Solubility Pattern of $CaSO_4{\cdot}2H_2O$ in the System NaCl + $CaCl_2$ + H_2O and Solution Densities at 35 °C: Non-ideality and Ion Pairing

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The solubility of $CaSO_4{\cdot}2H_2O$ was determined in aqueous NaCl solutions up to very high salinities and constant $CaCl_2$ concentrations at 35 °C. Addition of $CaCl_2$ into the aqueous NaCl system reduces the solubility of $CaSO_4{\cdot}2H_2O$ quite dramatically while maintaining the basic pattern of the solubility curve. Mean ionic activity coefficients $\gamma_\pm$ of $CaSO_4{\cdot}2H_2O$ derived using the extended Debye−Hückel law with quadratic terms decrease with an increase in ionic strength. A comparison of the value of the thermodynamic solubility product constant, $K_{sp(th)}$ of $CaSO_4{\cdot}2H_2O$ to the solubility product K_{sp} obtained from the observed solubility data indicate sizable differences. This has been explained through a combination of the extended Debye−Hückel law and ion association theory. We also measured accurate densities for the quaternary system $CaSO_4{\cdot}2H_2O$ + NaCl + $CaCl_2$ + H_2O at 35 °C. The density of the solution increases linearly with an increase in concentration. Solutions containing higher amounts of $CaCl_2$ were found to be less dense when compared at the same ionic strengths. Solubility and density data as a function of concentration have been correlated using polynomial and linear fits by the method of least squares. These studies are of relevance in the production of salt with low impurities of Ca^{2+} and SO_4^{2-} ions.

Introduction

Physicochemical properties of multicomponent electrolyte mixtures in water are important in understanding ionic equilibrium, ion−solvent and ion−ion interactions in natural waters. Accurate and reliable data on physicochemical properties of aqueous salt systems are necessary for many industrial processes where these systems are used as feed. We are continuing our research program on aqueous electrolyte solutions saturated with $CaSO_4{\cdot}2H_2O$, which is a predominantly sparingly soluble electrolyte present in seawater and industrial water systems. It precipitates and can form scale once its saturation limit exceeds a certain threshold limit. Therefore, it is quite important to have accurate data on solubility and other physical properties of the systems where $CaSO_4{\cdot}2H_2O$ is an important constituent. In earlier reports,[1−3] we studied a number of physicochemical properties for the ternary systems $CaSO_4{\cdot}2H_2O$ + NaCl + H_2O and $CaSO_4{\cdot}2H_2O$ + $CaCl_2$ + H_2O. Addition of NaCl increases the solubility of $CaSO_4{\cdot}2H_2O$ initially and then decreases after reaching a maximum value, whereas addition of $CaCl_2$ decreases the solubility of $CaSO_4{\cdot}2H_2O$ sharply at lower concentrations and decreases further with an increase in concentration. Therefore, we find it worth examining the counter effects of Ca^{2+} and Na^+ ions on the solubility of $CaSO_4{\cdot}2H_2O$ in the quaternary system $CaSO_4{\cdot}2H_2O$ + NaCl + $CaCl_2$ + H_2O up to very high salinities. A research paper by Atkinson et al.[4] provides a complete review of the solubilities of $CaSO_4{\cdot}2H_2O$ in water as well as in aqueous solutions of different electrolytes. Despite a number of investigations on the subject, a systematic study of the effect of added $CaCl_2$ on the solubility and other physicochemical properties of $CaSO_4{\cdot}2H_2O$ in saline water is lacking. In this paper, we determined the solubility behavior of $CaSO_4{\cdot}2H_2O$ in the quaternary system $CaSO_4{\cdot}2H_2O$ + NaCl + $CaCl_2$ + H_2O using analytical methods and present accurate results of density measurements as a function of concentration at 35 °C.

