1 mg. per liter of barium. Total sulfur was determined by a microreduction-colorimetric method (*4*). Use of the methylene blue colorimetric step directly on the sample without reduction gave the sulfide content, which was usually negligible. The sulfate content, based on the difference between total sulfur and sulfide, could be determined in the range of 1.0 to 45.0 mg. per liter of sulfate with a precision of 0.3 mg. per liter. For the concentrated solutions the percentage of total salts on drying at 110° C. was taken as sodium chloride.

Materials. All water used was distilled water which had been run through a mixed bed ion-exchange column and a Millipore filter. All chemicals were Baker Analyzed reagent grade. The reagent sodium chloride contained 0.0025% sulfate (microreduction method) and less than 0.0001% barium (spectrographic method). By a specially developed scheme involving solubility measurements in which the ratio of solid barium sulfate to brine volume was varied over a wide range, the reagent solid barium sulfate was found to contain 0.026% of excess soluble sulfate. Because of the proportions used, no account had to be taken of impurities in the reagent barium chloride or sodium sulfate.

Equilibration Procedure. In all cases 400 ml. of a solution was placed in a 500-ml. balloon flask, which was immersed in a water bath thermostat-controlled to within ±0.05° C. and equipped with a liquid seal stirrer. Each initial solution was mixed from calculated amounts of water, concentrated sodium chloride solution, 0.005 molar barium chloride solution, and 0.005 molar sodium sulfate, to obtain desired ionic strengths and Ba to SO_4 ratios and to allow equilibrium to be approached from either undersaturation or supersaturation. Each solution was initially seeded with 0.25 gram of reagent solid barium sulfate. Samples were taken through a sidearm by means of a Millipore hypodermic syringe filter attachment, after 24 and 48 hours of stirring. Sulfate determinations were made immediately on the undiluted samples; the samples for the barium determinations were diluted by weight with barium-free sodium chloride solution of the same concentration to prevent precipitation of barium sulfate on standing. For the measurements above room temperature, it was shown, by a few samplings under specially arranged isothermal conditions, that no precipitation occurred during the oridnary sampling procedure or during the short waiting period before sulfate analysis. Apparently so few nucleating centers remained after passage through the Millipore filter that the cooled solution was stable for at least several hours.

The molal concentration solubility product was designated by

$$K_s' = m_{Ba} \times m_{SO_4} \qquad (1)$$

while the thermodynamic solubility product was expressed as

$$K_s = \gamma_\pm^2 K_s' = \gamma_\pm^2 m_{Ba} m_{SO_4} \qquad (2)$$

Every solubility point was approached both from supersaturation and undersaturation. When both m_{Ba} and m_{SO_4} were experimentally determined in the equilibrium solution, K_s' was then known and no account had to be taken of the exact initial composition of the solution. However, about half these data were taken before the sulfate microreduction method was in use. In this case, when only barium was determined on the final solution, the final sulfate concentration could be calculated by material balance provided that the initial values of m_{Ba} and m_{SO_4} were known synthetically, that no occlusion occurred in the precipitate, and that all the chemicals were prefectly pure. Both the reagent grade sodium chloride and barium sulfate contained appreciable excesses of sulfate over barium, which required the use of corrections. In what follows, $(m_{Ba})_i$ and $(m_{SO_4})_i$ refer to the synthetically fixed hypothetical values for the initial solution based on the assumed exact purity of the reagents. For the final equilibrated solution $(m_{Ba})_f$ and $(m_{SO_4})_f$ are the actual values. For the conditions of the present measurements, one can then derive the following correction formula:

$$(m_{SO_4})_f = (m_{Ba})_f + \left\{ (m_{SO_4})_i - (m_{Ba})_i \right\} + (1.52 \times 10^{-5}) m_{NaCl} + (0.2 \times 10^{-5}) \qquad (3)$$

for calculating $(m_{SO_4})_f$ from $(m_{Ba})_f$ and the synthetic composition of the initial solution. The term $(1.52 \times 10^{-5}) m_{NaCl}$ represents the sulfate excess contributed by the sodium chloride, and (0.2×10^{-5}) represents that from the barium sulfate used for seeding.

RESULTS AND DISCUSSION

The kinetic features of precipitation as related to the presence of nucleating particles are illustrated in Figure 1. Each of the two runs presented concerned the continuous stirring at 35° C. of 400 ml. of 5.0% sodium chloride solution containing approximately equal molalities of barium chloride and sodium sulfate. Periodic analyses for barium were made. The initial values of m_{Ba} and m_{SO_4} were about three times the equilibrium values. In Run CU, 0.250 gram of barium sulfate was added initially; equilibrium was essentially attained after four hours. In Run C the initial seeding involved only a few specks of barium sulfate; up to 72 hours there was only a slow rate of precipitation. At the 72-hour point 0.250 gram of barium sulfate was added. Twenty-four hours later the system was definitely at equilibrium, since over the next six days the barium content was unchanged.

