enforce linearity in the pressure dependence of $C_{p,\phi}$.

Previous results on $C_{p,\phi}$ and $\{C_{p,\phi}(m_1) - C_{p,\phi}(m_2)\}$ for 1-1 electrolytes (*4*, *6*) have shown that absolute differences between the salts tend to increase as temperature increases but on a relative scale the opposite is true. This means that, as a fraction of the total effect, individuality decreases. A comparison of the present results for $MgCl_2$(aq) with previous results for $CaCl_2$(aq) shows the same trends: absolute differences increase with increasing temperature and relative differences (except at 0 mol kg^{-1} and 600 K) decrease. The exception for $C_{p,\phi}{}^0$ at 600 K may be due to the great inaccuracy of determining $C_{p,\phi}{}^0$ by extrapolation of the experimental measurements. Both $CaCl_2$(aq) and $MgCl_2$(aq) are strongly ion paired at the lowest experimental concentrations (*26*) and plots of $C_{p,\phi}$ vs $m^{1/2}$ exhibit slopes which are much less than the Debye–Hückel limiting law even at the lowest experimental molalities (*3*).

The $C_{p,\phi}$s presented in this paper, together with experimental standard Gibbs free energies and enthalpies at 298.15 K, allow calculations of the thermodynamic properties of $MgCl_2$(aq) at temperatures to 600 K. Calculation of standard Gibbs free energies by this route allows the calculation of equilibrium constants for chemical reactions involving $MgCl_2$(aq) under these conditions. The details of the calculations have been reported elsewhere (*27*, *28*).

Registry No. $MgCl_2$, 7786-30-3.

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Thermodynamics of "Scale" Mineral Solubilities. 1. $BaSO_4$(s) in H_2O and Aqueous NaCl

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A review of the solubilities of barium sulfate in water and aqueous NaCl is given. Equations to calculate $C_p{}^\circ$, ΔH°, ΔS°, ΔG° for all of the species in the solubility equilibrium are presented and the coefficients are computed. With these coefficients, all of the thermodynamic quantities and the equilibrium constant are expressed as a function of temperature. The calculated thermodynamic values are compared with the available literature values. Activity coefficients are calculated at the given NaCl concentration and temperature by using the Pitzer formalism. The best literature solubility data are used to calculate the needed coefficients. A computer program is used with these coefficients to predict the solubility of $BaSO_4$(s) in NaCl solutions up to 300 °C.

Introduction

"Scale" formation is the precipitation of a solid mineral from a brine. Although there are many industrial processes where scaling can be a concern there are and many possible scales, we have focused on those most common in oil and gas production. All petroleum reservoirs contain connate brines. These are ancient sea water modified chemically by millenia of interaction with the gas phase and the reservoir rock/clay matrix. In the reservoir the brine is in equilibria with its surroundings at their temperature and pressure. But as the brine is produced with the oil/gas, the equilibrium is disturbed by going to a lower temperature and pressure. This can lead to the precipitation of scale ranging from a minor annoyance to massive clogging of production tubing and above ground equipment. Scale formation can also be a problem during "water flood" operations. Here, water or brine is injected into a reservoir to maintain production pressure. If the injected water is quite different in composition with the connate brine,

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scale formation can occur around the bottom of the injection well or even further out in the reservoir. We are engaged in systematic and critical review of the thermodynamics of the most common scale minerals. This is a necessary first step for the development of better tools for scale prediction and treatment.

This first paper in the series describes our approach as applied to $BaSO_4$(s). $BaSO_4$(s) is the least soluble of the common sulfate scales in water. Unlike some common sulfate scales, it cannot normally be removed by chemical means. It must be removed mechanically or the equipment discarded.

Our general approach is the following. We use the best thermodynamic data of the ions and solids to derive a thermodynamic solubility constant expression as a function of temperature. Then the Pitzer formalism is used to develop expressions for activity coefficients. These expressions are "fine-tuned" with the best available solubility data. Finally our predicted solubilities in water and NaCl are compared with the best available literature data.

Literature

There are many references to the solubility of $BaSO_4$(s) in water, sea water, aqueous NaCl, and other electrolyte solutions at different temperature and pressures. We discuss the ones that we have critically examined.