While dealing electrolyte with solutions at high concentrations, departure from ideality and ion association become quite significant due to Coulombic interactions between ions. In addition, the ion−solvent and solvent−solvent interactions that are present even in dilute solution also become increasingly modified as the concentration increases, contributing further to the nonideality. The nonideality could be evaluated by activity coefficients, which can be based upon some theoretical models.[5−7] The ion association contribution can be studied both theoretically and experimentally.[8−13] From experimental results of solubility measurements we have evaluated deviations from ideality using a combination of the extended Debye−Hückel law and ion association theory.

Experimental Section

$CaSO_4{\cdot}2H_2O$ and NaCl (≥ 99.8 % mass fraction) obtained from S. D. Fine Chemicals, Bombay, India, were used after drying in an oven at 70 °C without further purification. Fused $CaCl_2$ obtained from E. Merck (India) Limited, Mumbai (≥ 98 % mass fraction), was recrystallized using Millipore grade water and was dried at 120 °C under vacuum. All solutions were prepared by weight, using an analytical balance with a precision of ± 0.0001 g (Denver Instrument APX-200) in Millipore grade water. Four aqueous $CaCl_2$ solutions with different concentrations were prepared by dissolving known amounts of $CaCl_2$ in Millipore grade water. Stock solutions were prepared by adding oven-dried NaCl to the solutions containing fixed amounts of $CaCl_2$. A range of solutions with different concentrations of NaCl saturated with $CaSO_4{\cdot}2H_2O$ were then made by diluting stock solutions with initially prepared aqueous $CaCl_2$ solutions and adding excess $CaSO_4{\cdot}2H_2O$. The resulting solutions were stirred in a thermostatically controlled water bath. After the

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Table 1. Molal Solubilities and Mean Ionic Activity Coefficients of $CaSO_4{\cdot}2H_2O$ in Aqueous NaCl Solutions of Fixed $CaCl_2$ Concentrations at 35 °C

NaCl m_1	$CaSO_4$ m_2	I	$\gamma_\pm$	NaCl m_1	$CaSO_4$ m_2	I	$\gamma_\pm$
	0 m $CaCl_2$				0.1072 m $CaCl_2$		
0	0.0151	0.0604	0.4256	0	0.0102	0.3625	0.2239
0.1796	0.0250	0.2796	0.2477	1.0078	0.0195	1.4075	0.1401
0.3184	0.0295	0.4364	0.209	1.4003	0.0227	1.8128	0.1319
0.4777	0.0350	0.6177	0.1836	1.8413	0.0248	2.2622	0.1274
0.7754	0.0410	0.9394	0.1584	2.3786	0.0252	2.8011	0.1258
1.1295	0.0460	1.3135	0.1428	2.7680	0.0250	3.1897	0.1266
1.4890	0.0490	1.6850	0.134	3.1576	0.0245	3.5773	0.1289
2.0024	0.0520	2.2104	0.1277	3.5513	0.0231	3.9654	0.1325
2.5153	0.0529	2.7269	0.1258	3.9921	0.0217	4.4006	0.1381
3.0303	0.0529	3.2419	0.1269	4.3834	0.0200	4.7851	0.1445
3.4906	0.0510	3.6946	0.1299		0.3676 m $CaCl_2$		
3.8350	0.0493	4.0322	0.1333	0	0.0080	1.1348	0.1491
4.2002	0.0471	4.3886	0.1379	0.8494	0.0097	1.9910	0.1297
	0.0396 m $CaCl_2$			1.2374	0.0100	2.3802	0.1267
0	0.0109	0.1624	0.3038	1.5797	0.0101	2.7229	0.1258
0.7960	0.0278	1.0260	0.1529	1.8811	0.0102	3.0247	0.1261
1.0378	0.0301	1.2770	0.1440	2.3294	0.0103	3.4734	0.1282
1.4765	0.0337	1.7301	0.1333	2.6792	0.0100	3.8220	0.1310
2.2545	0.0368	2.5205	0.1262	3.0296	0.0094	4.1700	0.1349
2.8867	0.0377	3.1563	0.1265	3.3195	0.0087	4.4571	0.1390
3.3263	0.0374	3.5947	0.1290	3.7567	0.0079	4.8911	0.1465
3.8598	0.0351	4.1190	0.1343	4.2999	0.0073	5.4319	0.1585
4.2968	0.0328	4.5468	0.1404				
4.4488	0.0317	4.6944	0.1428				
4.9943	0.0280	5.2251	0.1536				

