Solubility of Barium and Strontium Sulfates in Strong Electrolyte Solutions

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■ Knowledge of the solubilities of $BaSO_4$ and $SrSO_4$ in solutions containing NaCl, $CaCl_2$, $MgCl_2$, and $NaHCO_3$ is needed to solve geologic and petroleum production problems. Samples of the sulfates were tagged with ^{35}S and prepared by precipitation. The solubility was measured in various concentrations of the major solutes by use of a liquid scintillation technique to detect the SO_4^{2-} in solution. The observed solubilities plotted against ionic strength of the solution are similar for strong electrolytes. They reach a maximum at concentration levels beginning at ionic strength of near 1. The sulfate solubility in synthetic brines (principally NaCl) confirms the ionic strength–sulfate solubility relationships.

Extensive study of the $CaSO_4$–strong electrolyte systems has been reported. The work of Blount (1965) gives a complete treatment of the $CaSO_4$–H_2O and $CaSO_4$–NaCl–H_2O systems. The need for solubility data of the less soluble sulfates in waters, particularly those flowing from or produced in petroleum formations, was the prime reason for this study. Water produced with petroleum is often high in minerals, which has created many problems for this industry. Better methods of petroleum production and brine disposal await development of new techniques that maintain chemical equilibrium with all minerals in solution. Changes in temperature, pressure, and environment create additional stability problems. Dilution of these waters with relatively "pure" surface waters often causes precipitation of sulfates which clog pumps, filters, and pores of sedimentary rocks. This study revealed some of the solubility interrelationships of the barium and strontium sulfates in the presence of the strong electrolytes NaCl, $CaCl_2$, $MgCl_2$, KCl, and KBr, and for other electrolytes such as $NaHCO_3$ and $Na_2B_4O_7$ solutions.

In 1933, Neuman published results of studies of $BaSO_4$ solubility in aqueous solutions of potassium, magnesium, and lanthanum as chlorides and nitrates. His data show that $BaSO_4$ solubility increases with the increasing complexity of the major solute, and in the order $(3, -1) > (2, -1) > (1, -1)$ of equal molality solutions.

Recently, Gates and Caraway (1965) analyzed California oil-well scale and found in a $BaSO_4$-type scale significant amounts of strontium along with iron, calcium, magnesium, and some carbonate. Weintritt and Cowan (1967) studied the unique characteristics of $BaSO_4$-scale deposition and concluded "the presence of strontium in barium sulfate scales deposited from oil field waters appears to be common." All of the sulfate deposits analyzed contained strontium sulfate in concentrations ranging from 1.2 to 15.9% and barium sulfate in concentrations ranging from 63.7 to 97.5%.

Templeton (1960) studied the solubility of $BaSO_4$ in sodium chloride solutions at 25°C and at sodium chloride molalities between 0.1 and 5.0. He found that at constant ionic strength the solubility of $BaSO_4$ increases with increasing temperature, and observed that calcium sulfate exhibits an inverse reaction with increasing temperature.

Experimental

A radioisotope-tagged solution of Na_2SO_4 (^{35}S) was prepared, from which aliquots were taken. One aliquot was used to precipitate $BaSO_4$ by addition of excess $BaCl_2$; a second portion was used to precipitate $SrSO_4$ by addition of equivalents of $SrCl_2$. These suspensions were stirred and allowed to settle. Following a 24 to 48-hr settling period, the precipitates were washed onto a 0.45-μ pore size filter medium, and the washings were continued until the sulfate ion in the filtrates could not be further reduced. The tagged precipitate was removed from the filter, dried in an oven at 105°C, and transferred to storage vials. Standard samples of the sulfates were prepared by chelation in a $0.1N$ solution of EDTA. Various strengths of 5 to 80 mg/liter of $BaSO_4$ and 50 to 800 mg/liter of $SrSO_4$ were made and used as reference counting samples for all of the sulfate determinations.

