Thermodynamics of "Scale" Mineral Solubilities. 4. Experimental Measurements of $SrSO_4(s)$ in H_2O and Aqueous NaCl from 25 to 250 °C and from 1 to 500 bar

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The solubility of $SrSO_4(s)$ was determined in water and in 0.5, 1, 2, 3, and 4 *m* aqueous sodium chloride solutions for temperatures ranging from 25 to 250 °C and pressures ranging from 1 to greater than 500 bar. The range in each of the three independent variables was covered completely, and the solubility is reported at 80 unique points on the sodium chloride concentration–temperature–pressure grid. An expression for the temperature and pressure dependence of the thermodynamic solubility product and an empirical expression for calculating the mean activity coefficient as a function of temperature, pressure, and ionic strength are given. A predictive model of the solubility of $SrSO_4(s)$ at conditions common to oil field brines is described.

Introduction

In an earlier paper (*1*) we received the literature on the solubility of $SrSO_4(s)$ and described our calculational approach to modeling $SrSO_4(s)$ solubility in brines as a function of temperature and ionic strength. While the literature database included more than 200 individual solubility measurements by a number of researchers, there was no single study in which the entire ranges of temperature, pressure, and ionic strength common to oil field brines were covered in a systematic manner. Moreover, the aggregate of the literature data did not sufficiently cover the temperature–pressure–ionic strength grid to enable development of a reliable predictive model which includes the effect of pressure on the solubility. This was primarily due to a lack of solubility measurements at elevated pressures over the complete ranges of temperature and ionic strength. In addition, there were other deficiencies in the literature data, which is understandable considering the number of experimental points which can arise in a system of three independent variables.

Because of the deficiencies in the literature database, the present study was undertaken to determine the solubility of $SrSO_4(s)$ in water and in aqueous sodium chloride solution up to 4 *m*, at pressures from 1 to more than 500 bar, and temperatures of 25–250 °C.

Experimental Section

Solid $SrSO_4$ was prepared by mixing $SrCl_2$ and Na_2SO_4 solutions made from Fisher Certified ACS grade reagents and distilled water which had been passed through a Barnstead NANOpure 18.5 mΩ deionization unit. The $SrSO_4$ precipitate was removed from the solution by filtration and washed with distilled deionized water to remove all traces of NaCl.

Saturated aqueous solutions were prepared using a Barnes (*2*) hydrothermal apparatus, model RA-2A-1, assembled by the Tem-Press Division of LECO Corp., Bellefonte, PA. Because of corrosion of the original 316SS components of the apparatus, they were replaced with similar ones made of a titanium alloy which after many months of use show no signs of corrosion. A coarse (40–60 μm) fritted glass filter was mounted on the inside of the reaction vessel at the sampling port which prevented the passage of fine particles of the solid out of the vessel and into the sample.

In an experimental run, 4–5 g of dry strontium sulfate was placed in the vessel before it was sealed. After all the tubing and valves were fixed in place, the vessel was evacuated of atmospheric gases with a vacuum pump and filled and pressurized with water or sodium chloride solution by a high-pressure pump. A Heise gauge was used to measure the pressure to a precision of ±100 psi (±7 bar), and the temperature of the vessel was controlled to ±1 °C by a microprocessor-based proportional-integral-derivative temperature controller (Eurotherm Model 810).

After an equilibration time of about 24 h, approximately 5 g of saturated solution was withdrawn from the reaction vessel and collected into 50 g of distilled water. This brought about rapid cooling of the samples and also ensured that they were unsaturated with respect to $SrSO_4(s)$.

A Perkin-Elmer Model 2380 atomic absorption spectrophotometer was used to analyze the samples for strontium content. An air/acetylene flame was used with a wavelength of 460.7 nm and an integration time of 2 s. In order to minimize the suppression of the strontium signal by sulfate, the solutions were prepared with 1000 ppm EDTA (as Na_2-EDTA, Fisher Certified) as suggested by Van Loon (*3*). In addition, potassium chloride (Fisher Certified) was added to all samples to control strontium ionization (*4, 5*). Standard strontium solutions and a blank were prepared so that they would contain sodium chloride, potassium chloride, and EDTA in the same concentrations as the samples.

