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Effect of Nitrate Salts on Solubility Behavior of Calcium Sulfate Dihydrate (Gypsum) in the Aqueous Sodium Chloride System and Physicochemical Solution Properties at 308.15 K

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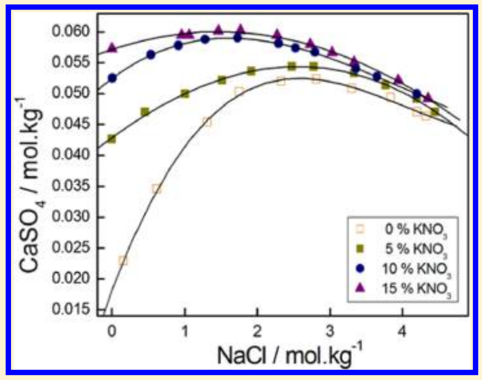
ABSTRACT: The effect of addition of nitrate salts (MNO_3, where M = Na, K, and NH_4) on the solubility behavior of calcium sulfate dihydrate (gypsum, $CaSO_4 \cdot 2H_2O$) in aqueous NaCl solutions has been examined at 308.15 K. The addition of nitrate salts in an aqueous NaCl system increased the $CaSO_4 \cdot 2H_2O$ solubility significantly, and the increase was higher at lower salinities. The order of increase in $CaSO_4 \cdot 2H_2O$ solubility with addition of different salts was NH_4NO_3 > $NaNO_3$ > KNO_3. The maximum solubility of $CaSO_4 \cdot 2H_2O$ in aqueous NaCl solutions with the addition of nitrate salts was found to shift toward the lower salinities. We also measured accurate density (ρ) and speed of sound (u) for the quaternary systems containing $CaSO_4 \cdot 2H_2O$, NaCl, nitrate salts, and H_2O at 308.15 K. Measurements of speed of sound and density have been used to determine solution isentropic compressibility (κ_S). Empirical equations describing the solubility, density, speed of sound, and isentropic compressibility in these systems are presented.



1. INTRODUCTION

Calcium sulfate dihydrate (gypsum, $CaSO_4 \cdot 2H_2O$), a nontoxic mineral, is one of the most commonly used material in diverse applications, such as, in cement industry, writing chalk, soil additive, or as a food additive, etc.[1,2] $CaSO_4 \cdot 2H_2O$ is precipitated in large quantities during the solar evaporation of natural brines prior to the production of common salt (NaCl). The solubility of $CaSO_4 \cdot 2H_2O$ in water is very low and increases slightly with the rise of temperature, the solubility curve attains a maximum, and then decreases with further increase of the temperature.[3−5] Most of the brines processed for the manufacture of industrial chemicals, such as soda ash or chlor-alkali contains Ca^{2+} and SO_4^{2-} ions (along with other ionic and nonionic impurities) which precipitates and forms $CaSO_4 \cdot 2H_2O$ scale in pipes and other production equipment once the concentration exceeds the solubility limit.[6] One way of prevention of scale formation could be to alter the solubility of $CaSO_4 \cdot 2H_2O$ by inhibiting the crystallization using various kinds of additives. However, the crystallization of $CaSO_4 \cdot 2H_2O$ is a complex phenomenon and is influenced by various parameters like temperature, pressure, dissolved electrolytes, or organics.[2] Therefore, understanding the solubility behavior of $CaSO_4 \cdot 2H_2O$ in the solutions containing additives, particularly the electrolytes (since practical industrial brines contains various electrolytes) is very important. Besides solubility, the knowledge of other physicochemical properties like density or compressibility of such solutions is also a necessary prerequisite while processing for the industrial applications. From the fundamental point of view these kinds of studies are important for understanding ionic-equilibrium, ion−solvent, and ion−ion interactions in natural waters.[7,8]