Liquid scintillation counting was found to be the most efficient counting technique, but problems were encountered in selecting a sample counting medium. Salts were precipitated when the more concentrated brines were added to the counting solution (fluor) and when 0.1-N EDTA solutions containing the reference-tagged sulfate (^{35}S), were added to the fluor. A nonionic detergent (Triton X-100) and toluene emulsion (Patterson and Greene, 1965) were prepared, whereby 1-cc sulfate samples in brine could be counted with greater than 20% efficiency. The emulsion forms a clear gel and permits a homogeneous dispersion of the aqueous phase in the fluor with no salting out.

Solutions of various salts, such as those usually found in formation waters, were made up in strengths of 0.005 to 1.77 m, and tagged solid barium or strontium sulfate was added. The chlorides of sodium, calcium, magnesium, and potassium were prepared, as were solutions of sodium bicarbonate, sodium borate, and potassium bromide. All of the solutions were stored in plastic bottles. To determine sulfate solubility, a 20-cc portion of one of the prepared salt solutions was transferred to a small plastic, stoppered vial, and 0.1 gram of the solid, tagged sulfate was added. This suspension was shaken in a wrist-action-type shaker for 72 hr and then allowed to settle a minimum of 24 hr without opening the vial. All samples were prepared in duplicate to assure equilibrium, and the operation was repeated when better precision was needed. The temperature of the suspension was raised briefly above the stabilized room temperature (25° ± 1°C) with a heat lamp during the shaking period, but no change

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Table I. Solubility of $BaSO_4$ and $SrSO_4$ in Electrolyte Solution

Major solute, *m*	$BaSO_4$–major solute system		$SrSO_4$–major solute system	
$CaCl_2$	$BaSO_4$, mg/liter	Total ionic strength	$SrSO_4$, mg/liter	Total ionic strength
0.010	(5.0)^{a} 6.2	0.03016	214	0.0347
0.015			247	0.0504
0.020	7.6	0.06013		
0.025			295	0.0814
0.045			260	0.1403
0.050	11.5	0.15020		
0.090			508	0.2819
0.100	15.5	0.30027		
0.136			590	0.4197
0.200	(17.3)^{a} 17.7	0.60030		
0.226			757	0.6959
0.300	16.2	0.90028		
0.400	16.3	1.20028		
0.456			1152	1.3947
0.500	16.6	1.50028		
0.934			1942	2.8438
1.000	(16.3)^{a} 11.3	3.00019		
2.000	(10.8)^{a} 2.5	6.00004		
$MgCl_2$				
0.005			172	0.0188
0.010	(2.9)^{a} 5.4	0.02979	203	0.0344
0.015			233	0.0499
0.020	6.9	0.05982		
0.025			295	0.0805
0.049			394	0.1571
0.050	9.8	0.14927		
0.074			422	0.2324
0.099	13.3	0.29693		
0.125			530	0.2866
0.196	18.0	0.58831		
0.254			731	0.7782
0.474	25.9	1.42244		
0.525			1063	1.5993
0.902	32.0	2.70655		
1.637	(44.5)^{a} 33.2	4.93257		
NaCl				
0.010	(5.3)^{a} 3.6	0.01006	134	0.0129
0.015			149	0.0182
0.020	(5.6)^{a} 4.2	0.02007		
0.025			172	0.0288
0.050	5.4	0.05009	199	0.0543
0.086			265	0.0914
0.100	(7.3)^{a} 7.1	0.10012		
0.172			332	0.1756
0.200	(11.3)^{a} 10.0	0.20017		
0.257			420	0.2667
0.431			525	0.4423
0.500	14.8	0.50025		
0.869			699	0.8840
1.000	(22.3)^{a} 20.2	1.00035		
1.771			760	1.7875
2.000	(35.7)^{a} 27.2	2.00047		
KCl				
0.010	(3.7)^{a} 4.2	0.01007	144	0.0131
0.015			169	0.0185
0.020	4.9	0.02008		
0.025			167	0.0286
0.050	6.3	0.05011		
0.067			375	0.0754

(*Continued on p 1041*)

Table I (*Continued*)