Hanor (*1*) studied the origin of barite and its solubility in sea water. Fresenius and Hintz (*2*) determined the solubility in water, 2.5 and 10% aqueous NH_4Cl, 2.5% aqueous NaCl, 10% HNO_3, and HCl. Fraps (*3*) studied the solubility in aqueous $FeCl_3$, $AlCl_3$, and $MgCl_2$. Rosseinsky (*4*) determined the solubility in water at 25 °C conductometrically. Ghosh et al. (*5*) determined the solubility in water using a resin membrane electrode. Kritsotakis (*6*) studied the solubility in 2 and 3 M aqueous NaCl at 25, 150, and 300 °C at total sulfate molarities of 10^{-1}, 10^{-3}, and 10^{-6} and over a wide pH range. Melcher (*7*) studied the solubility of $BaSO_4$(s) in water conductometrically at 18, 50, and 100 °C. Neuman (*8*) measured the solubility at 25 °C in aqueous potassium, magnesium, and lanthanum chloride and nitrate solutions but only up to ionic strength 0.04 *m*.

Some of the best solubility work on $BaSO_4$(s) was done by Templeton (*9*). The work was done in aqueous NaCl up to 5.0 *m* at 25, 35, 50, 65, 80, and 95 °C. Selivanova and Kapustinskii (*10*) determined the solubility in water at 25 °C polarographically and reported K_{sp} and ΔG°. Burton et al. (*11*) measured the solubility in water and sea water at 20 °C. In an important work Davies and Collins (*12*) studied the solubility at 25 ° in aqueous solutions of $CaCl_2$, NaCl, KCl, KBr, and $Na_2B_4O_7$. They observed a maximum in solubility near an ionic strength of 1.0 *m* similar to that found for $SrSO_4$ (*13*). Strubel (*14*) also looked at the solubility of $BaSO_4$(s) in aqueous NaCl as a function of temperature.

Blount (*15*) did a very extensive research on the solubility of $BaSO_4$(s) in water and aqueous NaCl as a function of temperature and pressure. He used activity coefficients calculated by an extended Debye–Hückel theory and reports K_{sp} and thermodynamic quantities as a function of temperature. Khodakovskiy et al. (*16*) expressed K_{sp} and thermodynamic parameters as a function of temperature using a method originally suggested by Barton (*17*). However, they used $C_p = AT$ which is not in accord with the literature. Consequently their thermodynamic parameters are not comparable with others. Egorov and Titova (*18*) give equations for ΔG° and log K_{sp} for some sulfates and carbonates. In some detailed work Malinin and his co-workers (*19*, *20*) studied $BaSO_4$(s) solubility in water and different concentrations of aqueous NaCl, KCl, $CaCl_2$, and $MgCl_2$ from 100 to 370 °C. Activity coefficients were calculated by the Debye–Hückel theory and K_{sp} is reported as a function of temperature.

Finally, Rogers (*21*) has applied the Pitzer formalism (*22*) to compute the solubility of $CaSO_4{\cdot}2H_2O$(s), $SrSO_4$(s), and $BaSO_4$(s) in saline waters at 25 °C. Her predicted values are in accord with the literature only up to 0.5 *m* NaCl.

Calculational Approach

For the solubility equilibrium

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

$$K_{sp} = a_{Ba^{2+}(aq)} a_{SO_4^{2-}(aq)} \tag{1}$$

For the dissolution of $BaSO_4$(s) in aqueous solution we can write

$$K_{sp} = s^2 \gamma_\pm^2 \tag{2}$$

where s is solubility (moles/kg of H_2O) and $\gamma_\pm$ is the mean ionic activity coefficient. It should be emphasized that s is the experimental fact. The literature values for K_{sp} are dependent on the assumptions made about $\gamma_\pm$. Our approach is to derive the values for ΔH°, ΔG°, and K_{sp} from the best available thermodynamic data. Then, using the critically evaluated s data, we derived expressions for activity coefficients within the context of the Pitzer formalism. Finally, the K_{sp} and $\gamma_\pm$ expressions are fine tuned to reproduce the best s data as closely as possible.

Our approach to the thermodynamics is based on the fact that the heat capacity for each species can be expressed as

$$C_{p_i} = A + BT + C/T^2 \tag{3}$$

This gives us the corresponding enthalpy as

$$\Delta H^\circ_i = AT + BT^2/2 - C/T + I_h \tag{4}$$

where I_h is an integration constant. Then the Gibbs free energy and entropy can be expressed as

$$\Delta G^\circ_i = -AT \ln T - BT^2/2 - C/2T + I_h + I_g T \tag{5}$$

$$\Delta S^\circ_i = A \ln T + BT - C/2T^2 + I_s \tag{6}$$

where I_g and I_s are additional integration constants.

