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Effect of Organic Additives on the Solubility Behavior and Morphology of Calcium Sulfate Dihydrate (Gypsum) in the Aqueous Sodium Chloride System and Physicochemical Solution Properties at 35 °C

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ABSTRACT: The effect of the addition of organic solvents, such as ethyl acetate (EA), glycerol (GLY), isopropyl alcohol (IPA), dimethylformamide (DMF), oxalic acid (OA), and propylamine (PA), on the solubility behavior of calcium sulfate dihydrate (gypsum, $CaSO_4 \cdot 2H_2O$) in aqueous NaCl solutions has been examined at 35 °C. Compared to organic solvent free system, the addition of EA slightly increased $CaSO_4 \cdot 2H_2O$ solubility, whereas only a little alteration in solubility was found with the addition of GLY. $CaSO_4 \cdot 2H_2O$ solubility decreased significantly and to nearly same extent with the addition of IPA or DMF. In the solutions containing PA or OA, $CaSO_4 \cdot 2H_2O$ dissolution was very limited probably due to precipitation of highly stable Ca salts of these organic solvents. Except OA, where no solubility maximum was observed, the addition of organic solvents did not shift the solubility maximum of $CaSO_4 \cdot 2H_2O$ as a function of NaCl concentration in solution, and the solubility pattern remained similar. Accurate data on density (ρ) and speed of sound (u) data have been recorded for the quaternary systems ($CaSO_4 \cdot 2H_2O$ + NaCl + H_2O + organic solvent) at 35 °C. Measurements of u and ρ have been used to determine the solution isentropic compressibility (κ_S). Empirical equations describing the solubility, density, speed of sound, and isentropic compressibility in these systems are presented. The morphology of $CaSO_4 \cdot 2H_2O$ recrystallized from different aqueous−organic solvent solutions and aqueous-NaCl-organic solvent solutions has also been examined from scanning electron microscopy (SEM).
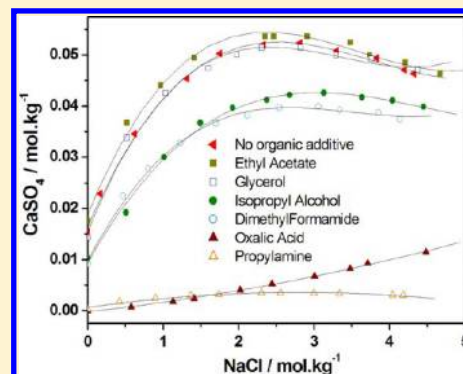
1. INTRODUCTION

Calcium sulfate dihydrate (gypsum, $CaSO_4 \cdot 2H_2O$) is either found in nature as a mineral or precipitated in large quantities during the solar evaporation of natural brines prior to the production of common salt (NaCl). $CaSO_4 \cdot 2H_2O$, a nontoxic mineral, is one of the most commonly used material in diverse applications, such as in the cement industry, writing chalk, soil additive, or as a food additive, and so forth.[1,2] $CaSO_4 \cdot 2H_2O$ is sparingly soluble in water, and its solubility slightly increases with temperature, attains a maximum, and then decreases with further increasing the temperature.[3−5] During the industrial water treatment $CaSO_4 \cdot 2H_2O$ precipitates and forms scale in pipes and other production equipment in desalination plants once its saturation limit exceeds a certain threshold limit.[6] The scale formation can be prevented either by altering the solubility to inhibit the crystallization or to modify the morphology of the crystalline $CaSO_4 \cdot 2H_2O$ using organic or inorganic additives. The crystallization of $CaSO_4 \cdot 2H_2O$ is influenced in a complex manner by temperature, pressure, dissolved electrolytes or organics, and the presence of its own or other minerals.[2] Therefore, the knowledge of solubility behavior of $CaSO_4 \cdot 2H_2O$ in the solutions containing electrolytes or organic additives is very important. Accurate and reliable data on physicochemical properties of such solutions is also a necessary prerequisite while processing for the industrial applications. These kinds of studies are also important for understanding ionic−equilibrium, ion−solvent, and ion−ion interactions in natural waters.[7,8]

The solubility of gypsum in brines has been extensively studied in the past.[9−15] Freyer and Vogt[2] and Marshall and Slusher[12] have nicely compiled the data in detail on crystallization, phase stability, and solubility behavior of $CaSO_4 \cdot 2H_2O$ in aqueous solution as well as in aqueous solutions of different electrolytes. Sensing the importance of such studies, we have also initiated a research program on the aqueous electrolyte solutions saturated with $CaSO_4 \cdot 2H_2O$ and reported 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)[16−18] and quaternary systems ($CaSO_4 \cdot 2H_2O$ + NaCl + $CaCl_2$ + H_2O and $CaSO_4 \cdot 2H_2O$ + NaCl + $MgCl_2$ + H_2O)[19,20] in the past few years. The effect of pH on the solubility of $CaSO_4 \cdot 2H_2O$ in the system