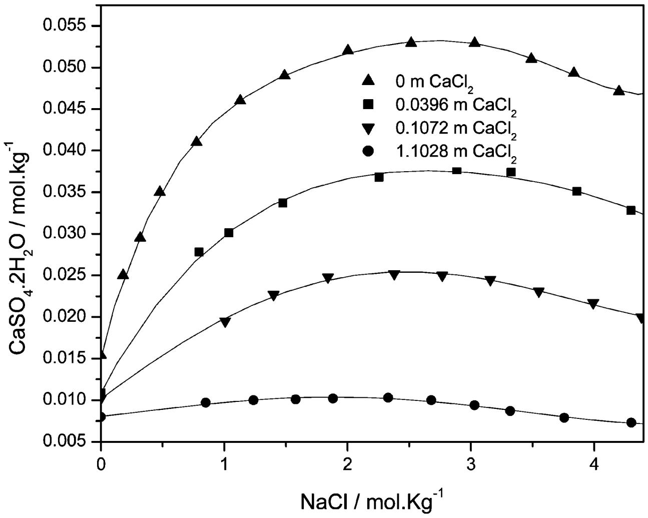

Figure 1. $CaSO_4{\cdot}2H_2O$ solubility at constant $CaCl_2$ concentration but varying NaCl concentration at 35 °C.

Table 2. Parameters A_i and Standard Deviations σ of Equation 1 for the System $CaSO_4{\cdot}2H_2O + NaCl + CaCl_2 + H_2O$ at 35 °C

$CaCl_2$ m	A_1	A_2	A_3	A_4	s
		Solubility/mol·kg^{-1}			
0	0.0150	0.0365	−0.0109	0.0010	0.0010
0.0396	0.0104	0.0179	−0.0028		0.0020
0.1072	0.0062	0.0125	−0.0020		0.0006
0.3676	0.0049	0.0035	−0.0006		0.0003
		Mean Ionic Activity Coefficients $\gamma_\pm$			
0	0.3447	−0.3320	0.1428	−0.0182	0.0447
0.0396	0.2926	−0.1970	0.0665	−0.0066	0.0163
0.1072	0.2119	−0.0669	0.0122		0.0113
0.3676	0.1468	−0.0220	0.0058		0.0020
		Density, $\rho/10^{-3}$ kg·m^{-3}			
0	0.9945	0.0379			0.0039
0.0396	1.0023	0.0369			0.0017
0.1072	1.0063	0.0365			0.0011
0.3676	1.0272	0.0357			0.0014

solutions were stirred with an electrical paddle for about 24 h, liquid samples were withdrawn periodically and analyzed for different ions as described elsewhere.[1,2]

The densities of the solutions were measured with an Anton Paar (model DMA 4500) vibrating-tube densimeter with a resolution of 5×10^{-2} kg·m^{-3}. The densimeter was calibrated with doubly distilled and degassed water, with dry air at atmospheric pressure, and also against the densities of NaCl(aq),[14] with an accuracy of 0.01 %. The temperature of the apparatus was controlled to within ± 0.03 K by a built-in peltier device. Reproducibility of the results was confirmed by performing at least three measurements for each sample.

Results and Discussion

Solubility. Experimental results of the solubility of $CaSO_4{\cdot}2H_2O$ in the aqueous NaCl solutions with fixed $CaCl_2$ concentrations are given in Table 1 and are visualized in Figure 1. Uncertainty in the solubility measurements was estimated to be less than 0.02 %. The composition dependence of $CaSO_4{\cdot}2H_2O$ solubility in aqueous NaCl solutions of fixed concentration was correlated by means of a polynomial type equation:

$$F(Q) = A_0 + A_1\,(m\text{NaCl}) + A_2\,(m\text{NaCl})^2 + A_3\,(m\text{NaCl})^3 \quad (1)$$