Then for the equilibrium

$$\Delta A = A_{Ba^{2+}(aq)} + A_{SO_4^{2-}(aq)} - A_{BaSO_4(s)} \tag{7}$$

and equivalent expressions for all the other constants. This allows us to express the equilibrium constant as

$$\ln K_{sp} = \frac{\Delta A \ln T}{R} + \frac{\Delta BT}{2R} + \frac{\Delta C}{2RT^2} - \frac{\Delta I_h}{RT} - \frac{\Delta I_g}{R} \tag{8}$$

where R = 8.314 35 J K^{-1} mol^{-1}. A, B, and C values for $BaSO_4$(s) were taken from the literature (*23*, *24*) whereas for the ions they were computed from the ΔH° values given by Barner and Scheurman (*25*). The I_h, I_g, and I_s values were evaluated from the ΔH°_i, ΔG°_i, and ΔS°_i values at 25 °C taken from the NBS tables (*26*, *27*). Finally, the I_h and I_g values were fine tuned so as to reproduce the best low-temperature K_{sp} values. Table I gives the A, B, C, I_h, I_g, and I_s values for the species and the Δ values for the equilibrium. ΔH°, ΔG°, ΔS°, and ΔC_p° values at different temperatures using eq 3–6 are calculated and given in Tables II and III.

The calculated values of log K_{sp} are given in Table IV and plotted versus temperature in Figure 1. Some log K_{sp} values from the literature are also shown. Note the maximum in log K_{sp} near 100 °C. Up to 100 °C there is really not much difference between our results, Blount's, Khodakovskiy's, and Templeton's. From 100 to 250 °C, our results are in good agreement with those of Blount and Malinin. Helgeson's values (*28*) are consistently higher at low temperature. In general,

Table I. Coefficients to Calculate the Thermodynamic Quantities for the Species and Equilibrium

species	A	B	$C \times 10^{-6}$	I_h	I_g	I_s
SO_4^{2-}(aq)	818.323	-1.84581	-49.7126	-1 237 946	5762.58	-4371.65
Ba^{2+}(aq)	-82.370	-0.06590	6.1124	-489 723	-683.58	532.96
$BaSO_4$(s)	141.419	0.0	-3.5271	-1 527 181	1338.88	-693.37
	ΔA	ΔB	$\Delta C \times 10^{-6}$	ΔI_h	ΔI_g	ΔI_s
equilibrium	594.534	-1.91171	-40.0731	-200 488	3740.12	-3145.32

Table II. Thermodynamic Quantities at Different Temperatures for the Species

T/°C	$\Delta H°$/kJ mol^{-1}	$\Delta G°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}	$\Delta C_p°$/J K^{-1} mol^{-1}
		SO_4^{2-}(aq)		
0.0	-901.28	-758.02	48.1	-352.2
25.0	-909.27	-744.54	20.1	-291.2
50.0	-916.04	-730.45	-1.7	-254.2
75.0	-922.12	-715.86	-19.9	-234.4
100.0	-927.87	-700.84	-35.8	-227.5
125.0	-933.57	-685.44	-50.6	-230.2
150.0	-939.44	-669.68	-64.9	-240.4
175.0	-945.64	-653.57	-79.1	-256.4
200.0	-952.30	-637.10	-93.6	-277.1
225.0	-959.53	-620.26	-108.5	-301.5
250.0	-967.40	-603.04	-123.9	-329.0
275.0	-975.99	-585.43	-139.9	-358.9
300.0	-985.36	-567.41	-156.6	-390.9
		Ba^{2+}(aq)		
0.0	-537.06	-558.95	11.9	-18.4
25.0	-537.71	-560.93	9.6	-33.3
50.0	-538.70	-562.84	6.5	-45.1
75.0	-539.95	-564.66	2.7	-54.9
100.0	-541.43	-566.38	-1.4	-63.1
125.0	-543.09	-568.00	-5.7	-70.0
150.0	-544.92	-569.51	-10.1	-76.1
175.0	-546.89	-570.91	-14.7	-81.5
200.0	-548.99	-572.19	-19.2	-86.2
225.0	-551.20	-573.36	-23.8	-90.6
250.0	-553.52	-574.41	-28.3	-94.5
275.0	-555.93	-575.35	-32.8	-98.2
300.0	-558.42	-576.19	-37.3	-101.5
		$BaSO_4$(s)		
0.0	-1475.64	-1371.72	123.6	94.1
25.0	-1473.19	-1362.31	132.2	101.7
50.0	-1470.57	-1353.12	140.7	107.6
75.0	-1467.81	-1344.14	148.9	112.3
100.0	-1464.96	1335.36	156.8	116.1
125.0	-1462.02	-1326.77	164.4	119.2
150.0	-1459.00	-1318.37	171.7	121.7
175.0	-1455.93	-1310.15	178.8	123.9
200.0	-1452.81	-1302.10	185.6	125.7
225.0	-1449.65	-1294.22	192.1	127.2
250.0	-1446.46	-1286.50	198.3	128.5
275.0	-1443.23	-1278.93	204.4	129.7
300.0	-1439.97	-1271.51	210.2	130.7

Malinin's values seem high at low temperatures and low at high temperatures. Over the entire temperature range we are in best agreement with Blount.