Physical phenomenon such as crystallization, phase stability, and solubility behavior of $CaSO_4 \cdot 2H_2O$ in aqueous solution as well as in aqueous solutions containing electrolytes have been widely investigated.[2,9] In particular, the solubility behavior of $CaSO_4 \cdot 2H_2O$ in brines has been extensively studied in the past.[9−16] Our research group is also actively engaged on a research program concerning investigations on solubility behavior of $CaSO_4 \cdot 2H_2O$ in brines in presence of various electrolytes[17−22] and nonelectrolytes,[23,24] and measurements on solution properties of such systems. As far as electrolytes containing systems are concerned, we have reported solubility behavior $CaSO_4 \cdot 2H_2O$ and other physicochemical properties for the ternary systems ($CaSO_4 \cdot 2H_2O$ + NaCl + H_2O and $CaSO_4 \cdot 2H_2O$ + $CaCl_2$ + H_2O),[17−20] quaternary systems ($CaSO_4 \cdot 2H_2O$ + NaCl + $CaCl_2$ + H_2O and $CaSO_4 \cdot 2H_2O$ + NaCl + $MgCl_2$ + H_2O)[21,22] in the past few years.

In continuation of our ongoing research program, herein we report new data on the effect of added nitrate salts ($NaNO_3$, KNO_3, and NH_4NO_3) on the solubility of $CaSO_4 \cdot 2H_2O$ in aqueous NaCl solutions at various concentrations. We also report the solution properties such as density and speed of sound for the systems $CaSO_4 \cdot 2H_2O$ + NaCl + MNO_3 (M = Na, K, and NH_4) + H_2O at 308.15 K. The primary data on density

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Table 1. Solubility of $CaSO_4 \cdot 2H_2O$ in Aqueous−NaCl Solutions in the Presence of Nitrate Salts, Solution Density ρ and Speed of Sound u at 308.15 K[a]