Results and Discussion

The solubility was determined in water and in 0.5, 1, 2, 3, and 4 *m* sodium chloride solutions. At each of these concentrations, the temperature and pressure were varied in order to provide an adequate coverage of the temperature–pressure–ionic strength grid. The experimental solubility values are given in Table I.

The results were normalized both graphically and with the SAS procedure G3GRID (*6*) with the SPLINE option. This routine utilizes a bivariate cubic spline routine, so the interpolation was accomplished in steps by interpolating with respect to two of the variables while holding the third constant. For example, the solubility values on a grid of temperature and pressure points were determined by interpolating at constant sodium chloride concentration. Further interpo-

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Table I. Solubility of $SrSO_4$, *s*, in Water and Aqueous NaCl

[NaCl]/*m*	*T*/C	*P*/bar	$10^3s/m$	[NaCl]/*m*	*T*/C	*P*/bar	$10^3s/m$	[NaCl]/*m*	*T*/C	*P*/bar	$10^3s/m$
0.0	24.4	1	0.62	1.0	50.0	107	3.63	3.0	25.0	1	4.76
0.0	24.4	1	0.64	1.0	50.0	198	3.90	3.0	28.6	1	4.75
0.0	24.4	1	0.66	1.0	50.0	198	3.85	3.0	28.6	1	4.75
0.0	25.0	216	0.76	1.0	50.0	198	3.86	3.0	49.7	1	4.29
0.0	25.0	415	0.88	1.0	50.0	303	4.17	3.0	49.7	1	4.28
0.0	25.0	415	0.87	1.0	50.0	303	4.24	3.0	76.1	1	3.82
0.0	24.5	546	1.00	1.0	50.2	400	4.42	3.0	76.1	1	3.80
0.0	24.5	546	1.05	1.0	50.2	400	4.38	3.0	103.6	1	3.47
0.0	99.5	1	0.29	1.0	50.0	502	4.67	3.0	103.6	1	3.45
0.0	99.5	1	0.29	1.0	50.0	502	4.65	3.0	103.6	1	3.44
0.0	99.4	227	0.38	1.0	75.8	1	3.06	3.0	149.4	5	2.86
0.0	99.4	227	0.38	1.0	75.7	1	3.02	3.0	220.1	23	2.19
0.0	99.5	401	0.48	1.0	100.9	1	2.54	3.0	220.1	23	2.12
0.0	99.5	401	0.45	1.0	100.9	1	2.59	3.0	248.9	39	1.92
0.0	99.8	566	0.53	1.0	100.0	186	2.97	3.0	251.5	41	1.99
0.0	99.8	566	0.51	1.0	100.0	186	3.00	4.0	25.0	1	4.13
0.0	150.8	5	0.11	1.0	100.0	186	3.02	4.0	25.0	1	4.11
0.0	150.8	5	0.11	1.0	101.6	277	3.50	4.0	26.4	149	4.34
0.0	149.8	198	0.15	1.0	100.2	432	3.94	4.0	26.4	149	4.35