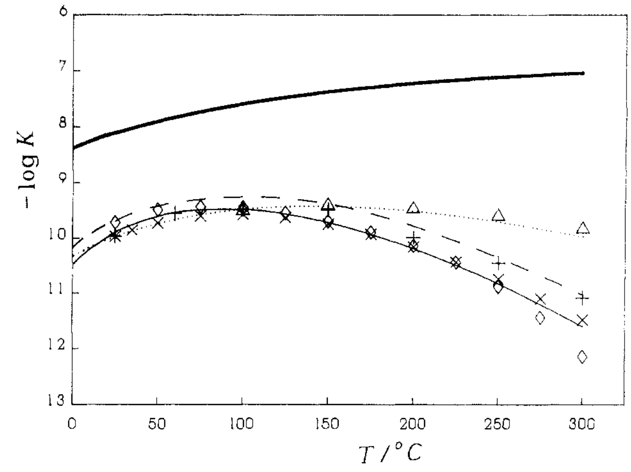

Figure 1. $-\log K_{sp}$ vs T/°C: (—) this work; (···) Khodakovskiy et al.; (- - -) Helgeson; (—) Egorov and Titova; (×) Blount; (◇) Malinin et al.; (△) Strubel; (+) ionic data.

The values of $\Delta G°$, $\Delta H°$, $\Delta S°$, and $\Delta C_p°$ for the solubility equilibrium are given at round temperatures in Table III. The table also compares our values with those reported by Blount and by Khodakovskiy. Also included are the values calculated by Blount from the ionic data of Criss and Cobble (*29*). Most of the differences can be attributed to the fact that our values are calculated from the available absolute heat capacity values while the Criss and Cobble values were calculated from average heat capacities.

Table IV compares the log K_{sp} values we recommend with those in the literature.

Activity Coefficients

In order to understand the behavior of ions in water or natural brines, we need to know the thermodynamic activity, a_i, of the ion. This means that we need to have some reasonable approach for the activity coefficients, γ_i. It should be noted that the major components in almost all natural brines are Na^+(aq) and Cl^-(aq).

In most of the early work on mineral solubility some form of the Debye–Hückel model (*30*) was used. In recent years Pitzer and co-workers (*22*, *31–36*) have developed a formalism that describes the thermodynamics of electrolytes up to high concentrations, pressures, and temperatures. Khoo et al. (*37*, *38*),

Table III. Thermodynamic Quantities for the Solubility Equilibrium

	$\Delta G°$/kJ mol^{-1}			$\Delta H°$/kJ mol^{-1}				$\Delta S°$/J K^{-1} mol^{-1}				$\Delta C_p°$/J K^{-1} mol^{-1}	
T/°C	this work	*15*	*16*	this work	*15*	*16*	*8*	this work	*15*	*16*	ionic	this work	*16*
25	56.84	56.94	54.06	26.21	26.57	23.05	26.36	-102.5	-101.7	-113.4	-102.5	-426.2	-142.7
60	61.26	61.67	61.71	11.78	12.43	14.35	13.81	-148.4	-147.7	-142.3	-142.3	-403.4	-159.8
80	64.47	65.10	64.68	3.74	4.35	11.05		-171.7	-172.0	-151.9		-401.9	-169.0
100	68.13	68.49	67.82	-4.34	-3.72	7.57	0.0	-194.0	-193.3	-161.5	-182.0	-406.6	-178.7
125	73.33	73.18	72.01	-14.65	-13.81	2.93		-220.7	-218.4	-173.2		-419.4	-190.8
150	79.18	78.83	76.48	-25.36	-23.93	-1.97	-16.74	-246.8	-242.7	-185.4	-221.8	-438.2	-202.9
175	85.68	85.31	81.25	-36.60	-34.02	-7.20		-272.6	-266.1	-197.5		-461.7	-214.6
200	92.82	92.55	86.36	-48.48	-44.14	-12.72	-37.24	-298.4	-288.7	-209.2	-270.3	-489.0	-226.8
225	100.61	100.37	91.71	-61.08	-54.22	-18.54		-324.3	-310.5	-221.3		-519.3	-238.9
250	109.05	107.03	97.40	-74.46	-64.31	-24.64	-60.25	-350.5	-329.7	-233.5	-316.7	-552.0	-250.6
275	118.15		103.39	-88.69		-31.05		-377.1		-245.2		-586.7	-262.8
300	127.92	125.52	109.66	-103.81	-84.52	-37.78	-85.35	-404.0	-365.3	-257.3	-361.9	-623.2	-274.5