where Q represents a general measured property (solubility and density) or derived function (mean ionic activity coefficient) and m is the concentration (mol·kg^{-1}) of NaCl in the solution. The values of the parameters A_i were evaluated by the method of least-squares with all points weighted equally. The parameters A_i and standard deviation σ are given in Table 2. The solubility of $CaSO_4{\cdot}2H_2O$ increases with an increase in the concentration of NaCl in solution and decreases with an increase in the concentration of $CaCl_2$, while retaining the basic pattern of the solubility curve intact. The solubility of the $CaSO_4{\cdot}2H_2O$ decreases with the additions of $CaCl_2$ in the solution significantly when compared to the ternary system.[2] The striking difference in solubility may be due to the addition of a common ion (Ca^{2+}) in the solution. For the same ionic strength, the maximum in the solubility curves appears to shift toward higher concentration with an increase of the $CaCl_2$ concentration in solution. The solubility equilibrium under study is

$$CaSO_4{\cdot}2H_2O(s) \Leftrightarrow Ca^{2+}(aq) + SO_4^{\ 2-}(aq) + 2H_2O(l) \quad (2)$$

that can be expressed by the solubility product constant

$$K_{sp} = a_{Ca^{2+}}{\cdot}a_{SO_4^{\ 2-}}{\cdot}a_{H_2O}^{\ \ 2}$$

$$= s^2{\cdot}\gamma_\pm^{\ 2}{\cdot}a_{H_2O}^{\ \ 2} < \quad (3)$$

where a is the activity coefficient of various species, s is the solubility of $CaSO_4{\cdot}2H_2O$ in mol·kg^{-1} of water, and $\gamma_\pm$ is the mean ionic activity coefficient. The extended Debye−Hückel law with quadratic terms was used to calculate mean ionic activity $\gamma_\pm$ of $CaSO_4{\cdot}2H_2O$:

$$\log \gamma_\pm = -A[z_+{\cdot}z_-]\,\sqrt{I}/(1 + A_{SP}\sqrt{I}) - BI/2 + CI^2/2 \quad (4)$$

where A is the Debye−Hückel limiting slope, I is the ionic strength, and $A_{SP} = ba^0$, b is a function of absolute temperature and dielectric constant, and a^0 is the "ion-size" parameter, and B and C are adjustable parameters that account for the variation of water activities with respect to ionic strength. Values of $A_{SP} = 1.52$, $B = -0.014$, and $C = 0.154$ at 35 °C were used from

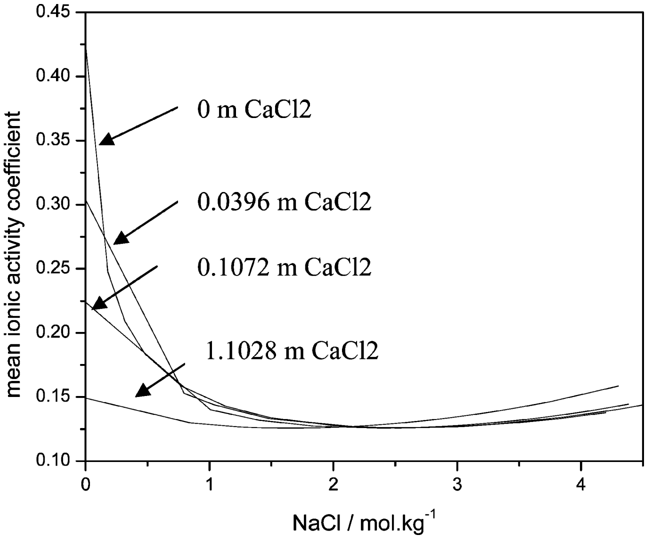

Figure 2. $\gamma_\pm$ of $CaSO_4{\cdot}2H_2O$ at constant $CaCl_2$ concentration but varying NaCl concentration at 35 °C.