Table 1. Solubility of CaSO$_4$·2H$_2$O in Aqueous−Organic Solvent−NaCl Solutions, Solution Density ρ, and Speed of Sound u at 35 °C

NaCl	CaSO$_4$	ρ	u	NaCl	CaSO$_4$	ρ	u
mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3}	m·s^{-1}	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3}	m·s^{-1}
EA				GLY			
0	0.0176	0.9978	1520.1	0	0.0143	1.0216	1557.6
0.5167	0.0367	1.0180	1553.1	0.5167	0.0338	1.0400	1585.1
0.9633	0.0441	1.0371	1577.5	1.0335	0.0425	1.0580	1609.7
1.4099	0.0495	1.0521	1606.4	1.5981	0.0474	1.0787	1642.3
2.3510	0.0536	1.0829	1659.4	1.9746	0.0501	1.0925	1660.6
2.4639	0.0536	1.0900	1668.1	2.3048	0.0514	1.1061	1681.8
2.9088	0.0536	1.1032	1694.1	2.8216	0.0514	1.1259	1710.5
3.4803	0.0525	1.1199	1728.9	3.2921	0.0500	1.1419	1730.7
3.7387	0.0500	1.1329	1740.6	3.7626	0.0492	1.1587	1758.0
4.2092	0.0485	1.1474	1769.0	4.3735	0.0470	1.1784	1791.2
4.6712	0.0463	1.1596	1797.8				
IPA				DMF			
0	0.0103	0.9849	1564.4	0	0.0092	0.9979	1565.9
0.5056	0.0192	1.0060	1587.7	0.4705	0.0225	1.0138	1590.4
1.0094	0.0300	1.0245	1610.8	0.7991	0.0277	1.0268	1609.1
1.4903	0.0367	1.0450	1630.2	1.2234	0.0327	1.0418	1631.1
1.9198	0.0397	1.0605	1651.5	1.6940	0.0367	1.0573	1652.9
2.3733	0.0412	1.0785	1671.5	2.1166	0.0382	1.0711	1675.5
2.6778	0.0422	1.0905	1685.9	2.5409	0.0397	1.0892	1697.1
3.1313	0.0426	1.1078	1705.5	3.0594	0.0400	1.1060	1726.0
3.6377	0.0417	1.1274	1728.5	3.3417	0.0392	1.1160	1740.1
4.0415	0.0411	1.1438	1747.1	3.8585	0.0387	1.1339	1766.2
4.4488	0.0399	1.1603	1764.2	4.1408	0.0375	1.1456	1782.0
OA				PA			
0	0	1.0308	1525.1	0	0.0003	0.9826	1568.4
0.5749	0.0007	1.0468	1549.2	0.4226	0.0018	1.0001	1588.8
1.1293	0.0018	1.0612	1572.5	0.8932	0.0024	1.0192	1607.2
1.4099	0.0024	1.0692	1584.8	1.3620	0.0030	1.0403	1630.6
2.0208	0.0040	1.0854	1609.3	1.7385	0.0032	1.0552	1646.4
2.4434	0.0053	1.0980	1628.6	2.3031	0.0035	1.0807	1671.5
3.0081	0.0068	1.1130	1650.4	2.5563	0.0035	1.0925	1683.5
3.4786	0.0082	1.1264	1671.9	2.9995	0.0034	1.1110	1704.4
3.7130	0.0093	1.1334	1682.9	3.3383	0.0033	1.1270	1718.8
4.4830	0.0115	1.1537	1715.0	4.0433	0.0031	1.1568	1750.1
				4.1836	0.0030	1.1628	1757.7

CaSO$_4$·2H$_2$O + NaCl + H$_2$O has also been examined by our research group.[21]