Table IV. Thermodynamic Solubility Products at Different Temperatures

	-log K								
T/°C	this work	Blount (1977)	Khodakovskiy et al. (1966)	Egorov and titova (1962)	Malinin et al. (1969)	Templeton (1960)	Helgenson (1969)	Strubel (1967)	ionic data
25	9.959	9.973	9.991	8.119	9.72	9.958	9.70		9.97
35	9.821	9.861	9.883	8.028		9.837	9.42		
50	9.672	9.732	9.749	7.905	9.49	9.714			
60	9.605						9.34		9.56
75	9.546	9.608	9.586	7.732	9.44				
100	9.537	9.581	9.488	7.591	9.45		9.22	9.50	9.49
125	9.620	9.635	9.441	7.474	9.55				
150	9.774	9.758	9.436	7.377	9.70		9.34	9.40	9.50
175	9.986	9.940	9.467	7.296	9.90				
200	10.247	10.173	9.528	7.227	10.15		9.76	9.47	10.00
225	10.549	10.450	9.614	7.169	10.45				
250	10.888	10.766	9.721	7.120	10.90		10.34	9.60	10.47
275	11.259	11.117	9.848	7.077	11.45				
300	11.658	11.499	9.990	7.041	12.15		11.05	9.83	11.10

Table V. Sources for Pitzer Coefficients

pair	at 25 °C	ref	at other temp	ref
$BaSO_4$	$CaSO_4$ model	*21*	$MgSO_4$ model	*50*
Ba-Cl	$BaCl_2$ actual	*21*	$CaCl_2$ model	*45*
Na-SO_4	Na_2SO_4 actual	*21*	Na_2SO_4 actual	*53*
Na-Cl	NaCl actual	*21*	NaCl actual	*54*

Boyd (*39*), Bates and co-workers (*40*, *41*), Roy et al. (*42*), Atkinson and co-workers (*43-47*) among others have successfully applied the approach to a variety of electrolyte problems. Recently, Harvie and Weare (*48*, *49*) have successfully reproduced $CaSO_4$(s) and $CaCO_3$(s) solubilities in natural waters at 25 °C using the Pitzer formalism. Rogers (*21*) has estimated the Pitzer parameters for gypsum in NaCl(aq) at 25 °C and reproduced the solubility in sea water within experimental error. She used the same parameters for $SrSO_4$(s) and $BaSO_4$(s) and compared her calculated solubilities with the literature values. For $BaSO_4$(s) the calculated solubility in NaCl(aq) is less than those of Templeton (*9*) and Strubel (*14*) but close to that reported by Davies and Collins (*12*). At NaCl(aq) > 0.5 m the calculated values start deviating from the Davies and Collins work. Pitzer and co-workers (*31-36*), Holmes and Mesmer (*50*), Ananthaswamy and Atkinson (*45*) have extended the formalism to higher temperatures but no attempt has been made to predict solubilities other than at 25 °C.

There are numerous articles which give complete details of the Pitzer equations. Therefore, we present only the final equations for the mean activity coefficients of $BaSO_4$ in NaCl mixture as

$$\begin{aligned}\ln \gamma_{\pm} = {} & 4f^{\gamma} + m_{M}[2B_{MS} + 2EC_{MS}] + \\ & m_{N}[B_{MC} + B_{NS} + EC_{MC} + EC_{NS}] + \\ & m_{M}^{2}[4B'_{MS} + 2C_{MS}] + m_{M}m_{N}[4B'_{MC} + 4B'_{NS} + 2C_{MC} + \\ & 2C_{NS}] + m_{N}^{2}[4B'_{NC} + 2C_{NC}] + m_{N}[{}^{E}\theta_{mN} + {}^{E}\theta_{SC}] + \\ & 4m_{M}m_{N}[\theta'_{MN} + \theta'_{SC}] + m_{N}[{}^{s}\theta_{MN} + {}^{s}\theta_{SC}] + \\ & m_{M}m_{N}[\psi_{MNS} + \psi_{MSC}] + \frac{m_{N}^{2}}{2}[\psi_{MNC} + \psi_{NSC}] \qquad (9)\end{aligned}$$

where the subscripts M, N, S, and C refer to Ba^{2+}(aq), Na^{+}(aq), SO_4^{2-}(aq), and Cl^{-}(aq) ions, respectively. As the $Z_M = |Z_S|$ and $Z_N = |Z_C|$, the ${}^{E}\theta_{MN} = {}^{E}\theta_{SC}$ and $\theta'_{MN} = \theta'_{SC}$ and all the symbols have their usual significance.