Major solute, m	$BaSO_4$–major solute system		$SrSO_4$–major solute system	
	$BaSO_4$, mg/liter	Total ionic strength	$SrSO_4$, mg/liter	Total ionic strength
KCl				
0.100	8.6	0.10015		
0.200	11.2	0.20019		
0.202			396	0.2109
0.338			502	0.3492
0.500	16.8	0.50029		
0.684			742	0.7001
1.000	21.6	1.00037		
1.396			802	1.4139
2.000	(25.8)[a] 27.2	2.00047		
KBr				
0.010	(3.6)[a] 4.1	0.01007	152	0.0133
0.015			163	0.0186
0.020	4.7	0.02008		
0.042			215	0.0467
0.050	6.3	0.05011		
0.084			262	0.0900
0.100	8.2	0.10014		
0.126			320	0.1335
0.200	11.0	0.20019		
0.211			420	0.2207
0.426			509	0.4378
0.500	16.2	0.50028		
0.866			669	0.8812
1.000	21.8	1.00037		
2.000	(23.9)[a] 26.7	2.00046		
$Na_2B_4O_7$				
0.010	6.0	0.03010		
0.013			320	0.0462
0.020	7.8	0.06014		
0.039			600	0.1307
0.050	12.9	0.15022		
0.065			690	0.2100
0.100	(23.7)[a] 21.0	0.30036		
0.200	(33.9)[a] 34.8	0.60060		
Pure water	2.5	0.00004	114	0.0025

[a] Parentheses indicate barium ion and sulfate ion determinations made separately.

was permitted during the last 24 hr nor during the settling period. When the sample container was opened, it was quickly filtered through a double Whatman no. 42 filter paper and 1 ml was transferred to a counting vial which contained 12 ml of the Triton emulsion and 7 ml of deionized water. The sample then was counted in a liquid scintillation counter for 50 min. The chelated sulfate standards were counted in the same time period. By this method, the correction for radioactive decay could be omitted and the soluble sulfate values determined from a graph of the chelated standards (in milligrams/liter) vs. the counts per minute. Barium was analyzed by emission spectroscopy (American Petroleum Institute, 1968), but adequate precision at levels of 1 mg/liter and less was difficult to achieve in the presence of ionic-strength salts encountered in some solutions.

Results and Discussion

The values obtained from solubility measurements are tabulated in Table I. The amounts of the alkaline sulfates which dissolve in other electrolyte solutions are tabulated alongside the total ionic strength of each solution. The term "ionic strength" is the most useful concept yet developed to include the combined effects of the activities of several ionic species in a solution. Lewis and Randall (1923) state, "in dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength." It is defined as $s = {}^1/_2\Sigma m_i Z_i^2$, where m_i is the ionic molality and Z_i is the charge on the ion in solution, the summation being taken over all ions, positive and negative. By definition, the activity of the dissolved species approaches the concentration value (molality) at infinite dilution.

Since the thermodynamic solubility product $Ka = m_M \times m_{SO_4} \times \gamma^2$ and since γ equals unity at zero ionic strength, a plot of log m_{SO_4} vs. the ionic strength function would extrapolate to zero concentration where $\log Ka^{1/2} = \log m_{SO_4}$. Figures 1–3 give plots representing six electrolytes and the values of Ka are determined graphically. The value for the sulfate solubilities in pure water (major solute = zero concentration) was determined experimentally and agreed with values in the literature.

In Figure 1, the plot of $BaSO_4$ solubility vs. $\sqrt{s}$ for the six electrolytes is almost identical at low ionic strength, a

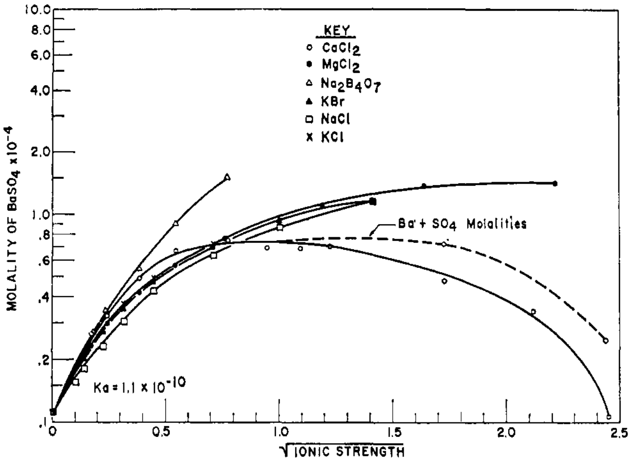

Figure 1. Concentration of saturated $BaSO_4$ in electrolyte solution

phenomenon to be expected from the statements above. The extrapolated $Ka^{1/2}$ values of all systems are 1.05×10^{-5} (within experimental limits). The fact must be correlated with the nature of the equation defining ionic strength. The square of the ionic valence gives the Mg and Ca ions four times the numerical weight of the Na and K ions. Molality values would indicate that the bivalent ions cause increased solubility effects.