0.0	149.8	198	0.15	1.0	100.2	432	3.63	4.0	25.3	247	4.56
0.0	150.0	216	0.16	1.0	101.3	466	3.82	4.0	25.3	247	4.68
0.0	150.0	216	0.16	1.0	101.3	466	3.67	4.0	25.3	247	4.65
0.0	149.5	422	0.19	1.0	152.0	5	1.96	4.0	25.3	247	4.55
0.0	149.5	422	0.18	1.0	152.2	5	1.94	4.0	25.3	366	4.84
0.0	150.3	576	0.23	1.0	150.2	70	2.25	4.0	25.3	366	4.81
0.0	150.3	576	0.21	1.0	150.2	70	2.23	4.0	25.7	511	5.03
0.5	24.9	1	2.54	1.0	150.2	70	2.13	4.0	25.7	511	5.02
0.5	24.9	1	2.67	1.0	150.2	70	2.15	4.0	49.8	1	4.06
0.5	50.1	1	2.54	1.0	150.0	215	2.33	4.0	49.8	1	4.17
0.5	50.1	1	2.60	1.0	150.8	246	2.41	4.0	49.8	1	4.06
0.5	75.2	1	2.25	1.0	150.8	246	2.35	4.0	75.6	1	3.69
0.5	75.2	1	2.23	1.0	150.8	408	2.63	4.0	75.6	1	3.69
0.5	100.2	1	1.92	1.0	150.8	408	2.51	4.0	100.8	1	3.57
0.5	100.2	1	1.93	1.0	151.1	508	2.58	4.0	100.8	1	3.49
0.5	100.2	1	1.89	1.0	151.1	508	2.57	4.0	100.0	1	3.70
0.5	151.7	5	1.22	1.0	200.3	16	1.37	4.0	100.0	1	3.70
0.5	151.7	5	1.22	1.0	200.3	16	1.40	4.0	100.0	133	3.82
0.5	199.4	15	0.75	1.0	249.9	40	0.94	4.0	100.0	133	3.80
0.5	199.4	15	0.75	1.0	250.0	40	0.96	4.0	100.0	288	4.11
0.5	249.6	39	0.48	1.0	251.2	41	0.96	4.0	100.0	288	4.07
0.5	249.6	39	0.44	1.0	252.0	41	0.96	4.0	100.0	398	4.61
1.0	25.0	1	3.57	1.0	252.0	41	0.95	4.0	100.0	508	4.54
1.0	25.0	1	3.68	1.0	252.0	41	0.98	4.0	100.0	508	4.67
1.0	25.0	1	3.59	2.0	25.0	1	4.57	4.0	151.0	5	3.26
1.0	26.9	229	4.04	2.0	50.8	1	4.12	4.0	151.0	5	3.17
1.0	26.9	229	4.11	2.0	50.8	1	4.12	4.0	151.5	113	3.61
1.0	26.9	229	3.98	2.0	76.3	1	3.68	4.0	151.5	252	3.78
1.0	25.9	331	4.32	2.0	76.3	1	3.65	4.0	151.0	335	3.91
1.0	25.9	331	4.43	2.0	97.7	1	3.29	4.0	151.0	335	3.78
1.0	25.0	431	4.69	2.0	97.7	1	3.35	4.0	152.2	473	4.08
1.0	25.0	431	4.59	2.0	150.7	5	2.67	4.0	152.2	473	4.03
1.0	25.0	431	4.64	2.0	150.6	5	2.74	4.0	200.1	16	2.68
1.0	25.3	508	5.21	2.0	200.0	16	2.11	4.0	200.1	16	2.66
1.0	25.3	508	5.25	2.0	200.0	16	2.07	4.0	253.5	42	2.51
1.0	50.1	1	3.47	2.0	250.0	40	1.71	4.0	253.5	42	2.54
1.0	50.1	1	3.44	2.0	250.0	40	1.80				
1.0	50.0	107	3.57	3.0	25.0	1	4.82				