The main problem in calculating the activity coefficients is caused by the virial coefficients for $BaSO_4$. This salt is so slightly soluble in water that the Pitzer coefficients cannot be obtained from the pure salt data. The following approach for $BaSO_4$-NaCl mixtures illustrates our general solution to these problems. Each of the Pitzer coefficients for $BaSO_4$ can be described by an equation of the form given by Holmes and Mesmer (*50*) for $MgSO_4$

$$\beta^{(i)} = a + b(T - T_r) + c(T^2 - T_{r_2}) \qquad (10)$$

where T_r is the reference temperature, 298.15 K, a is the $\beta^{(i)}$ value for $BaSO_4$ at 25 °C, and b and c are the coefficients of the $MgSO_4$ fit. We then use the coefficient sources given in Table V The coefficient values for $BaSO_4$ and $BaCl_2$ are given in Table VI for ready reference.

${}^{s}\theta_{ij}$ and ψ_{ijk} values which are considered to be independent of I are reported at 25 °C only. However, considerable deviations are observed in these parameters. Recently Atkinson and his co-workers (*43*, *46*, *47*) observed that ${}^{s}\theta_{ij}$ and ψ_{ijk} parameters depend upon I. These observations are contrary to Pitzer's assumptions. However, Mayer showed that second and third virial coefficients, λ_{ij} and μ_{ijk} for charged species are ionic strength dependent. For ψ_{ijk} (which is a combination of μ_{ijk}'s) Pitzer ignored the ionic strength dependence, assuming it to be very small. In NaCl-$CaCl_2$ (*43*), $CaCl_2$-$CaBr_2$ (*46*), and NaBr-$CaBr_2$ (*47*) mixtures Atkinson and co-workers have showed that these coefficients are distinct functions of ionic strength, but due to the lack of sufficient literature on these mixing parameters in several other systems, they have not discussed it further.

Recently Rogers (*21*) has applied the Pitzer formalism to calcium, strontium, and barium sulfates in saline waters at 25 °C, predicted the solubilities, and compared with literature values. For $BaSO_4$ the predicted solubilities are in good agreement with those of Davies and Collins (*12*) up to 0.5 m NaCl but are below the measured values at higher NaCl concentrations. The differences are more pronounced with Templeton (*9*) and Strubel (*14*) data even at low concentrations of NaCl itself. The plot for the solubility against concentrations of the added salt was shown up to 2 m. If the Pitzer's equation with ${}^{s}\theta_{ij}$ and ψ_{ijk} are used up to 4 m NaCl to predict the solu-

Table VI. Coefficients for $BaSO_4$ and $BaCl_2$ in the Equations for β's and C^{ϕ} as $\beta^{(i)}$ or $C^{\phi} = a + b(T - T_r) + (T^2 - T_r^2) + d(1/T - 1/T_r) + e \ln (T/T_r)$

salt	function	a	b	c	d	e
$BaSO_4$	$\beta^{(0)}$	0.20	0.002916	-3.872×10^{-6}	0	0
	$\beta^{(1)}$	3.1973	0.00124	1.809×10^{-5}	0	0
	$\beta^{(2)}$	-54.24	0.8283	-0.001782	0	0
$BaCl_2$	$\beta^{(0)}$	0.2628	-0.1390	6.826×10^{-5}	5108.0	46.48
	$\beta^{(1)}$	1.4963	-0.01647	2.346×10^{-5}	-498.20	0
	C^{ϕ}	-0.01938	0.2462	-1.184×10^{-4}	-9676.0	-84.83

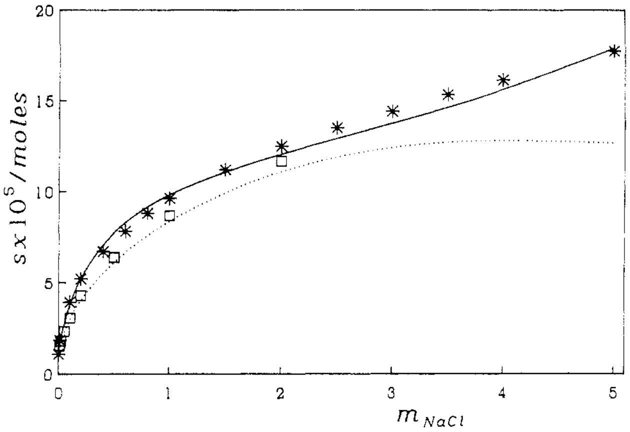

Figure 2. Calculated and experimental solubility vs m_{NaCl} at 25 °C: (—) this work; (···) Pitzer formalism; (*) Templeton; (□) Davies and Collins.