Borates are present in many subterranean waters and $Na_2B_4O_7$ solutions were investigated to find differences in the sulfate solubility in electrolytes containing a complex ion. As shown in Figures 1 and 3, the solubility deviated from that of monatomic electrolytes, and the relationship described does not hold at higher solubilities of electrolytes containing complex ions.

Another ion commonly found in mineral waters is the bicarbonate ion. Many water-bearing zones contain limestone and dolomite which slowly erode in water of low pH. The water carries away carbonates and bicarbonates. In this study, $NaHCO_3$ solutions of 0.005 to 1.0 *m* were saturated with tagged $BaSO_4$. However, only trace amounts of Ba were found in solution, though the sulfate content increased with the amount of $NaHCO_3$ in solution. This apparent anomaly can be reconciled by the ionization of the HCO_3^- ion into CO_3^{2-}, which in appreciable concentration would reduce the Ba ion concentration according to the solubility product $K_{sp} = M_{Ba} \times M_{CO_3}$.

The effect of high concentration of $CaCl_2$ on $BaSO_4$ solubility is indicated by the solid curve of Figure 1. At concentrations of 2 *m*, the $BaSO_4$ solubility has dropped to values close to that of the compound in pure H_2O. The maximum value is reached between 0.2 and 0.4 *m* where the decline begins. The accompanying broken line of Figure 1 which is a plot of $Ba^{2+} + SO_4^{2-}$ ions determined separately, shows the reduced solubility of the Ba ion caused by the equilibrium $Ca^{2+} + SO_4^{2-} \rightleftarrows CaSO_4$ ($K_{sp} < 1.95 \times 10^{-4}$).

The effect of the ions of strong electrolyte solutions on $SrSO_4$ solubility is similar to that observed when $BaSO_4$ solubility was studied. The Na^+, K^+, Cl^-, and Br^- ions have approximately equal effect, and all determined values fall on a common curve. The increase in sulfate solubility is marked in dilute solutions but reaches a maximum at concentrations with ionic strength near 1. This is the average value calculated for seawater. When bivalent ions Mg^{2+} are used in the strong electrolyte (Figure 3), the $SrSO_4$ solubility remains of the same relation to the total ionic strength as for the monovalent ions.