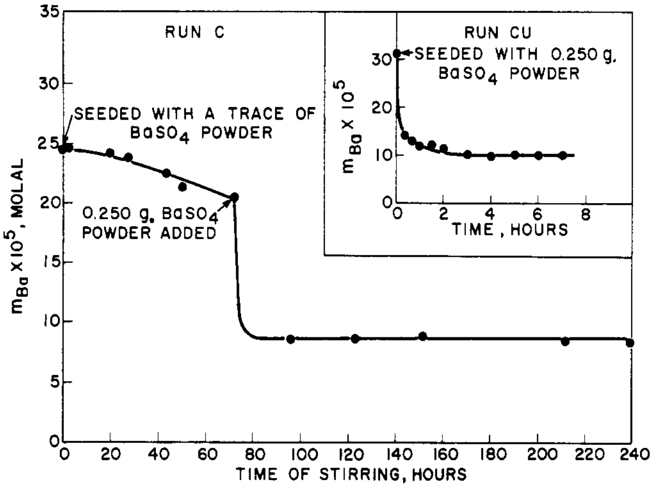

Figure 1. Kinetics of precipitation of $BaSO_4$ in 5% sodium chloride solution at 35° C.

Solution volume = 400 ml. $m_{Ba}/m_{SO_4} \approx 1$

To investigate the constancy of K'_s at a given temperature and ionic strength, K'_s was determined at 35° C. at constant sodium chloride content while m_{Ba} to m_{SO_4} was varied from about 0.1 to 10. This was done for sodium chloride weight percentages of 1.0, 5.0, and 10.0, with the results summarized in Table I. Average values are shown with the average deviations from the mean. No systematic trend of K'_s with m_{Ba} to m_{SO_4} was discernible. For each salinity, K'_s is seen to be constant within the precision of the analytical techniques used.

Table I. Summary of K'_s Data at Constant Salinity and Varying m_{Ba} to m_{SO_4} at 35° C.

Wt. % NaCl	Number of Systems	$[(K'_s)^{1/2} \pm (\text{Av. dev.})] \times 10^5$
1.0	6	5.6 ± 0.8
5.0	21	9.2 ± 0.6
10.0	6	13.4 ± 0.2

Measurements were then made at six temperatures (25° C., 35° C., 50° C., 65° C., 80° C., and 95° C.) for sodium chloride concentrations between 0.2 and 20.0 weight per cent. For most of the systems the m_{Ba} to m_{SO_4} ratio was near unity. All points were checked from both supersaturation and undersaturation. Values of $(K'_s)^{1/2}$ for $m_{NaCl} = 0$ were calculated from data in the International Critical Tables (*3*). For each temperature log $(K'_s)^{1/2}$ was plotted *vs.* $\mu^{1/2}$, where μ is the ionic strength. When $m_{NaCl} > 0.01$, $\mu^{1/2}$ is equivalent to $(m_{NaCl})^{1/2}$ for all practical purposes. For each such plot a smooth curve was drawn, the course of which at extreme dilution was guided by the results of Neuman (*6*) for the $BaSO_4$-KCl-H_2O system at 25° C., in which the slope at first exceeded the Debye-Hückel limiting slope. A set of smooth data read from these graphs was then replotted on a composite log $(K'_s)^{1/2}$ *vs.* $1/T$ (° K.) graph. On the latter plot, lines were drawn for constant m_{NaCl} values. A new set of smooth data was read from these curves, which was then used to readjust the log $(K'_s)^{1/2}$ *vs.* $\mu^{1/2}$ curves. These processes were alternated until one set of smooth data was compatible with both types of plots. These are the data which are recorded in Table II. Figure 2 shows the final log $(K'_s)^{1/2}$ *vs.* $\mu^{1/2}$ plot for 25° C., which typifies the degree of deviation of the actual points from the smoothed data.

The first line of Table II contains $(K'_s)^{1/2}$ values for the $BaSO_4$-H_2O system. The Debye-Hückel limiting law was

Table II. Smoothed Solubility Data for $BaSO_4$–$NaCl$–H_2O System at Various Temperatures

	$(K'_s)^{1/2} \times 10^5$, Molal					
m_{NaCl}	25° C.	35° C.	50° C.	65° C.	80° C.	95° C.
0.000	1.08	1.25	1.44	1.54	1.62	1.68
0.001	1.28	1.46	1.69	1.83	1.92	1.97
0.005	1.60	1.81	2.10	2.31	2.47	2.55
0.01	1.84	2.08	2.43	2.70	2.90	3.05
0.05[a]	3.02	3.49	4.00	4.37	4.67	4.85
0.1	3.92	4.47	5.20	5.78	6.13	6.30
0.2	5.2	5.8	6.9	7.7	8.4	8.8
0.4	6.7	7.5	8.9	10.3	11.7	12.7
0.6	7.8	8.8	10.5	12.4	14.3	15.8
0.8	8.8	9.8	11.7	14.2	16.3	18.3
1.0	9.6	10.6	12.8	15.5	18.1	20.5
1.5	11.2	12.4	14.9	18.0	21.2	24.9
2.0	12.5	13.8	16.5	19.9	23.7	28.1
2.5	13.5	14.8	17.7	21.2	25.2	30.6
3.0	14.4	15.7	18.7	22.3	26.5	32.8
3.5	15.3	16.6	19.7	23.2	27.7	34.7
4.0	16.1	17.5	20.6	24.1	28.8	36.4
4.5	16.9	18.5	21.4	25.1	29.9	38.0
5.0	17.7	19.4	22.2	26.0	30.9	39.7