Table VII. Coefficients in Eq 26

$B_1 = -2.5611728 \times 10^5$
$B_2 = 2.9466777 \times 10^5$
$B_3 = -8.6886170 \times 10^4$
$B_4 = 1.6663294 \times 10^3$
$B_5 = -1.8958779 \times 10^3$
$B_6 = 5.6166103 \times 10^2$
$B_7 = -3.5590300$
$B_8 = 4.0215636$
$B_9 = -1.19877908$
$B_{10} = 2.5053231 \times 10^{-3}$
$B_{11} = -2.8178237 \times 10^{-3}$
$B_{12} = 8.4842450 \times 10^{-4}$

bilities, the differences are continuously increasing (Figure 2) with ionic strength, suggesting that ${}^s\theta_{ij}$ and ψ_{ijk} terms might be functions of I or some more additional terms which are functions of I have to be added to the equation.

By considering the above facts, another approach could be done in the following way. Let

$$\ln \gamma_\pm = \ln \gamma_\pm^* + f(I,T) \qquad (11)$$

and $\gamma_\pm^*$ is calculated from Pitzer equation without the ${}^s\theta_{ij}$ and ψ_{ijk} terms in eq 9.

Now γ_{exptl} is calculated from the experimental solubility in NaCl(aq) and the calculated K_{sp} (from eq 8) by the relation

$$\gamma_{exptl} = (K_{sp}/s^2)^{1/2} \qquad (12)$$

This γ_{exptl} is equated to $\gamma_\pm^*$ and $f(I,T)$ by the equation

$$\ln \gamma_{exptl} = \ln \gamma_\pm^* + m_M[(B_1 + B_2I^{1/2} + B_3I) + (B_4 + B_5I^{1/2} + B_6I)T + (B_7 + B_8I^{1/2} + B_9I)T^2 + (B_{10} + B_{11}I^{1/2} + B_{12}I)T^3] \qquad (13)$$

The coefficients are calculated using a nonlinear least-squares program and given in Table VII. The data base in computing the above coefficients are of Templeton's (*19*), Strubel's (*14*), and Blount's (*15*) data.

Solubility Check

Finally, a program has been developed to predict the solubilities of $BaSO_4$ in aqueous NaCl solutions (up to 4 *m*) at any temperature up to 300 °C. A flow chart for this program is given in Figure 3. With this program one can predict the solubility within ±10% deviation.

The experimental solubility vs added NaCl concentration at 25 °C are given in Figure 2. Our predicted values are in excellent agreement with Templeton's and Strubel's data, but up to 22% higher than the data of Davies and Collins. They are up to 5% lower for $I = 2$ than Templeton's data but always greater than those predicted by Rogers (*21*).

At high temperatures the predicted values are in agreement with literature values. The predicted solubilities are plotted against concentration of NaCl at 100, 200, and 250 °C in Figure 4. At 100 °C, the percent deviation with that of Blount (*15*) is only 7% and with Strubel's data (*14*) is 6% except at 0.1 *m* NaCl (12%). In fact, at 0.1 *m* NaCl Blount reported the solubility as 5.8 × 10^{-5} *m* whereas Strubel's value is 6.73 × 10^{-5} *m* (16% difference). Our predicted value is 6.01 × 10^{-5} *m*. At 200 and 250 °C also, our predicted values deviated by only 6%. The percent deviation is 50 and 25 for Strubel's data in 2 *m* NaCl at 200 and 250 °C, respectively. Strubel has reported the solubilities as 62.7 × 10^{-5} and 63.7 × 10^{-5} *m*; Blount's values are 43.0 × 10^{-5} and 49.5 × 10^{-5} *m*, whereas our predicted values are 41.7 × 10^{-5} and 50.6 × 10^{-5} *m* at 200 and 250 °C, respectively, in 2 *m* NaCl.