Table 3. Thermodynamic Functions for the Equilibria $CaSO_4{\cdot}2H_2O(s) \Leftrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O(l)$ at 35 °C[4]

$\Delta G°$/kJ·mol^{-1}	$\Delta H°$/kJ·mol^{-1}	$\Delta S°$/J·K^{-1}·mol^{-1}
27.19	−3.84	−100.7

Marshall and Slusher.[15] Contribution of BI and CI^2 terms to the calculated mean ionic activity coefficient shows an error of ± 1 %. Overall error in the estimation of $\gamma_\pm$ is less than 1.5 % at higher concentrations. Estimated values of $\gamma_\pm$ are presented in Table 1 and are depicted as a function of ionic strength in Figure 2. $\gamma_\pm$ decreases with an increase in the NaCl concentration in solution. At lower concentration the decrease is sharp. Additions of $CaCl_2$ in the solution decrease the $\gamma_\pm$ and reduce the sharpness of the curve at lower concentrations. On the other hand, the thermodynamic solubility product constant, $K_{sp(th)}$, of the same salt can be calculated from $\Delta G°$ of equilibrium 2:

$$K_{sp(th)} = e^{-\Delta G_{diss}°}/RT \tag{5}$$

where $\Delta G°_{diss} = \Delta H°_{diss} - T\Delta S°_{diss}$, and all symbols have their usual meaning.

Thermodynamic functions for the calculation of $K_{sp(th)}$ are given in Table 3. $K_{sp(th)}$ calculated from eq 5 using thermodynamic functions given in Table 3 is equal to 2.46×10^{-5}. The average solubility product K_{sp} of $CaSO_4{\cdot}2H_2O$ derived from the experimental solubilities and mean ionic activity coefficients $\gamma_\pm$ comes out to be 4.23×10^{-5}, 2.18×10^{-5}, 8.84×10^{-6}, and 1.55×10^{-6} for (0, 0.0396, 0.1072, and 0.3676) m $CaCl_2$ concentrations in aqueous NaCl solutions, respectively. The K_{sp} values presented in Figure 3 as a function of $CaCl_2$ ionic strength in aqueous NaCl solutions decrease exponentially with an increase in the $CaCl_2$ concentration in the solution. We have compared K_{sp} and $K_{sp(th)}$ of $CaSO_4{\cdot}2H_2O$ in aqueous NaCl system with no $CaCl_2$ in the solution to check the nonideality. Comparison reveals that K_{sp} is almost double $K_{sp(th)}$. This large difference can be attributed to the formation of $Ca^{2+}SO_4^{2-}$ ion pairs. If x denotes the concentration of the $Ca^{2+}SO_4^{2-}$ ion pair in the saturated solution of $CaSO_4{\cdot}2H_2O$ at 35 °C, then $(s - x)$ will represent the concentration of Ca^{2+} or SO_4^{2-} in the free state in the solution. So $K_{sp(th)}$ can be expressed as

$$K_{sp(th)} = a_{Ca^{2+}free}{\cdot}a_{SO_4^{2-}free} = [Ca^{2+}]_{free}[SO_4^{2-}]_{free}{\cdot}\gamma_\pm^{\,2} = (s-x)^2{\cdot}\gamma_\pm^{\,2} \tag{6}$$

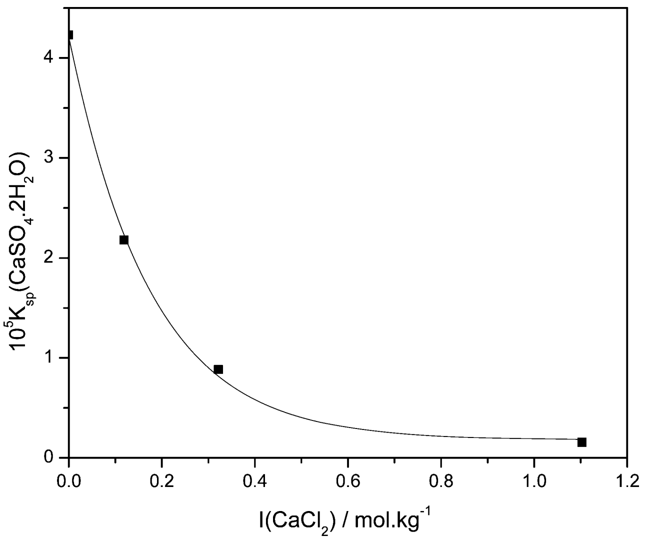

Figure 3. $CaSO_4{\cdot}2H_2O$ solubility product at different $CaCl_2$ ionic strength in aqueous NaCl solutions at 35 °C.