NaCl	$CaSO_4$	ρ	u	NaCl	$CaSO_4$	ρ	u
$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$m \cdot s^{-1}$	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$m \cdot s^{-1}$
		5% $NaNO_3$				10% $NaNO_3$	
0	0.0382	1.0312	1549.5	0	0.0397	1.0573	1567.5
0.4877	0.0463	1.0458	1570.5	0.6194	0.0508	1.0791	1595.2
0.8282	0.0514	1.0626	1590.4	0.9754	0.0544	1.0938	1618.4
1.3638	0.0558	1.0798	1619.2	1.5109	0.0574	1.1096	1642.9
1.7956	0.0565	1.0906	1638.7	1.9507	0.0576	1.1241	1666.8
2.2465	0.0558	1.1134	1661.8	2.1937	0.0574	1.1340	1677.7
2.7327	0.0544	1.1238	1683.7	2.7806	0.0561	1.1527	1708.8
3.2250	0.0520	1.1415	1710.5	3.2683	0.0537	1.1700	1733.2
3.5610	0.0507	1.1495	1728.7	3.5609	0.0518	1.1807	1747.3
4.0041	0.0477	1.1635	1752.1	4.0041	0.0492	1.1962	1771.8
4.3908	0.0463	1.1785	1773.1	4.1444	0.0481	1.2013	1778.8
		15% $NaNO_3$				5% KNO_3	
0	0.0455	1.0906	1592.6	0	0.0426	1.0295	1539.5
0.4651	0.0506	1.1028	1611.1	0.4535	0.0470	1.0458	1561.8
0.9756	0.0551	1.1190	1635.9	1.0078	0.0499	1.0658	1592.2
1.4630	0.0580	1.1356	1660.2	1.5161	0.0521	1.0838	1618.4
1.7077	0.0587	1.1431	1671.4	1.9199	0.0544	1.0951	1635.6
2.1458	0.0583	1.1564	1695.0	2.4795	0.0544	1.1146	1662.5
2.4880	0.0573	1.1694	1714.3	2.7806	0.0544	1.1243	1679.6
2.9278	0.0558	1.1843	1734.8	3.3350	0.0529	1.1425	1707.3
3.5609	0.0527	1.2031	1763.8	3.7697	0.0522	1.1572	1728.5
3.7081	0.0514	1.2089	1773.6	4.1957	0.0499	1.1700	1751.4
4.0041	0.0499	1.2178	1786.1	4.4490	0.0470	1.1802	1764.7
		10% KNO_3				15% KNO_3	
0	0.0525	1.0603	1558.1	0	0.0573	1.0900	1578.1
0.5344	0.0563	1.0788	1585.7	0.5713	0.0595	1.1187	1619.5
0.9127	0.0578	1.0939	1603.8	1.0609	0.0595	1.1218	1624.2
1.2817	0.0588	1.1096	1623.9	1.4630	0.0595	1.1339	1641.1
1.7284	0.0591	1.1241	1645.2	1.7676	0.0602	1.1438	1658.5
2.2916	0.0581	1.1425	1673.0	2.2724	0.0595	1.1590	1679.8
2.5246	0.0574	1.1527	1684.8	2.7293	0.0573	1.1729	1701.1
2.7965	0.0567	1.1605	1697.1	3.0305	0.0558	1.1813	1715.2
3.3597	0.0541	1.1807	1722.4	3.3350	0.0551	1.1900	1726.8
3.6509	0.0527	1.1911	1736.5	3.9425	0.0521	1.2062	1753.5
4.1947	0.0499	1.2106	1762.9	4.3480	0.0492	1.2174	1772.0
		5% NH_4NO_3				10% NH_4NO_3	
0	0.0470	1.0202	1536.8	0	0.0527	1.0367	1557.9
0.4706	0.0521	1.0367	1562.3	0.7700	0.0572	1.0649	1594.6
1.0233	0.0558	1.0555	1589.4	1.2663	0.0589	1.0825	1617.9
1.4151	0.0576	1.0716	1610.2	1.5109	0.0595	1.0909	1629.8
1.9507	0.0583	1.0906	1639.2	2.0465	0.0600	1.1102	1654.5
2.3066	0.0583	1.1020	1656.6	2.4384	0.0599	1.1260	1674.6
2.6814	0.0573	1.1176	1677.0	2.8747	0.0595	1.1422	1695.2
3.2204	0.0549	1.1352	1704.0	3.3658	0.0575	1.1590	1717.7
3.5130	0.0531	1.1474	1721.3	3.7560	0.0549	1.1734	1737.6
3.6841	0.0514	1.1550	1730.7	4.0965	0.0509	1.1867	1754.8
3.9493	0.0489	1.1653	1742.8	4.6201	0.0449	1.2037	1779.4
				15% NH_4NO_3			
0	0.0568	1.0536	1568.6	2.6084	0.0626	1.1394	1688.1
0.5072	0.0584	1.0702	1592.1	3.0352	0.0609	1.1543	1705.9
1.0750	0.0603	1.0890	1618.1	3.5639	0.0585	1.1708	1730.8
1.3842	0.0611	1.0983	1631.8	3.9745	0.0557	1.1854	1749.6
1.8894	0.0624	1.1149	1653.5	4.3776	0.0509	1.1995	1769.4
2.2215	0.0627	1.1266	1668.6				

[a]Standard uncertainties are $\rho(T) = 1$ K, $u(T) = 0.03$ K, $\rho = 5 \cdot 10^{-2}$ kg·m^{-3}, $u = 0.1$ m·s^{-1}.

Table 2. Parameters A_i and Standard Deviations σ of eq 1 for the Systems $CaSO_4 \cdot 2H_2O$−NaCl−Water−Nitrate Salts at 308.15 K