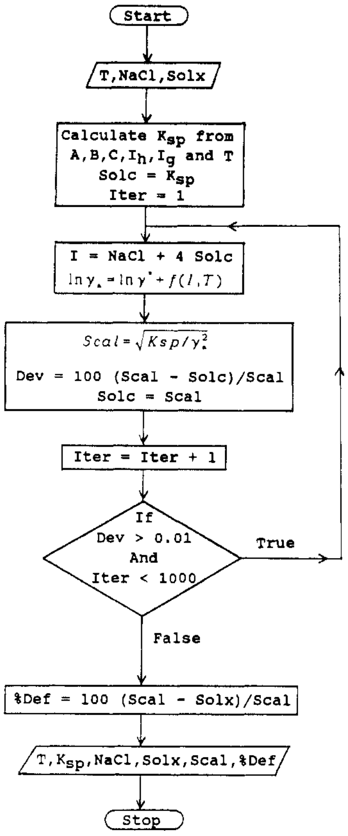

Figure 3. Flow chart for the solubility prediction.

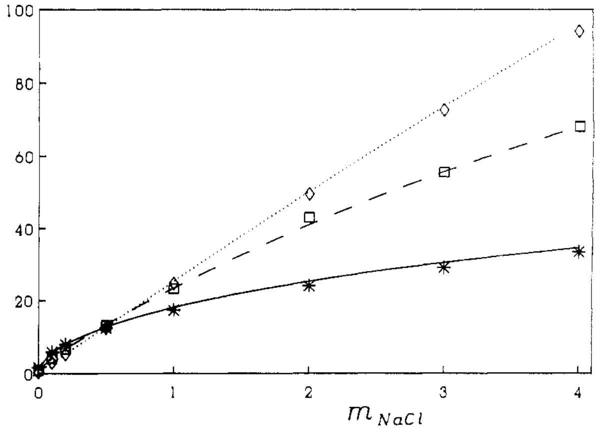

Figure 4. Calculated and experimental solubility (Blount's data) vs m_{NaCl} at higher temperatures: (* and —) 100 °C; (□ and ---) 200 °C; (◇ and ···) 250 °C.

The percent deviation for Templeton's data from 25 to 95 °C and from 0 to 5 *m* NaCl is 4.4% (90 points); for Strubel's data up to 100 °C is 6.7% (36 points); for Blount's data from 0 to 4 *m* NaCl and from 100 to 250 °C is 3.1% (31 points).

The program is effective up to 200 °C and 4 *m* NaCl. As the temperature increases further, it is not able to converge at the highest NaCl concentration, for example, in 4 *m* NaCl at 250 °C and 3 and 4 *m* NaCl at 300 °C.

Registry No. $BaSO_4$, 7727-43-7; NaCl, 7647-14-5.

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Apparent Molal Volumes and Heat Capacities of Aqueous HCl and $HClO_4$ at 15–55 °C

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The apparent molal volumes and apparent molal heat capacities of dilute (0.01–0.25 *m*) aqueous HCl and $HClO_4$ solutions have been determined at 15, 25, 35, 45, and 55 °C. These apparent molal quantities have been extrapolated to zero concentration to obtain the limiting values at infinite dilution, which are the same as the infinite dilution partial molal values. The apparent molal quantities were fitted with the equation $\phi_J = \phi_J^0 + A_J m^{1/2} + B_J m$. Taking $\phi_J^0(H^+) = 0$, conventional ionic ϕ_J^0's are obtained for the Cl^- and ClO_4^- anions at each temperature.

Introduction

The apparent molal properties of HCl and $HClO_4$ at 25 °C are well-known. The data become ambiguous and scattered at temperatures other than 25 °C. We have determined values of ϕ_V^0 and $\phi_{C_p}^0$ at 15, 25, 35, 45, and 55 °C for both HCl and $HClO_4$. These results are important since we use the standard convention and set $\phi_J^0(H^+) = 0$ at all temperatures; thus the acid values yield the conventional anion values. These anion values are then used to calculate other ionic values from salt data. Any error in these original anion values is propagated throughout subsequent calculations of ionic ϕ_J^0's. Determination of these anion ϕ_J^0's will provide a consistent data base from which all other ionic ϕ_J^0 values can be calculated in later work.

Experimental Section

The densities were measured with a Paar Mettler DMA 602 vibrating tube densimeter and the heat capacities with a Sodev flow calorimeter. The densimeter was calibrated with NaCl solutions by using the data of Millero (*1*). The operation of a vibration tube densimeter has been previously described (*2*). The calorimeter performance was verified with NaCl solutions against the data of Desnoyers (*3*). Both measurements were carried out at 15, 25, 35, 45, and 55 °C. The densimeter cell temperature was controlled to within ±0.005 °C with an accuracy of 0.001 °C by using a miniature PRT and a Neslab bath combination. The calorimeter cell temperature was maintained within ±0.005 °C and an accuracy of 0.05 °C with a closed loop circulation system Model CT-L provided by Sodev. The values of the density and heat capacity of pure water used

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