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Effect of $MgCl_2$ on the Solubility of $CaSO_4 \cdot 2H_2O$ in the Aqueous NaCl System and Physicochemical Solution Properties at 35 °C

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The solubility of $CaSO_4 \cdot 2H_2O$ was determined in aqueous NaCl solutions up to very high salinities and at constant $MgCl_2$ concentrations at 35 °C. The addition of $MgCl_2$ into the aqueous NaCl system enhances the solubility of $CaSO_4 \cdot 2H_2O$ significantly at lower NaCl concentrations. The solubility maximum of $CaSO_4 \cdot 2H_2O$ also shifts slightly toward the lower salinities with the addition of $MgCl_2$. We also measured accurate density (ρ) and speed of sound (u) for the quaternary system $CaSO_4 \cdot 2H_2O + NaCl + MgCl_2 + H_2O$ at 35 °C. Measurements of the speed of sound and density have been used to determine solution isentropic compressibility (κ_S) and ion-hydration characteristics. Empirical equations describing the solubility, density, speed of sound, and isentropic compressibility in these systems are presented.

Introduction

Physicochemical properties of multicomponent electrolyte mixtures in water are important for understanding ionic equilibrium, ion−solvent, and ion−ion interactions in natural waters.[1,2] Accurate and reliable data on the 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 predominant sparingly soluble electrolyte present in seawater and industrial water systems. It precipitates and forms 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 we have studied a number of physicochemical properties for the ternary systems $CaSO_4 \cdot 2H_2O + NaCl + H_2O$ and $CaSO_4 \cdot 2H_2O + CaCl_2 + H_2O$ and quaternary system $CaSO_4 \cdot 2H_2O + NaCl + CaCl_2 + H_2O$ and have also examined the effect of pH on the solubility of $CaSO_4 \cdot 2H_2O$ in the system $CaSO_4 \cdot 2H_2O + NaCl + H_2O$.[3−7] In aqueous NaCl solutions the solubility of $CaSO_4 \cdot 2H_2O$ increases initially and then decreases after reaching a maximum value, whereas in aqueous $CaCl_2$ solutions the solubility of $CaSO_4 \cdot 2H_2O$ decreases sharply at lower concentrations and keeps decreasing steadily with a further increase in concentration as a consequence of the common ion Ca^{2+}. In the quaternary system $CaSO_4 \cdot 2H_2O + NaCl + CaCl_2 + H_2O$ a competing effect of Ca^{2+} and Na^+ in opposite directions has been observed on the solubility of $CaSO_4 \cdot 2H_2O$. In present work we have determined the solubility of $CaSO_4 \cdot 2H_2O$ in the quaternary system $CaSO_4 \cdot 2H_2O + NaCl + MgCl_2 + H_2O$ up to very high salinities and also determined solution properties such as density and speed of sound. A research paper by Atkinson and Raju[8] provides a complete review of the solubility of $CaSO_4 \cdot 2H_2O$ in aqueous solution 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 $MgCl_2$ on the solubility of $CaSO_4 \cdot 2H_2O$ in saline water can be rarely found. The solubility of $CaSO_4 \cdot 2H_2O$ in the $NaCl + MgCl_2 + H_2O$ system has been determined by Ostroff et al. at different temperatures with $MgCl_2$ in the concentration range of (0.01 to 0.325) *m*.[9] The solubility data for $CaSO_4 \cdot 2H_2O$ in saline water having $MgCl_2$ concentrations higher than 0.325 *m* are not available in the literature. On the other hand, solution physicochemical properties such as density and speed of sound of these systems are not known. In this paper we determined the solubility behavior of $CaSO_4 \cdot 2H_2O$ in the $NaCl + MgCl_2 + H_2O$ system with very high concentrations of $MgCl_2$ ((0.34 and 0.68) *m*) and up to very high salinities at 35 °C using analytical methods. We also report the density and speed of sound over a range of salt concentration for the system $CaSO_4 \cdot 2H_2O + NaCl + MgCl_2 + H_2O$ at 35 °C. The primary data on density and speed of sound have been used to determine solution isentropic compressibility and the hydration characteristics of ions.