nitrate salt	A_0	A_1	A_2	A_3	σ
			solubility/mol·kg^{-1}		
5% $NaNO_3$	0.0038	0.0214	−0.0075	$6.9 \cdot 10^{-4}$	$3.56 \cdot 10^{-4}$
10% $NaNO_3$	0.0398	0.0213	−0.0075	$6.97 \cdot 10^{-4}$	$2.95 \cdot 10^{-4}$
15% $NaNO_3$	0.0431	0.0186	−0.0066	$6.10 \cdot 10^{-4}$	$2.42 \cdot 10^{-4}$
5% KNO_3	0.0429	0.0086	−0.0015	$5.78 \cdot 10^{-5}$	$2.65 \cdot 10^{-4}$
10% KNO_3	0.0525	0.0088	−0.0034	$2.77 \cdot 10^{-4}$	$9.21 \cdot 10^{-4}$
15% KNO_3	0.0572	0.0039	−0.0014	$1.04 \cdot 10^{-4}$	$2.83 \cdot 10^{-4}$
5% NH_4NO_3	0.0472	0.0115	−0.00302	$5.94 \cdot 10^{-5}$	$1.99 \cdot 10^{-4}$
10% NH_4NO_3	0.0526	0.0061	$-7.02 \cdot 10^{-4}$	$-2.13 \cdot 10^{-4}$	$3.87 \cdot 10^{-4}$
15% NH_4NO_3	0.0567	0.0033	$4.75 \cdot 10^{-4}$	$-3.48 \cdot 10^{-4}$	$2.27 \cdot 10^{-4}$
			Density, ρ/g·cm^{-3}		
5% $NaNO_3$	1.0327	0.0330			0.0019
10% $NaNO_3$	1.0579	0.0344			0.0010
15% $NaNO_3$	1.0869	0.0328			0.0009
5% KNO_3	1.0311	0.0334			0.0010
10% KNO_3	1.0612	0.0357			0.0013
15% KNO_3	1.0902	0.0294			0.0011
5% NH_4NO_3	1.0192	0.0366			0.0011
10% NH_4NO_3	1.0366	0.0364			0.0007
15% NH_4NO_3	1.0530	0.0332			0.0006
			Speed of Sound, u/m·s^{-1}		
5% $NaNO_3$	1547.75	50.86			1.75
10% $NaNO_3$	1566.32	50.32			1.42
15% $NaNO_3$	1586.97	50.12			1.45
5% KNO_3	1539.91	50.24			1.35
10% KNO_3	1560.25	48.56			1.27
15% KNO_3	1577.41	44.89			1.28
5% NH_4NO_3	1536.64	52.34			0.87
10% NH_4NO_3	1557.17	48.03			0.60
15% NH_4NO_3	1568.48	45.60			0.85
			Isentropic Compressibility, $10^{12} \cdot \kappa_S$/Pa^{-1}		
5% $NaNO_3$	404.34	−38.96	1.95		1.44
10% $NaNO_3$	384.80	−36.44	1.72		0.86
15% $NaNO_3$	365.79	−34.29	1.80		0.61
5% KNO_3	409.03	−39.27	1.95		1.00
10% KNO_3	388.02	−37.85	2.11		0.63
15% KNO_3	368.85	−31.05	1.47		0.54
5% NH_4NO_3	444.67	−41.17	1.95		0.57
10% NH_4NO_3	397.28	−37.08	1.70		0.36
15% NH_4NO_3	386.49	−34.09	1.55		0.76

and speed of sound has been used to determine solution isentropic compressibility and the hydration characteristics of ions.

2. EXPERIMENTAL SECTION

Inorganic salts $CaSO_4 \cdot 2H_2O$, NaCl, $NaNO_3$, KNO_3, and NH_4NO_3 (> 99.5 % by mol) obtained from SD. Fine Chemicals (Bombay) were dried in an oven at 70 °C and used 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. Stock solutions were prepared by adding oven-dried NaCl to the solutions containing fixed amounts of nitrate salts. A range of solutions with different NaCl and fixed nitrate salt concentrations saturated with the $CaSO_4 \cdot 2H_2O$ were then made by diluting stock solutions with initially prepared aqueous $NaNO_3$/KNO_3/or NH_4NO_3 solutions and adding excess $CaSO_4 \cdot 2H_2O$. The resulting solutions were stirred with an electrical paddle in a thermostatically controlled water bath, and solubility equilibrium was ensured by analyzing samples at different time intervals; 24 h was found sufficient for attaining the equilibrium as no more dissolution was observed from chemical analysis of samples taken after stirring for even longer time periods. Liquid samples were withdrawn periodically and analyzed for different ions as described elsewhere.[17] In brief, Ca^{2+} and Cl^- concentrations were determined volumetrically using standard EDTA and $AgNO_3$ solutions, respectively, with an error of < 0.2 %, and SO_4^{2-} concentration was determined gravimetrically using barium chloride precipitation as per the standard analytic procedure with an estimated error of < 0.1 %. The solubility of $CaSO_4 \cdot 2H_2O$ in water thus determined was 0.0151 mol/kg which is fairly close to the literature solubility of $CaSO_4 \cdot 2H_2O$ (0.0154 mol/kg[12] and 0.0157 mol/kg[16] 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} at 308.15 K. The densimeter was calibrated with doubly distilled and degassed water, with dry air at atmospheric pressure, and also against the densities of NaCl (aq),[25] with an accuracy of 0.01%. The sample temperature 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 51600 Hz using a concentration analyzer (model 87, SCM Laboratory Sonic Composition Monitor) based on the sing-around technique[26] at 308.15 K with a single transducer cell, immersed in a water bath with temperature controlled to ±1 K. The analyzer was calibrated by measurements of speeds of sound in water as a reference, with an estimated error < ± 0.1 $m \cdot s^{-1}$.[26] Measurements were carried out in a specially designed sample jar of low volume capacity. The reproducibility of the results was ensured by performing at least three experiments for each concentration.