Though the effect of electrolytes on solubility behavior of CaSO$_4$·2H$_2$O in brines has been studied extensively and systematically, a little attention has been paid toward the investigations on effect of organic solvents/water−organic solvent systems.[22] Organic solvents are often added to control hydrate formation. However, such practice has an adverse effect on scale formation since the mineral salts are generally less soluble in the cosolvent. Different organic additives alter the magnitude of mineral scaling to a different extent. Therefore, a comprehensive physicochemical data is required on brine solutions containing organic solvents and CaSO$_4$·2H$_2$O. The data will be useful to test or develop the models of the solubility of mineral salts in hydrate inhibitors/water/salt solutions. Such investigations can be also useful in drowning out precipitation of soluble salts at ambient temperature and obtaining crystals of high purity, desired size, and morphology.[23−27] In this pursuit, very recently we investigated the effect of ethylene glycol and its derivatives on the solubility behavior of CaSO$_4$·2H$_2$O in brines and determined physicochemical solution properties.[28]

Studies revealed that the addition of ethylene glycol reduced the solubility of CaSO$_4$·2H$_2$O, and the replacement of the hydroxyl group of ethylene glycol by the methoxy group further decreased the solubility of CaSO$_4$·2H$_2$O. In the present work we have investigated the effect of diverse organic solvents (10 wt %) (ethyl acetate (EA), glycerol (GLY), isopropyl alcohol (IPA), dimethylformamide (DMF), oxalic acid (OA), and propylamine (PA)) on the dissolution behavior of CaSO$_4$·2H$_2$O in aqueous NaCl solutions to examine the efficacy of these solvents to alter solubility behavior of CaSO$_4$·2H$_2$O and determined physicochemical solution properties as an aid toward the assessment of the potential drowning out precipitation using organic solvents as a separation technique.

In a normal course of precipitation CaSO$_4$·2H$_2$O forms small needle-like crystals having a monoclinic, prismatic structure with water molecules between the calcium and sulfate ions in the unit cell.[29] However, this is shown that CaSO$_4$·2H$_2$O with varying morphologies can be prepared using organic additives, surfactants, microemulsions, or in organic media.[25−27,29−31] Therefore, out of curiosity, we have regenerated CaSO$_4$·2H$_2$O crystals from various solutions at room temperature and

assessed the morphology changes using scanning electron microscopy (SEM).

2. EXPERIMENTAL SECTION

$CaSO_4 \cdot 2H_2O$, and NaCl (> 99.5 % by mol) obtained from SD. Fine Chemicals (Bombay) were used after drying in an oven at 70 °C without further purification. EA (> 99 mol %), GLY (> 98 mol %), IPA (> 99.5 mol %), DMF (> 99.5 mol %), OA (> 99.8 mol %), and PA (> 99.5 mol %) were obtained from SD Fine Chemicals, Bombay. All of the organic liquids were used after drying over the 0.4 nm molecular sieves and under vacuum at ambient conditions. 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 aqueous solutions containing fixed amounts of organic solvent (10 wt %). The pH of the solutions containing different organic solvents was: 6.5, 7.0, 7.1, 2.0, 7.1, and 10.0, respectively, for GLY, EA, DMF, OA, IPA, and PA. A range of solutions of different NaCl concentrations saturated with $CaSO_4 \cdot 2H_2O$ were then prepared by diluting the stock solutions of sodium chloride with an aqueous solution of organic solvents 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, the solutions were kept unstirred for (6 to 8) h, and the superlayer clear solution then was filtered through a simple filter paper. No liquid−liquid demixing was observed in any of the solvent−NaCl−water system even at very high NaCl concentration at 35 °C. Liquid samples were withdrawn periodically and analyzed for different ions as described elsewhere.[16] In brief: Ca^{2+} and Cl^- concentrations were determined volumetrically using standard EDTA and $AgNO_3$ solutions, respectively. Repeated analytical experiments showed an error of < 0.2 %. The SO_4^{2-} concentration was determined gravimetrically using barium chloride as a precipitating agent with an estimated error of < 0.1 %.

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 35 °C. The densimeter was calibrated with doubly distilled and degassed water, with dry air at atmospheric pressure, and also against the densities of NaCl(aq),[32] with an accuracy of 0.01 %. The temperature of the apparatus was controlled to within ± 0.03 K by a built-in Peltier device. The 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[33] at 35 °C with a single transducer cell, immersed in a water bath with temperature controlled to ± 0.01 °C. The analyzer was calibrated by measurements of speeds of sound in water as a reference, with an estimated error < ± 0.1 m·s^{-1}.[33] 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. At least three experiments were performed for each concentration to ensure the reproducibility of the results.

Scanning electron micrographs of the gypsum crystals grown from different aqueous−organic solvent systems were taken from a LEO 1430 VP Carl Zeiss scanning electron microscope.