Table 4. Successive Calculations in Order To Achieve a Reasonable Value of $Ca^{2+}SO_4^{2-}$ Ion Pair at Three Arbitrary NaCl Concentrations

iteration	I/mol·kg^{-1}	$\gamma_\pm$	$x = Ca^{2+}SO_4^{2-}$/mol·kg^{-1}
	0 m NaCl		
1	0.0151	0.4256	0.00347
2	0.0116	0.4604	0.00435
3	0.0108	0.471	0.0046
4	0.0105	0.4741	0.0047
5	0.0104	0.4754	0.0047
	2.7269 m NaCl		
1	0.0529	0.1258	0.0136
2	0.0394	0.1258	0.0136
	4.2002 m NaCl		
1	0.0471	0.1379	0.0112
2	0.0359	0.1372	0.0110
3	0.0361	0.1373	0.0110

The value of x can be obtained from eqs 4 and 6. We take $I = s$ at the first approximation and calculate an approximate value of x and name it x_1. Then, iterating the calculation, but taking $I = s - x_1$, we can obtain a more precise value of x and name it x_2. We iterate the procedure until the difference between two successive x values becomes less than 1 %. So the final value of x will reasonably represent the concentration of $Ca^{2+}SO_4^{2-}$ ion pair in the saturated solution of $CaSO_4{\cdot}2H_2O$ at 35 °C.[13] The values are given in Table 4. We have chosen three arbitrary concentrations of NaCl (0, 2.7269, and 4.2002 m) for estimating the $Ca^{2+}SO_4^{2}$ ion pairs in solution. From Table 4, we can see that the concentration of the $[Ca^{2+}SO_4^{2-}]$ ion pair increases with an increase in the NaCl concentration in the solution but decreases with a further increase in concentration. The association constant K_A for the reaction $Ca^{2+}(aq) + SO_4^{2-}(aq) \Leftrightarrow Ca^{2+}SO_4^{2-}$(ion pair) is

$$K_A = \frac{[Ca^{2+}SO_4^{\ 2-}]\gamma}{[Ca^{2+}][SO_4^{\ 2-}]\gamma_\pm^{\,2}} \tag{7}$$

K_A at the three arbitrary NaCl concentrations (0, 2.7269, and 4.2002 m) comes to be 192, 554, and 448, respectively. Our values of K_A are comparable to the K_A values (178, 549, and 407, respectively) estimated from the solubility data of Marshall and Slusher[15] at similar NaCl concentrations. At zero ionic strength, Smith and Martell[16] report the K_A value of 200, whereas our value estimated from experimentally determined

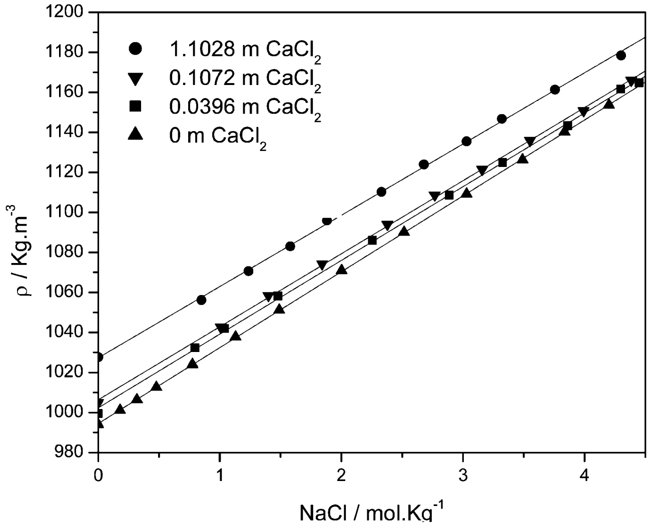

Figure 4. Density of aqueous NaCl solutions saturated with $CaSO_4{\cdot}2H_2O$ at constant $CaCl_2$ concentrations at 35 °C.