3. RESULTS AND DISCUSSION

Experimental results of $CaSO_4 \cdot 2H_2O$ solubility in aqueous-NaCl solutions containing various nitrate salts, MNO_3, (M = Na, K and NH_4) and the solution densities and speed of sounds at 308.15 K are given in Table 1. The dependence of $CaSO_4 \cdot 2H_2O$ solubility and other solution properties in NaCl + MNO_3 (M = Na, K, and NH_4) + H_2O systems as a function of NaCl concentration has been 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, density, speed of sound) or derived function (isentropic compressibility) and m is the concentration ($mol \cdot kg^{-1}$) of NaCl in the solution. The values of the parameters A_i were evaluated by the method of least-squares using nonlinear method with all points weighted equally. The parameters A_i and standard deviations σ are given in Table 2. The solubility pattern of $CaSO_4 \cdot 2H_2O$ in pure brines and brines containing different nitrate salt additives (5 wt % to 15 wt %) is compared in Figures 1 to 3. In general all the investigated nitrate salts, that is, $NaNO_3$, KNO_3, and NH_4NO_3 increased the solubility of $CaSO_4 \cdot 2H_2O$ in brine solutions. The solubility increased to nearly same extent with the increase in amount of added salt irrespective of the nature of cation. The increase in solubility maximum of $CaSO_4 \cdot 2H_2O$ in brine solutions for 15 wt % addition of $NaNO_3$, KNO_3, or NH_4NO_3 was 11.7 %, 12.0 %, and 12.5 %, respectively. The solubility maximum was found to shift toward lower NaCl concentrations in the solutions containing $NaNO_3$ and KNO_3 salts, whereas it did not alter in the solutions containing NH_4NO_3. No alteration in solubility maximum of gypsum in solutions containing NH_4NO_3 may be due to less perturbation of water structure by NH_4^+ ions because of nearly same size as that of water.

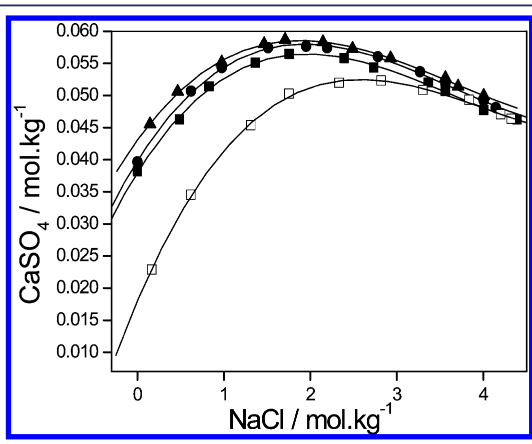

Figure 1. Comparison of solubility of $CaSO_4 \cdot 2H_2O$ at 308.15 K in aqueous NaCl-solutions containing □, 0 %; ■, 5 %; ●, 10 %; and ▲, 15 % $NaNO_3$. Lines are polynomial fit to the experimental data.