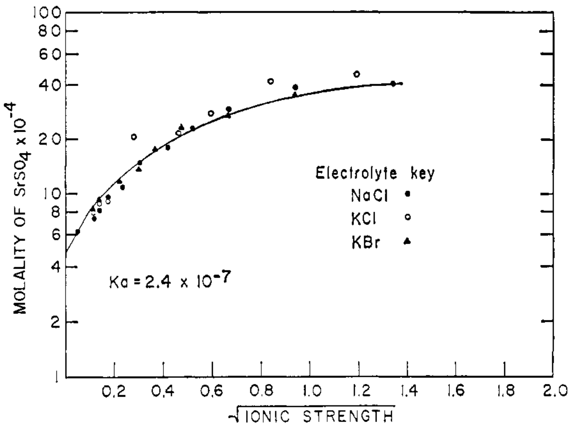

Figure 2. Concentration of saturated $SrSO_4$ in strong electrolyte solution

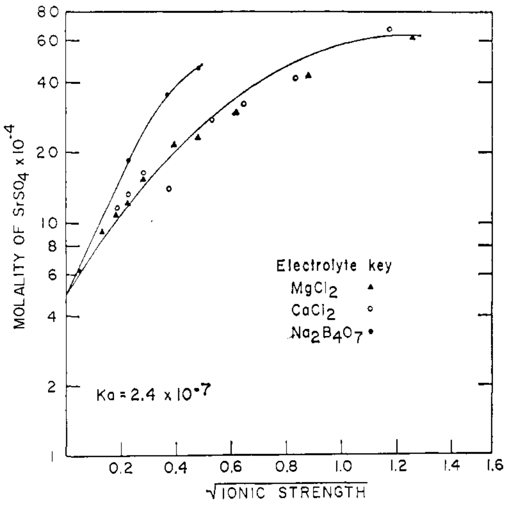

Figure 3. Concentration of saturated SrO_4 in electrolyte solution

A study of the system $SrSO_4$-$NaHCO_3$-H_2O was limited by the insolubility of $SrCO_3$. The ionization of the bicarbonate to H^+ and CO_3^{2-} would result in the precipitation of any Sr which dissolves and leaves the SO_4^{2-} in solution. This relationship is similar to the $BaSO_4$-$NaHCO_3$-H_2O system and is worthy of special note. That is, when carbonate or bicarbonate waters are diluted or intermixed with the waters containing alkaline earths Ba or Sr, an unstable solution is formed.

Experimental data reported by the authors indicate maximum sulfate solubility in strong electrolytes beginning at ionic strength of approximately 1. When the principal cation in solution is the Ca ion, sulfate solubility decreases after the ionic strength exceeds unity. Blount (1965), when measuring solubility of $CaSO_4$ in the system $CaSO_4$-NaCl-H_2O, and Lucchesi and Whitney (1962), when measuring $SrSO_4$-NaCl-H_2O, solubility equilibria, found similar maximums. The works of the authors extend the knowledge to other systems which contain other dissolved solids found in petroleum-associated waters. By use of the ionic strength calculations in place of weight per unit volume, the predictions of

Table II. Sulfate Solubilities in Synthetic Brines

Concentration, *m*	Brine 1	Brine 2	Brine 3
Na^+	1.2179	1.7399	2.4359
Ca^{2+}	0.0250	0.0374	0.0499
Mg^{2+}	0.0206	0.0823	0.0411
K^+	0.0051	0.0051	0.0193
Cl^-	1.3019	1.9650	2.6113
Br^-	0.0125	0.0188	0.0250
I^-	<0.0001	0.0000	0.0001
Barium sulfate solubility			
$BaSO_4$, mg/liter	60	63	66
$BaSO_4$, *m*	2.57×10^{-4}	2.70×10^{-4}	2.83×10^{-4}
Ionic strength (*s*)	1.3600	2.1038	3.0278
Strontium sulfate solubility			
$SrSO_4$, mg/liter	813	922	958
$SrSO_4$, *m*	44.26×10^{-4}	50.19×10^{-4}	52.18×10^{-4}
Ionic strength (*s*)	1.3777	2.1239	3.0487

mineral water stability became more accurate and dilutions more feasible. Further study of the systems where such electrolytes as the borates and bicarbonates are present with the insoluble sulfates seems necessary.

Three synthetic brines were made with salts concentrations in the range of many formation waters and containing the major salts found in these waters. Table II gives these concentrations and the results of a $BaSO_4$ and a $SrSO_4$ solubility determination. The values found when plotted against the ionic strength function of the brine fall on the same curve as the barium salt in Figure 1 and the strontium salt in Figure 2. No carbonates were added to these synthetic brines.

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Literature Cited

American Petroleum Institute, "Analysis of Oil Field Water," Dallas, Texas, API RP 45, November 1968.
Blount, C. W., Dissertation, University of California, Los Angeles, Calif., 1965.
Gates, G. L., Caraway, W. H., Bur. Mines Rept. Invest. 6658 (1965).
Lewis, G. N., Randall, H. M., "Thermodynamics," McGraw-Hill, New York, N.Y., 1923, pp 373-374.
Lucchesi, P. J., Whitney, E. D., *J. Appl. Chem.* **12,** 277 (1962).
Neuman, E. W., *J. Amer. Chem. Soc.* **55,** 879 (1933).
Patterson, M. S., Greene, R. C., *Anal. Chem.* **37** (7), 854 (1965).
Templeton, C. C., *J. Chem. Eng. Data* **5** (4), 514 (1960).
Weintritt, D. J., Cowan, J. C., *J. Petrol. Technol.* **19** (10), 1381 (1967).

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