Table 5. Densities of the Quaternary $CaSO_4{\cdot}2H_2O + NaCl + CaCl_2 + H_2O$ System at 35 °C as a Function of Ionic Strength

NaCl m_1	density ρ/kg·m^{-3}	NaCl m_1	density ρ/kg·m^{-3}	NaCl m_1	density ρ/kg·m^{-3}	NaCl m_1	density ρ/kg·m^{-3}
0 *m* $CaCl_2$		0.0396 *m* $CaCl_2$		0.1072 *m* $CaCl_2$		0.3676 *m* $CaCl_2$	
0	994.0	0	999.3	0	1004.9	0	1027.6
0.1796	1001.1	0.7960	1013.3	1.0078	1041.0	0.8494	1056.2
0.3184	1006.4	1.0378	1042.1	1.4003	1058.5	1.2374	1070.7
0.4777	1012.6	1.4765	1058.7	1.8413	1074.3	1.5797	1083.0
0.7754	1024.0	2.2545	1088.5	2.3786	1094.1	1.8811	1096.0
1.1295	1037.8	2.8867	1108.6	2.7680	1108.7	2.3294	1110.3
1.4890	1051.2	3.3263	1125.0	3.1576	1121.5	2.6792	1124.0
2.0024	1071.0	3.8598	1143.5	3.5513	1136.0	3.0296	1135.5
2.5153	1090.1	4.2968	1161.8	3.9921	1150.8	3.3195	1146.8
3.0303	1109.2	4.4488	1164.8	4.3834	1166.1	3.7567	1161.4
3.4906	1126.3	4.9943	1182.6			4.2999	1178.5
3.8350	1140.2						
4.2002	1153.7						

solubility is 192. Relative error in estimated K_A values from literature is within ± 1 %. Ionic association increases up to a certain concentration of NaCl in solution but decreases with a further increase in concentration. This behavior is consistent with the solubility behavior of $CaSO_4{\cdot}2H_2O$ in aqueous salt solutions. A very high value of K_A suggests a large association between Ca^{+2} and SO_4^{2-} ions in the system.

Density. Density values for the system $CaSO_4{\cdot}2H_2O + NaCl + CaCl_2 + H_2O$ at 35 °C as a function of NaCl concentration and at fixed $CaCl_2$ concentrations are reported in Table 5 and are shown in Figure 4 as a function of NaCl concentration. The composition dependence of densities is fitted to eq 1. The parameters A_i and standard deviation σ are given in Table 2. Density values increase linearly with an increase in the concentration of electrolytes in solution. When compared at the same ionic strength, the densities are lower for the solutions having a higher concentration of $CaCl_2$. This may be due to the higher concentration of Ca^{2+} ions, which have a high structure making capacity when compared to other ions present in solution. Water becomes more structured in the presence of Ca^{2+} ions creating void space and hence less dense thereby resulting in lower density of solutions when compared at similar ionic strengths.

Conclusions

$CaSO_4{\cdot}2H_2O$ solubility decreases with the additions of $CaCl_2$ in aqueous NaCl solutions without altering the basic pattern of the solubility curve. The solubility maximum appears to shift toward higher concentrations for higher concentrations of $CaCl_2$ in the solution. Aqueous NaCl solutions saturated with $CaSO_4{\cdot}2H_2O$ are far from ideal. The nonideality of the solution can be accounted partly to physical contribution (activity coefficients) and partly to chemical contribution (ion association). Furthermore, the addition of $CaCl_2$ in the system makes the solution less dense due to a water structure enhancement effect of the Ca^{+2} ions.

Acknowledgment

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