lations were carried out at constant temperature over a grid of pressure and sodium chloride concentrations, and at constant pressure over a grid of temperature and sodium chloride concentrations. This resulted in 1470 normalized solubility values over the entire grid of all three variables. A portion of these normalized values are given in Table II.

Our method for determining the temperature dependence of the thermodynamic solubility product was described in the first paper of this series (*7*). In the present analysis, we began with expressions for the temperature dependence of the infinite dilution partial molar heat capacities of the ions and the solid. The temperature dependence of the infinite dilution ionic partial molar heat capacities was obtained using expressions for the temperature dependence of the infinite dilution partial molar heat capacities of $SrCl_2$, HCl, Na_2SO_4, and NaCl from the work of Pitzer and co-workers (*8–11*) and the additivity principle (*12*). By integrating the heat capacity expressions, the enthalpy, free energy, and equilibrium constant can be obtained as described in our previous papers (*1, 7*). Unfortunately, Pitzer and co-workers did not use the same mathematical expression for the temperature dependence of the infinite dilution partial molar heat capacity of the various electrolytes so the resulting expression for the equilibrium constant is somewhat complex and is given as

$$\ln K_{\mathrm{sp}}(T) = -4762.71 - 0.878035(T/\mathrm{K}) + \\ 1.84788 \times 10^{-4}(T/\mathrm{K})^2 - \frac{320587.4}{(T/\mathrm{K})} + 731.756 \ln (T/\mathrm{K}) + \\ \frac{99430.6 \ln (T/\mathrm{K})}{(T/\mathrm{K})} - 2.98111\left(\frac{T/\mathrm{K} - 263}{T/\mathrm{K}}\right) \ln (T/\mathrm{K} - 263) \tag{1}$$