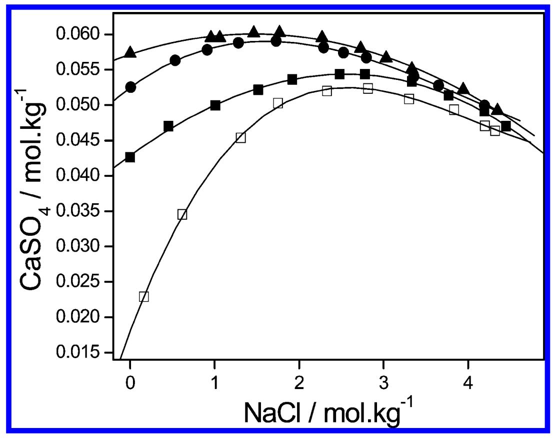

Figure 2. Comparison of solubility of $CaSO_4 \cdot 2H_2O$ at 308.15 K in aqueous NaCl-solutions containing □, 0 %; ■, 5 %; ●, 10 %; and ▲, 15% KNO_3. Lines are polynomial fit to the experimental data.

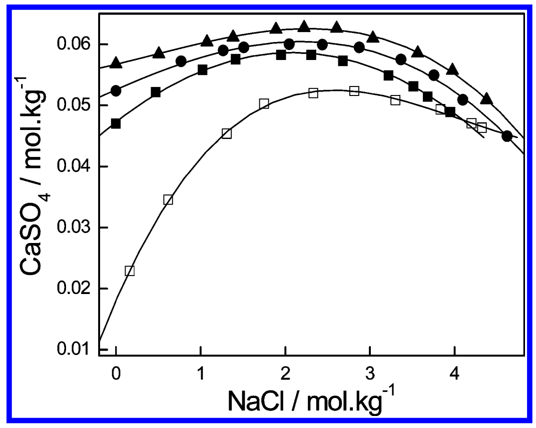

Figure 3. Comparison of solubility of $CaSO_4 \cdot 2H_2O$ at 308.15 K in aqueous NaCl-solutions containing □, 0 %; ■, 5 %; ●, 10 %; and ▲, 15% NH_4NO_3. Lines are polynomial fit to the experimental data.

Density (ρ) and speed of sound (u) values for the systems $CaSO_4 \cdot 2H_2O$ + NaCl + MNO_3 (M = Na, K, and NH_4) + H_2O at 308.15 K at fixed nitrate salt concentrations and as function of NaCl concentration are plotted in Figures 4 to 6. Both the ρ and u were found to increase linearly with an increase in NaCl concentration in the solution. As expected, the solution density also increased with the addition of nitrate salts. However, at similar concentration of nitrate salts in the solution, NH_4NO_3 salt made less dense solution as compared to $NaNO_3$ or KNO_3 salts. At a similar concentration of nitrate salts in the solution, the speed of sound, u, in solutions followed the order: $NaNO_3$ > KNO_3 > NH_4NO_3. Assuming negligible ultrasonic absorption under the experimental conditions we derived the solution isentropic compressibility κ_S from the u and ρ values by using the Newton–Laplace equation[27]

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

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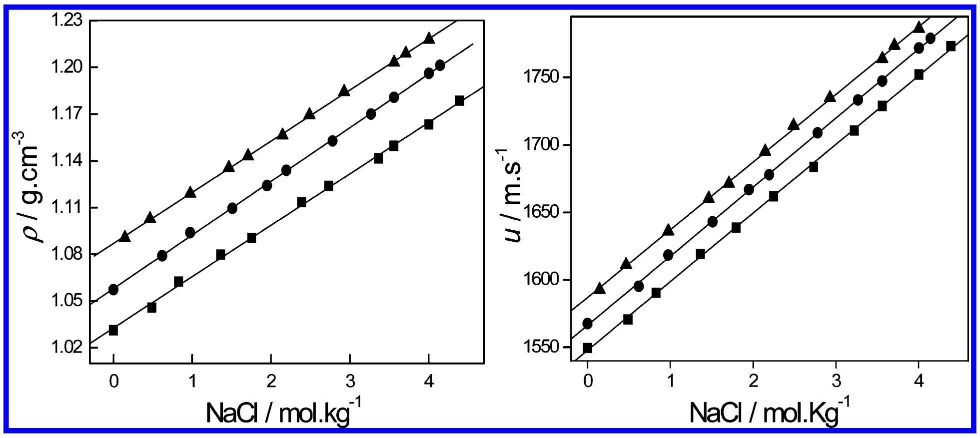