Experimental Section

$CaSO_4 \cdot 2H_2O$, $MgCl_2$, and NaCl (> 99.5 % by mol), obtained from S.D. Fine Chemicals (Bombay), were used after drying in the oven at 70 °C without further purification. Solutions were prepared by weight, using an analytical balance with a precision of ± 0.0001 g (Denver Instrument APX-200) in Millipore grade water. Aqueous $MgCl_2$ solutions with different concentrations were prepared by dissolving known amounts of $MgCl_2$ in Millipore grade water. Stock solutions were prepared by adding oven-dried NaCl to the solutions containing fixed amounts of $MgCl_2$. A range of solutions with different NaCl and fixed $MgCl_2$ concentrations saturated with the $CaSO_4 \cdot 2H_2O$ were then made by diluting stock solutions with initially prepared aqueous $MgCl_2$ solutions and adding excess $CaSO_4 \cdot 2H_2O$. The resulting solutions were stirred in a thermostatically controlled water bath. After the solutions were stirred with an electrical paddle for about 24 h, liquid samples were withdrawn periodically and analyzed for different ions as described elsewhere.[3] In brief, Mg^{2+}, Ca^{2+}, and Cl^- concentrations were determined volumetrically using standard ethylenediaminetetraacetic acid (EDTA)

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and $AgNO_3$ solutions, respectively. The SO_4^{2-} concentration was determined gravimetrically using barium chloride precipitation as per the standard analytical procedure. The solubility of 0.0151 *m* $CaSO_4 \cdot 2H_2O$ in water thus determined is fairly close to the literature solubility of $CaSO_4 \cdot 2H_2O$ (0.0154[10] and 0.0157[9] at 38 °C).

The density (ρ) of the solutions was measured with an Anton Paar (model DMA 4500) vibrating-tube densimeter with a resolution of $5 \cdot 10^{-2}$ 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),[11] 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.

Speed of sound (u) in the salt solutions was measured at 51 600 Hz using a concentration analyzer (model 87, SCM laboratory sonic composition monitor) based on the sing-around technique[12] with a single transducer cell, immersed in a water bath with temperature controlled to ± 0.01 K. The analyzer was calibrated by measurements of speeds of sound in water as a reference, and the error was estimated to be less than ± 0.1 m·s^{-1}.[12] Measurements were carried out in a specially designed sample jar of low volume capacity. Sample jars were provided with an airtight Teflon covering to keep the samples moisture-free during measurements. To check the reproducibility of the results, not less than three experiments were performed for each concentration.

Results and Discussion

Experimental results of solubility of $CaSO_4 \cdot 2H_2O$ in aqueous NaCl solutions with fixed $MgCl_2$ concentrations are given in Table 1 and are visualized in Figure 1. For comparing the solubility of $CaSO_4 \cdot 2H_2O$ at different $MgCl_2$ concentrations at varying salinity, the data collected by Ostroff and Metler[9] at 38 °C are also plotted in Figure 1. The composition dependence of $CaSO_4 \cdot 2H_2O$ solubility in the $NaCl + MgCl_2 + H_2O$ system was correlated by means of a polynomial-type equation,

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

where Q represents a general measured property (solubility, density, or speed of sound) or derived function (isentropic compressibility) 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 deviations σ are given in Table 2. As can be seen from Figure 1, the solubility of $CaSO_4 \cdot 2H_2O$ increases markedly at lower salinities, and this increase is significant up to approximately 3.0 *m* NaCl. At still higher concentrations of NaCl, the difference in solubility of $CaSO_4 \cdot 2H_2O$ in NaCl or $NaCl + MgCl_2$ solutions continues to reduce, indicating only a small effect of Mg^{2+} ions on the solubility of $CaSO_4 \cdot 2H_2O$ at very high salinities. Further the addition of $MgCl_2$ shifts the solubility maximum of $CaSO_4 \cdot 2H_2O$ slightly toward lower NaCl concentrations. The solubility maximum is shifted about 0.5 *m* in the concentration of NaCl toward the left when the $MgCl_2$ concentration is changed from (0 to 0.68) *m* in the system. When compared as a function of ionic strength, the solubility of $CaSO_4 \cdot 2H_2O$ follows the same pattern in general, but the solubility maximum is shifted toward higher ionic strengths with increased $MgCl_2$ concentration in the solution.