Table II. Smoothed Values of the Solubility of $SrSO_4$, *s*, in Water and Aqueous NaCl

[NaCl]/*m*	*T*/°C	*P*/bar	$10^3s/m$
0	25	1	0.58
0.5	25	1	2.61
1	25	1	3.61
1.5	25	1	4.18
2	25	1	4.57
3	25	1	4.77
0	50	1	0.57
0.5	50	1	2.57
1	50	1	3.46
1.5	50	1	3.87
2	50	1	4.12
3	50	1	4.29
4	50	1	3.92
0	75	1	0.47
0.5	75	1	2.24
1	75	1	3.04
1.5	75	1	3.43
2	75	1	3.67
3	75	1	3.81
4	75	1	3.69
0	100	1	0.29
0.5	100	1	1.91
1	100	1	2.57
1.5	100	1	3.02
2	100	1	3.32
3	100	1	3.45
4	100	1	3.53
0	150	5	0.22
0.5	150	5	1.20
1	150	5	1.93
1.5	150	5	2.40
2	150	5	2.72
3	150	5	3.08
4	150	5	3.34
0	200	15	0.13
0.5	200	15	0.73
1	200	15	1.34
1.5	200	15	1.91
2	200	15	2.37
3	200	15	2.85
4	200	15	3.23
0	250	40	0.06
0.5	250	40	0.40
1	250	40	0.96
1.5	250	40	1.57
2	250	40	2.09
3	250	40	2.70
4	250	40	3.16
0	25	100	0.69
0.5	25	100	2.80
1	25	100	3.81
1.5	25	100	4.39
2	25	100	4.77
3	25	100	4.85
4	25	100	4.26
0	50	100	0.59
0.5	50	100	2.66
1	50	100	3.59
1.5	50	100	4.08
2	50	100	4.39
3	50	100	4.50
4	50	100	4.07
0	75	100	0.49
0.5	75	100	2.40
1	75	100	3.23
1.5	75	100	3.68
2	75	100	3.94
3	75	100	4.05
4	75	100	3.89
0	100	100	0.36
0.5	100	100	2.07
1	100	100	2.83
1.5	100	100	3.32
2	100	100	3.65
3	100	100	3.80
4	100	100	3.74
0	150	100	0.23
0.5	150	100	1.43
1	150	100	2.23
1.5	150	100	2.70
2	150	100	2.99
3	150	100	3.32
4	150	100	3.58
0	200	100	0.14
0.5	200	100	0.91
1	200	100	1.57
1.5	200	100	2.09
2	200	100	2.49
3	200	100	3.01
4	200	100	3.41
0	250	100	0.06
0.5	250	100	0.53
1	250	100	0.98
1.5	250	100	1.59
2	250	100	2.15
3	250	100	2.74
4	250	100	3.27
0	25	200	0.75
0.5	25	200	2.90
1	25	200	3.99
1.5	25	200	4.61
2	25	200	4.94
3	25	200	4.90
4	25	200	4.48
0	50	200	0.64
0.5	50	200	2.70
1	50	200	3.88
1.5	50	200	4.41
2	50	200	4.65
3	50	200	4.60
4	50	200	4.29
0	75	200	0.52
0.5	75	200	2.45
1	75	200	3.53
1.5	75	200	4.06
2	75	200	4.28
3	75	200	4.35
4	75	200	4.10
0	100	200	0.38
0.5	100	200	2.15
1	100	200	3.07
1.5	100	200	3.67
2	100	200	4.05
3	100	200	4.12
4	100	200	3.94
0	150	200	0.25
0.5	150	200	1.56
1	150	200	2.31
1.5	150	200	2.83
2	150	200	3.17
3	150	200	3.51
4	150	200	3.73
0	200	200	0.15
0.5	200	200	1.04
1	200	200	1.62
1.5	200	200	2.11
2	200	200	2.54
3	200	200	3.12
4	200	200	3.53
0	250	200	0.06
0.5	250	200	0.61
1	250	200	0.99
1.5	250	200	1.60
2	250	200	2.20
3	250	200	2.78
4	250	200	3.35
0	25	300	0.80
0.5	25	300	3.09
1	25	300	4.29
1.5	25	300	4.93
2	25	300	5.21
3	25	300	5.12
4	25	300	4.72
0	50	300	0.67
0.5	50	300	2.81
1	50	300	4.20
1.5	50	300	4.84
2	50	300	5.06
3	50	300	4.89
4	50	300	4.53
0	75	300	0.54
0.5	75	300	2.52
1	75	300	3.95
1.5	75	300	4.60
2	75	300	4.79
3	75	300	4.69
4	75	300	4.33
0	100	300	0.42
0.5	100	300	2.22
1	100	300	3.56
1.5	100	300	4.21
2	100	300	4.48
3	100	300	4.43
4	100	300	4.12
0	150	300	0.27
0.5	150	300	1.63
1	150	300	2.49
1.5	150	300	3.03
2	150	300	3.33
3	150	300	3.64
4	150	300	3.82
0	200	300	0.16
0.5	200	300	1.12
1	200	300	1.65
1.5	200	300	2.15
2	200	300	2.60
3	200	300	3.20
4	200	300	3.59
0	250	300	0.07
0.5	250	300	0.68
1	250	300	0.98
1.5	250	300	1.57
2	250	300	2.18
3	250	300	2.83
4	250	300	3.40
0	25	400	0.87
0.5	25	400	3.34
1	25	400	4.54
1.5	25	400	5.25
2	25	400	5.59
3	25	400	5.40
4	25	400	4.89
0	50	400	0.73
0.5	50	400	2.99
1	50	400	4.40
1.5	50	400	5.13
2	50	400	5.44
3	50	400	5.21
4	50	400	4.75
0	75	400	0.59
0.5	75	400	2.63
1	75	400	4.07
1.5	75	400	4.84
2	75	400	5.18
3	75	400	5.01
4	75	400	4.60
0	100	400	0.47
0.5	100	400	2.29
1	100	400	3.60
1.5	100	400	4.38
2	100	400	4.78
3	100	400	4.72
4	100	400	4.40
0	150	400	0.29
0.5	150	400	1.69
1	150	400	2.57
1.5	150	400	3.13
2	150	400	3.45