Figure 4. Density (left) and speed of sound (right) data of aqueous-NaCl solutions saturated with $CaSO_4 \cdot 2H_2O$ and containing ■, 5 %; ●, 10 %; and ▲, 15 % $NaNO_3$ at 308.15 K. Lines are linear fit to the experimental data.

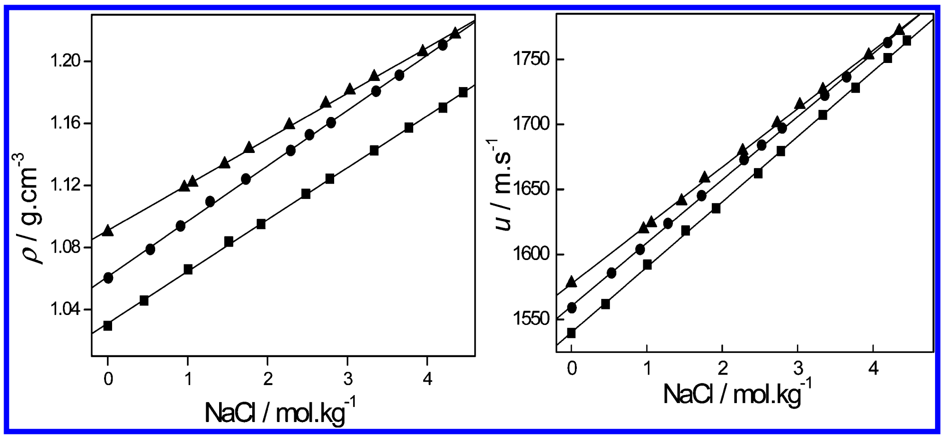

Figure 5. Density (left) and speed of sound (right) data of aqueous-NaCl solutions saturated with $CaSO_4 \cdot 2H_2O$ and containing: ■, 5 %; ●, 10 %; and ▲, 15 % KNO_3 at 308.15 K. Lines are linear fit to the experimental data.

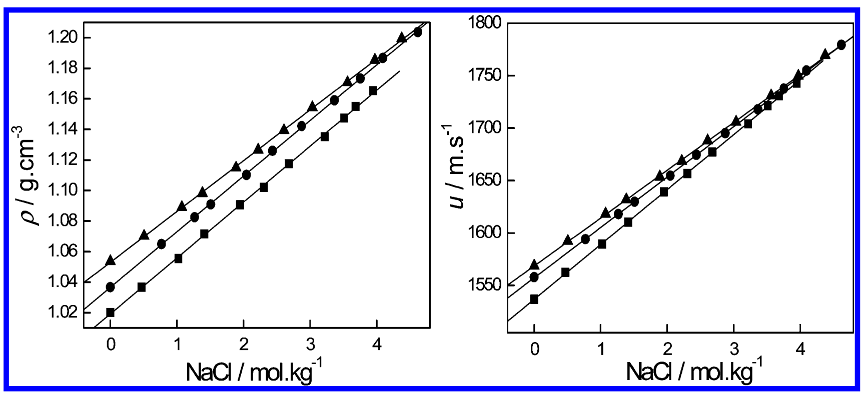

Figure 6. Density (left) and speed of sound (right) data of aqueous-NaCl solutions saturated with $CaSO_4 \cdot 2H_2O$ and containing: ■, 5 %; ●, 10 %; and ▲, 15 % NH_4NO_3 at 308.15 K. Lines are linear fit to the experimental data.