Table 1. Molal Solubilities of $CaSO_4 \cdot 2H_2O$ in Aqueous NaCl Solutions at Fixed $MgCl_2$ Concentrations, Solution Density ρ, Speed of Sound u, and Isentropic Compressibility κ_S at 35 °C

NaCl	$CaSO_4$		ρ	u	$10^{12} \cdot \kappa_S$
m_1	m_2	I	kg·m^{-3}	m·s^{-1}	Pa^{-1}
		0 *m* $MgCl_2$			
0	0.0151	0.0604	996.1	1521.4	433.7
0.1796	0.0250	0.2796	1004.4	1532.6	423.9
0.3184	0.0295	0.4364	1010.5	1541.1	416.7
0.4777	0.0351	0.6181	1017.4	1550.4	408.9
0.7754	0.0410	0.9394	1030.1	1568.0	394.8
1.1295	0.0462	1.3143	1042.3	1585.3	381.8
1.4890	0.0491	1.6854	1054.4	1603.7	368.8
2.0024	0.0520	2.2104	1076.6	1634.1	347.8
2.5153	0.0529	2.7269	1094.2	1660.4	331.5
3.0303	0.0529	3.2419	1114.2	1688.1	314.9
3.4906	0.0510	3.6946	1127.8	1711.3	302.8
3.7350	0.0493	3.9322	1140.2	1725.1	294.7
4.2002	0.0471	4.3886	1153.7	1746.5	284.2
		0.34 *m* $MgCl_2$			
0	0.0551	1.2404	1029.6	1563.6	397.3
0.45343	0.0576	1.70383	1046.9	1588.1	378.7
0.89831	0.0592	2.15511	1065.0	1613.2	360.8
1.36372	0.0601	2.62412	1080.3	1636.3	345.7
1.78636	0.0602	3.04716	1097.5	1660.5	330.5
2.25006	0.0594	3.50766	1114.5	1683.9	316.4
2.61794	0.058	3.86994	1129.1	1705.1	304.6
3.11757	0.0558	4.36077	1145.0	1728.5	292.3
3.40845	0.054	4.64445	1157.2	1744.0	284.1
3.94915	0.0503	5.17035	1173.6	1769.5	272.1
4.30505	0.0477	5.51585	1188.4	1784.0	264.4
		0.68 *m* $MgCl_2$			
0	0.0611	2.2844	1052.7	1593.5	374.1
0.4611	0.0625	2.7511	1066.9	1614.4	359.6
1.018	0.0633	3.3112	1083.8	1643.6	341.6
1.1554	0.0635	3.4494	1087.8	1651.2	337.2
1.5025	0.0636	3.7969	1099.7	1666.5	327.4
2.1473	0.0626	4.4377	1121.7	1700.4	308.3
2.4696	0.0617	4.7564	1131.4	1713.7	301.0
2.9991	0.0587	5.2739	1148.1	1739.3	287.9
3.423	0.0561	5.6874	1163.5	1758.1	278.1
4.2241	0.0499	6.4637	1191.6	1795.8	260.2

Density (ρ) and speed of sound (u) values for the system $CaSO_4 \cdot 2H_2O + NaCl + MgCl_2 + H_2O$ at 35 °C as a function of NaCl concentration are reported in Table 1 and are shown in Figures 2 and 3, respectively. Both the density and the speed of sound increase with an increase of concentration of electrolytes in the solution. The density of the system increases linearly

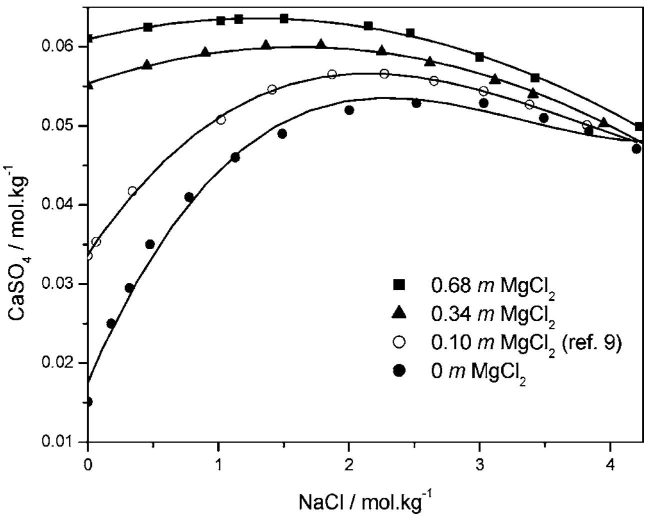

Figure 1. $CaSO_4 \cdot 2H_2O$ solubility at constant $MgCl_2$ concentrations but varying NaCl concentration at 35 °C (data from ref 9 at 38 °C).