Table II. (Continued)

[NaCl]/*m*	*T*/°C	*P*/bar	$10^3 s/m$	[NaCl]/*m*	*T*/°C	*P*/bar	$10^3 s/m$	[NaCl]/*m*	*T*/°C	*P*/bar	$10^3 s/m$
3	150	400	3.77	0.5	100	500	2.38	2	50	600	5.95
4	150	400	3.95	1	100	500	3.80	3	50	600	5.60
0	200	400	0.17	1.5	100	500	4.58	4	50	600	4.99
0.5	200	400	1.19	2	100	500	4.98	0	75	600	0.70
1	200	400	1.67	3	100	500	4.90	0.5	75	600	2.92
1.5	200	400	2.20	4	100	500	4.55	1	75	600	4.51
2	200	400	2.70	0	150	500	0.30	1.5	75	600	5.29
3	200	400	3.30	0.5	150	500	1.76	2	75	600	5.54
4	200	400	3.67	1	150	500	2.57	3	75	600	5.33
0	250	400	0.08	1.5	150	500	3.18	4	75	600	4.84
0.5	250	400	0.74	2	150	500	3.56	0	100	600	0.54
1	250	400	0.99	3	150	500	3.91	0.5	100	600	2.50
1.5	250	400	1.63	4	150	500	4.11	1	100	600	3.96
2	250	400	2.30	0	200	500	0.18	1.5	100	600	4.72
3	250	400	2.86	0.5	200	500	1.26	2	100	600	5.03
4	250	400	3.47	1	200	500	1.72	3	100	600	4.98
0	25	500	0.98	1.5	200	500	2.24	4	100	600	4.66
0.5	25	500	3.62	2	200	500	2.77	0	150	600	0.33
1	25	500	5.17	3	200	500	3.40	0.5	150	600	1.87
1.5	25	500	5.84	4	200	500	3.79	1	150	600	2.82
2	25	500	6.06	0	250	500	0.09	1.5	150	600	3.38
3	25	500	5.66	0.5	250	500	0.81	2	150	600	3.68
4	25	500	5.02	1	250	500	1.04	3	150	600	4.04
0	50	500	0.82	1.5	250	500	1.63	4	150	600	4.27
0.5	50	500	3.19	2	250	500	2.28	0	200	600	0.19
1	50	500	4.65	3	250	500	2.92	0.5	200	600	1.37
1.5	50	500	5.49	4	250	500	3.57	1	200	600	1.91
2	50	500	5.77	0	25	600	1.06	1.5	200	600	2.42
3	50	500	5.46	0.5	25	600	3.90	2	200	600	2.90
4	50	500	4.89	1	25	600	5.55	3	200	600	3.52
0	75	500	0.65	1.5	25	600	6.19	4	200	600	3.95
0.5	75	500	2.77	2	25	600	6.33	0	250	600	0.10
1	75	500	4.25	3	25	600	5.84	0.5	250	600	0.91
1.5	75	500	5.09	4	25	600	5.13	1	250	600	1.20
2	75	500	5.45	0	50	600	0.89	1.5	250	600	1.79
3	75	500	5.23	0.5	50	600	3.40	2	250	600	2.40
4	100	500	4.75	1	50	600	5.05	3	250	600	2.95
0	100	500	0.50	1.5	50	600	5.80	4	250	600	3.70

Table III. Coefficients for Calculating the Temperature Dependence of the Partial Molar Properties

species	$A_V/(\mathrm{cm^3\ mol^{-1}})$	$B_V/(\mathrm{cm^3\ mol^{-1}\ K^{-1}})$	$C_V/(\mathrm{cm^3\ mol^{-1}\ K^{-2}})$	$A_K/(\mathrm{cm^3\ mol^{-1}\ bar^{-1}})$	$B_K/(\mathrm{cm^3\ mol^{-1}\ bar^{-1}\ K^{-1}})$	$C_K/(\mathrm{cm^3\ mol^{-1}\ bar^{-1}\ K^{-2}})$
$SrCl_2$	−248.2	1.616	−0.002 436	353.2	−2.09	0.003 13
HCl	−61.3	0.493	−0.000 764	124.6	−0.75	0.001 12
Sr^{2+}	−125.6	0.630	−0.000 908	104.0	−0.59	0.000 89
Na_2SO_4	−248.2	1.547	−0.002 268	384.0	−2.19	0.003 21
NaCl	−101.6	0.701	−0.001 023	174.9	−1.01	0.001 48
SO_4^{2-}	−167.6	1.131	−0.001 750	284.2	−1.67	0.002 49
$SrSO_4$	44.0	0.007	0.0	0.1	0.0	0.0
equilibrium	−337.2	1.754	−0.002 658	388.1	−2.26	0.003 38

The effect of pressure on the solubility product may determined using (*13*)

$$\ln\left[\frac{K_{sp}(T,P)}{K_{sp}(T,P_{ref})}\right] = \frac{-\Delta\bar{V}^\circ(P-P_{ref})}{RT} + \frac{\Delta\bar{K}^\circ(P-P_{ref})^2}{2RT} \qquad (2)$$

in which R is 83.314 41 cm³ bar K⁻¹ mol⁻¹. The reference pressure P_{ref} is taken as 1 bar for temperatures of 100 °C or less and the saturated water vapor for temperatures greater than 100 °C. To compute the reference pressure at temperatures above 100 °C, the equation of Ambrose and Lawrenson (*14*) was used.