Figure 7 shows a comparison of κ_S of the $CaSO_4 \cdot 2H_2O$ + NaCl + MNO_3 (M = Na, K and NH_4) + H_2O systems. The addition of nitrate salts in water decreased the solution compressibility in general. The solutions containing $NaNO_3$ were found least compressible, whereas NH_4NO_3 solutions were more compressible. The compressibility of aqueous electrolyte solutions comprises configurational as well as vibrational effects with the former effect playing a dominant role in dilute solutions.[28] At higher concentrations the isentropic compressibility is largely determined by the compression of the hydration shell of the ions. The κ_S differences can be explained on the basis of the partial molar volumes and charge densities of the respective ions. In the case of NH_4NO_3, the ammonium ions have partial molar volume close to that of water (~18 cm^3 mol^{-1}), and these do not change appreciably with concentration.[29] Hence the perturbation of the water structure is small. The high hydrophobic hydration (because of comparatively bigger size and polarizability) and good compatibility of ammonium ions with water molecules meant little reduction in free volume of solution. On the other hand, the sodium ions due to the high charge density have a pronounced electrostrictive effect and cause disorder in

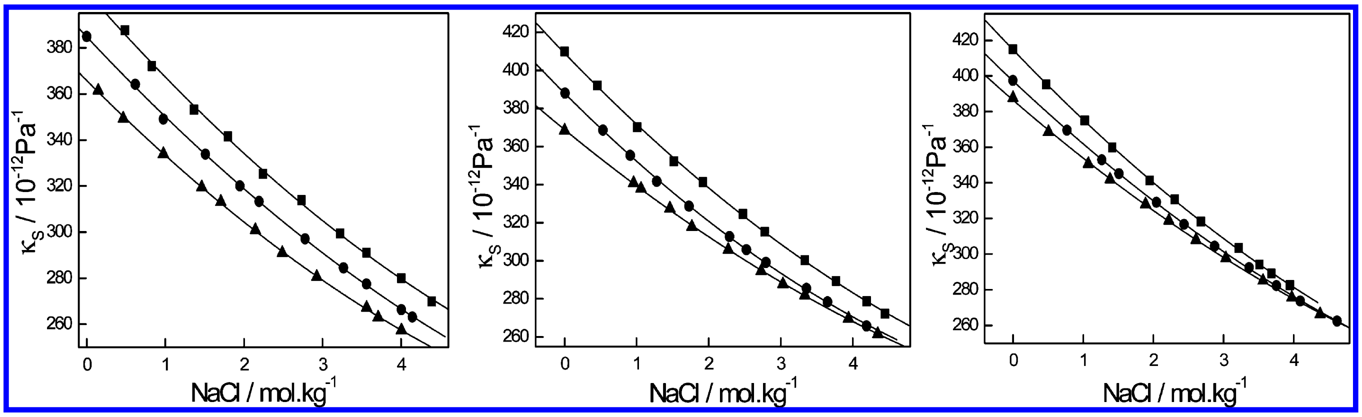

Figure 7. Isentropic compressibility of aqueous-NaCl solutions saturated with $CaSO_4 \cdot 2H_2O$ and containing ■, 5 %; ●, 10 %; and ▲, 15 % nitrate salts (left) $NaNO_3$, (middle) KNO_3, and (right) NH_4NO_3 at 308.15 K. Lines are polynomial fit to the experimental data.

the normal hydrogen bonding of water to a great extent, which is also confirmed from FTIR measurements,[30] and hence $NaNO_3$ containing solutions had higher reduction in free volume and thus were found to be least compressible.

4. CONCLUSION

The solubility of $CaSO_4 \cdot 2H_2O$ in aqueous sodium chloride solutions increases with the addition of nitrate salts and follow the order: NH_4NO_3 > $NaNO_3$ > KNO_3. The solubility maximum was found to shift toward lower NaCl concentrations in the solutions containing $NaNO_3$ and KNO_3 salts, whereas it did not change in the solutions containing NH_4NO_3. The solution properties, that is, solubility, density, and speed of sound for the systems $CaSO_4 \cdot 2H_2O$ + NaCl + MNO_3 (M = Na, K and NH_4) + H_2O have been measured at 308.15 K. Solubility was fitted into a second order polynomial equation, whereas density and speed of sound were fitted to a linear equation. The accurate data produced herein will be highly useful in industrial applications where brines containing gypsum are utilized.

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Notes

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