Table 2. Parameters A_i and Standard Deviations σ of Equation 1 for the System $CaSO_4 \cdot 2H_2O$ + NaCl + $MgCl_2$ at 35 °C

$MgCl_2$ m	A_1	A_2	A_3	σ
		Solubility, $mol \cdot kg^{-1}$		
0	0.0150	0.0365	−0.0109	0.0010
0.34	0.0554	0.0057	−0.0018	0.0003
0.68	0.0610	0.0041	−0.0016	0.0002
		Density, $\rho / kg \cdot m^{-3}$		
0	999.2	37.2		1.9
0.34	1031.0	36.7		1.4
0.68	1051.0	32.8		1.2
		Speed of Sound, $u / m \cdot s^{-1}$		
0	1522.2	57.8	−1.1	1.3
0.34	1562.8	57.0	−1.2	1.2
0.68	1592.6	50.8	−0.7	1.1
		Isentropic Compressibility, $10^{12} \cdot \kappa_S / Pa^{-1}$		
0	432.1	−47.93	3.0	1.1
0.34	397.1	−41.7	2.5	0.6
0.68	374.3	−33.8	1.6	0.5

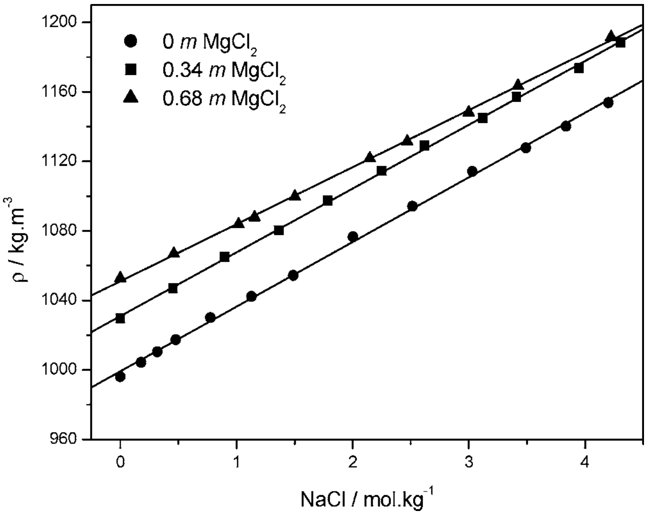

Figure 2. Density of aqueous NaCl solutions saturated with $CaSO_4 \cdot 2H_2O$ at constant $MgCl_2$ concentrations at 35 °C.

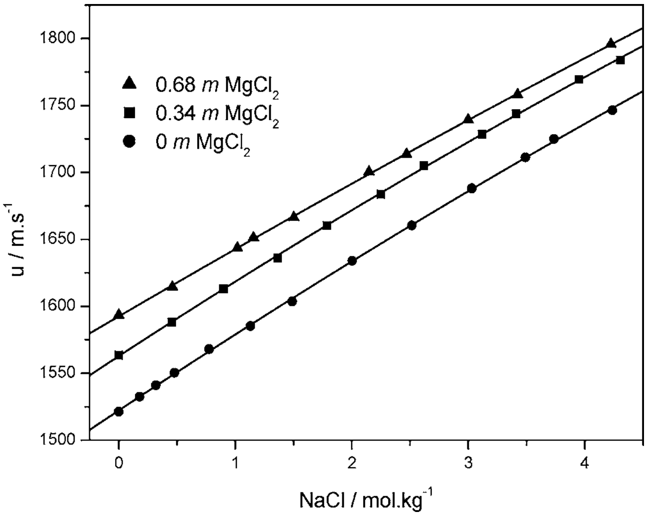

Figure 3. Speed of sound in aqueous NaCl solutions saturated with $CaSO_4 \cdot 2H_2O$ at constant $MgCl_2$ concentrations at 35 °C.