$\Delta\bar{V}^\circ$ in eq 2 is the infinite dilution partial molar volume change for the dissolution reaction. It is the difference between the infinite dilution partial molar volumes of the products (Sr^{2+} and SO_4^{2-}) and the reactant ($SrSO_4$). Similarly, $\Delta\bar{K}^\circ$ is the change in the infinite dilution partial molar compressibility for the equilibrium and is calculated as the difference between the infinite dilution partial molar compressibilities of the ionic products and the solid reactant. The $\bar{V}^\circ_i$ and $\bar{K}^\circ_i$ for the ions are determined in a manner completely analogous to that used for the heat capacities by determining ionic values from electrolyte values using the additivity principle. Again, the electrolytes used were $SrCl_2$, Na_2SO_4, HCl, and NaCl. Values for the electrolyte infinite dilution partial molar properties at temperatures ranging from 0 to 200 °C were taken from the literature (*15–17*) and were fitted to functions of absolute temperature given by

$$\bar{V}^\circ(T) = A_V + B_V T + C_V T^2 \qquad (3)$$

and

$$-10^3\bar{K}^\circ(T) = A_K + B_K T + C_K T^2 \qquad (4)$$

The coefficients for the temperature dependence of the partial molar properties of the electrolytes and the ions along with values from the *International Critical Tables* (*18*) for the temperature dependence of the partial molar properties of $SrSO_4$(s) are summarized in Table III.

The changes in the infinite dilution partial molar volume and compressibility for the equilibrium are both negative. This is due to the compressive field of the divalent ions acting on the water molecules. The ionic compression causes a decrease in the volume of the water molecules near the ions

Table IV. B_i Values for Calculating the Mean Activity Coefficient with Equation 6

parameter	term	value and estimated error
B_0	constant	-40.3990 ± 1.0696
B_1	$I^{1/2}$	-4.3373 ± 0.0754
B_2	I	-16.5963 ± 0.7323
B_4	T	$(-2.66525 \pm 0.05080) \times 10^{-2}$
B_6	$\ln T$	8.4768 ± 0.2119
B_7	$I^{1/2}P$	$(-7.975 \pm 0.537) \times 10^{-3}$
B_{10}	IT	$(-9.8857 \pm 0.3365) \times 10^{-3}$
B_{11}	$I^{1/2}/T$	444.1 ± 29.6
B_{14}	$I \ln T$	3.59225 ± 0.14493
B_{15}	TP	$(-2.004 \pm 0.333) \times 10^{-6}$
B_{17}	$P \ln T$	$(1.5358 \pm 0.2304) \times 10^{-4}$
B_{18}	$I^{1/2}TP$	$(1.1716 \pm 0.0697) \times 10^{-5}$
B_{20}	$I^{1/2}P/T$	1.3554 ± 0.1032

relative to water molecules in bulk solution. Since both $\Delta\bar{V}^\circ$ and $\Delta\bar{K}^\circ$ are negative, the two terms in eq 2 are opposite in sign. However, the first term (volume) is numerically larger than the second term (compressibility) for the range of pressure common to oil field brines.

From the thermodynamic equilibrium constant calculated using eqs 1–4 and the solubility, the mean ionic activity coefficient can be computed by

$$\gamma_\pm = K_{sp}^{1/2}/s \qquad (5)$$

where s is the concentration of the strontium and sulfate ions in solution.

The activity coefficients were calculated from the interpolated solubilities using eq 5 and were fitted to an empirical function of ionic strength, temperature, and pressure given by

$$\ln[\gamma_\pm] = B_0 + B_1 I^{1/2} + B_2 I + B_3 P + B_4 T + B_5/T + B_6 \ln T + B_7 I^{1/2} P + B_8 IP + B_9 I^{1/2} T + B_{10} IT + B_{11} I^{1/2}/T + B_{12} I/T + B_{13} I^{1/2} \ln T + B_{14} I \ln T + B_{15} TP + B_{16} P/T + B_{17} P \ln T + B_{18} I^{1/2} TP + B_{19} ITP + B_{20} I^{1/2} P/T + B_{21} IP/T + B_{22} I^{1/2} P \ln T + B_{23} IP \ln T \qquad (6)$$

We fit eq 6 to the 1470 activity coefficient value using the SAS REG procedure with the SELECTION=MAXR option (*19*) and used the method based on Mallow's C_p statistic as described by Daniel and Wood (*20*) to find an optimum subset model of eq 6 that contains 13 rather than 24 terms. The numerical values of the B_i fitting parameters along with their estimated errors are given in Table IV.