[a] Approximate lowest ionic strength experimentally studied in present work.

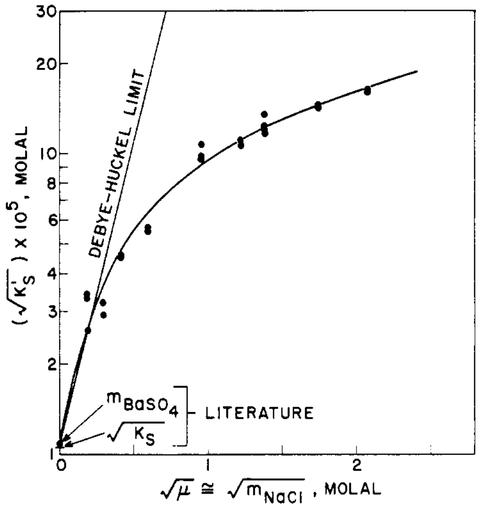

Figure 2. Variation of K_s' with ionic strength at 25° C.

used to estimate $\gamma_\pm$ in the same system, an approximation which should be allowable within the precision of the data. Table III lists the activity solubility products which were then calculated by Equation 2.

The solubility data of Table II for the $BaSO_4$-$NaCl$-H_2O system can be converted to mean activity coefficient data for barium sulfate $[\gamma_\pm = (K_s)^{1/2}/(K_s')^{1/2}]$. In Figure 3 such activity coefficients at 25° C. are compared with those of zinc sulfate in the $ZnSO_4$-H_2O system (2), of magnesium sulfate in the $MgSO_4$-H_2O system (2), and of calcium sulfate in the $CaSO_4$-$NaCl$-H_2O system. For $CaSO_4$, $\gamma_\pm$ was calculated from the solubility data of Madgin and Swales (5), being made to coincide with the $ZnSO_4$ curve at low ionic strengths. For the gypsum-$NaCl$-H_2O system, water activities were estimated from the data for the $NaCl$-H_2O system listed by Robinson and Stokes (7). Equivalent results for $\gamma_\pm$ are obtained from solutions saturated with either gypsum or anhydrite. When $\gamma^{1/2}$ is less than 0.25 all of these 2-2 sulfates essentially follow a common curve, the effects of cationic individuality being more important at higher ionic strengths.

Table III. Activity Solubility Products for Barium Sulfate

Temp. ° C.	$(K_s)^{1/2} \times 10^5$ Molal
25[a]	1.05
35	1.21
50	1.39
65	1.48
80	1.55
95	1.60

[a] A very recent conductometric study by Rosseinsky, (8) gives K_s at 25° C. as $(1.014 \pm 0.01) \times 10^{-10}$.

The increase in solubility of barium sulfate with increasing temperature at constant ionic strength is opposite to the behavior of calcium sulfate. Hence barium sulfate scaling would be aggravated by cooling a supersaturated brine, whereas calcium sulfate scaling troubles increase on heating a brine.

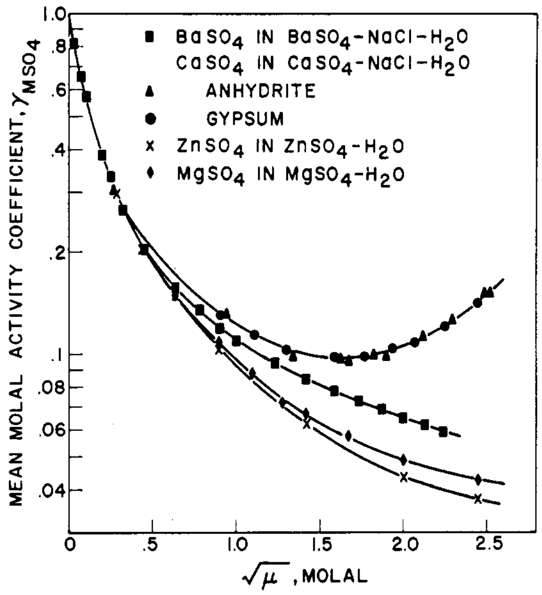

Figure 3. Activity coefficients of sulfates of bivalent metals at 25° C.

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