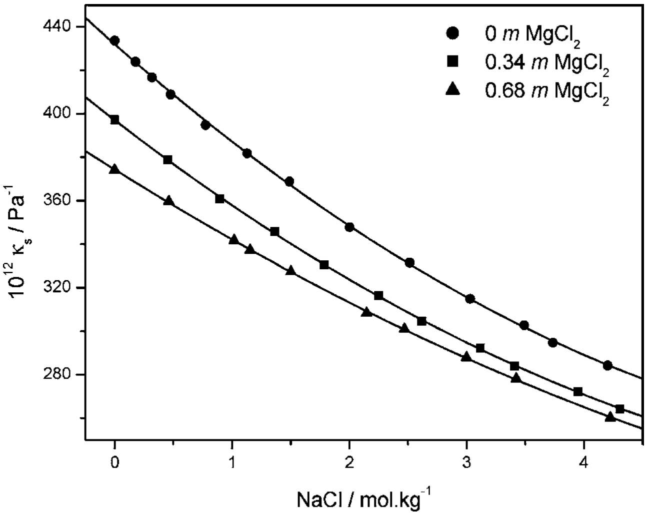

Figure 4. Isentropic compressibility of aqueous NaCl solutions saturated with $CaSO_4 \cdot 2H_2O$ at constant $MgCl_2$ concentrations at 35 °C.

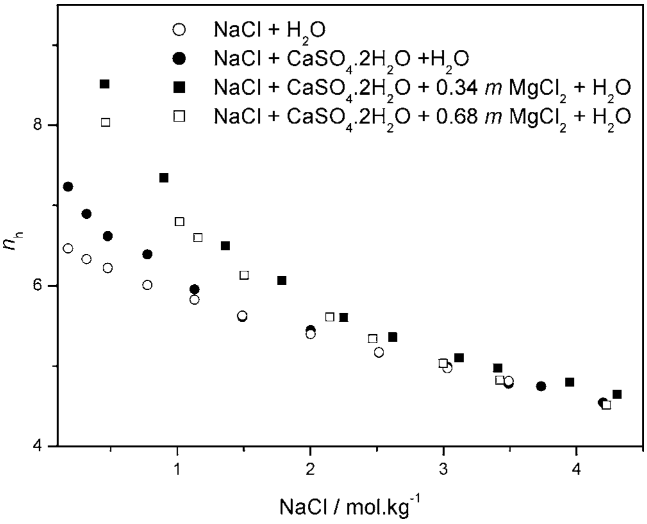

Figure 5. Total hydration number of ionic species for the system NaCl + $CaSO_4 \cdot 2H_2O$ (saturated) + $MgCl_2$ + H_2O at 35 °C.

whereas the speed of sound increases monotonically. The composition dependence of density and speed of sound is well-fitted to eq 1. The parameters A_i and standard deviations σ are given in Table 2. Assuming negligible ultrasonic absorption under the experimental conditions, we derived the isentropic compressibility κ_S from the u and ρ values by using the Newton−Laplace equation

$$\kappa_S = 1/u^2\rho \qquad (2)$$

Figure 4 shows a comparison of κ_S of the solution for the NaCl + $CaSO_4 \cdot 2H_2O$ + $MgCl_2$ + H_2O system as a function of NaCl concentration. κ_S decreases monotonically with an increase of the NaCl concentration in the solution. Addition of $MgCl_2$ also decreases the solution compressibility quite significantly which may be due to the weakening of hydrogen bonding of bulk water thereby making the solutions more rigid. The compressibility of aqueous electrolyte solutions is comprised of configurational as well as vibrational effects, with the former effect playing a dominant role in dilute solutions.[13] At higher concentrations the isentropic compressibility is largely determined by the compression of the hydration shell of the ions. This is in accordance with our calculations of the hydration number as shown in Figure 5. The total hydration number n_h of the ionic species was obtained using the approximate equation[13]

$$n_h = \frac{n_w}{n_s}\left(1 - \frac{\kappa_S}{\kappa_{S,0}}\right) \qquad (3)$$

where $\kappa_{S,0}$ and κ_S are the isentropic compressibilities of the pure water and the aqueous electrolyte solution and n_w and n_s are the number of moles of water and solute, respectively. As can be seen from Figure 5, the hydration number is higher at lower concentrations and then decreases with an increase in concentration in all of the solutions. The total hydration number of the ionic species at lower salt concentrations enhances significantly with the addition of $CaSO_4 \cdot 2H_2O$ and $MgCl_2$. However, at higher molalities of NaCl ($\approx$ 20.5 *m*) the effect of $CaSO_4 \cdot 2H_2O$ or $MgCl_2$ on the ionic hydration is not noticeable wherein the hydration shells coincide due to the disappearance of bulk water with all of the water molecules being incorporated into the hydration shells of ions. Beyond this concentration the cospheres of the cations and anions overlap, leading to the formation of ion pairs.[14]

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