The experimental and calculated solubility values along with values from the literature at 25 and 100 °C and 1 bar are plotted in Figures 1 and 2. Our experimental and calculated values compare well with the bulk of the literature data at these as well as other temperatures and pressures which gives us confidence in our data at temperatures and pressures beyond the range of those from the literature.

The mathematical model developed provides excellent agreement with our experimental data for the region of the temperature–pressure–ionic strength grid common to oil field brines, that is, ionic strengths of 0.5–4 m, temperatures of 25–150 °C, and pressures of 1–500 bar. Outside this region, the model provides a fair estimate of the solubility but should be used with caution, particularly for high ionic strength solutions (greater than 3 m) at high temperature (greater than 200 °C). The utility of the model lies in the ability to predict the solubility of strontium sulfate which provides a means to protect above-ground equipment and oil and gas formations from scale formation.

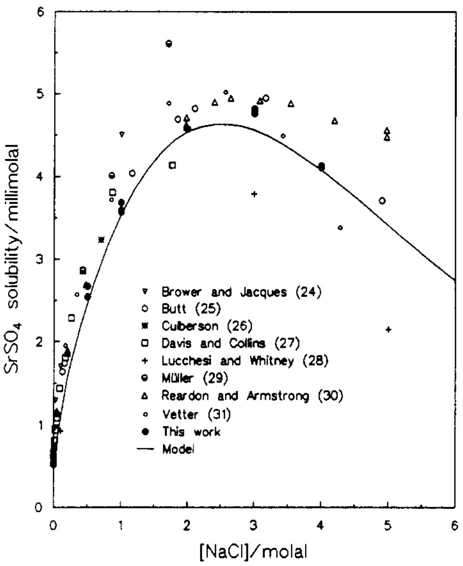

Figure 1. Comparison of the experimental and predicted solubility with literature data at 25 °C and 1 bar.

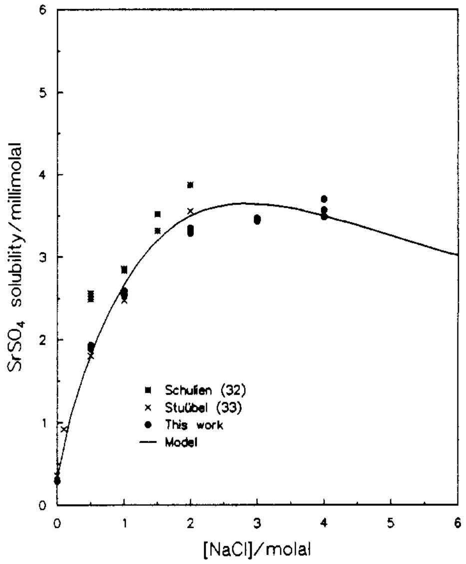

Figure 2. Comparison of the experimental and predicted solubility with literature data at 100 °C and 1 bar.

Glossary

K_{sp}	thermodynamic solubility product constant
I	ionic strength (m)
T	absolute temperature (K)
P	pressure (bar)
s	$SrSO_4$ solubility (m)
$\Delta\bar{V}^\circ$	molar volume change on dissolution (cm^3 mol^{-1})
A_V, B_V, C_V	temperature dependence parameters for $\Delta\bar{V}^\circ$
$\Delta\bar{K}^\circ$	molar compressibility change on dissolution (cm^3 mol^{-1} bar^{-1})
A_K, B_K, C_K	temperature dependence parameters for $\Delta\bar{K}^\circ$
$\gamma_\pm$	mean activity coefficient
B_i	coefficients in ln $\gamma_\pm$ expression

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