Gypsum as the solid phase was confirmed through energy-dispersive X-ray (EDX) spectrometry.
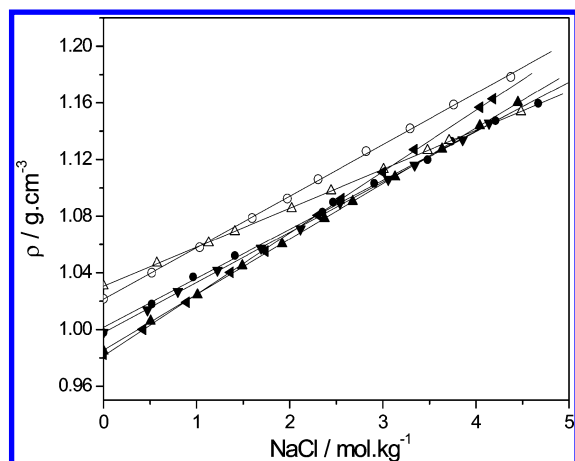
3. RESULTS AND DISCUSSION

Experimental results of solubility and solution properties (density and speed of sound) of $CaSO_4 \cdot 2H_2O$ in aqueous−

Table 2. Parameters A_i and Standard Deviations σ of eq 1 for the System $CaSO_4 \cdot 2H_2O$−NaCl−Water−Organic Solvent at 35 °C
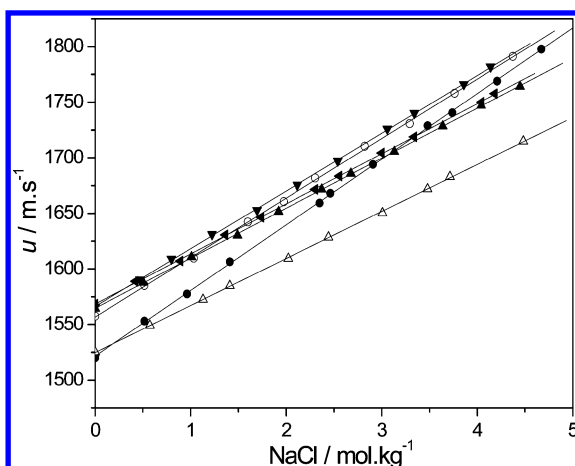
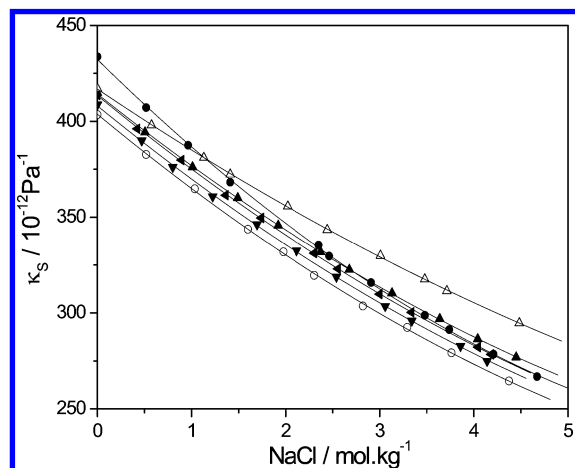| organic solvent	A_0	A_1	A_2	A_3	σ
Solubility/mol·kg^{-1}					
EA	0.0189	0.0359	−0.0113	0.0010	0.0012
GLY	0.0155	0.0368	−0.0119	0.0012	0.0013
IPA	0.0094	0.0263	−0.0065	0.0005	0.0009
DMF	0.0099	0.0282	−0.0085	0.0008	0.0007
OA	−0.0002	0.0016	0.0002		0.0002
PA	0.0007	0.0021	−0.0004		0.0002
Density, ρ/g·cm^{-3}					
EA	1.0015	0.0346			0.003
GLY	1.0213	0.0364			0.001
IPA	0.9855	0.0392			0.001
DMF	0.9977	0.0355			0.001
OA	1.0305	0.0275			0.001
PA	0.9814	0.0433			0.001
Speed of Sound, u/m·s^{-1}					
EA	1521.6	59.1			1.4
GLY	1556.7	53.5			1.8
IPA	1564.7	45.0			0.7
DMF	1566.3	51.9			1.0
OA	1524.7	42.3			0.8
PA	1568.5	45.1			0.9
Isentropic Compressibility, $10^{12} \cdot \kappa_S$/Pa^{-1}					
EA	432.2	−48.3	2.8		1.1
GLY	403.7	−40.8	2.1		0.9
IPA	414.3	−39.3	1.9		0.4
DMF	408.1	−40.2	2.0		0.7
OA	416.8	−33.1	1.3		0.5
PA	413.4	−40.2	1.9		0.5
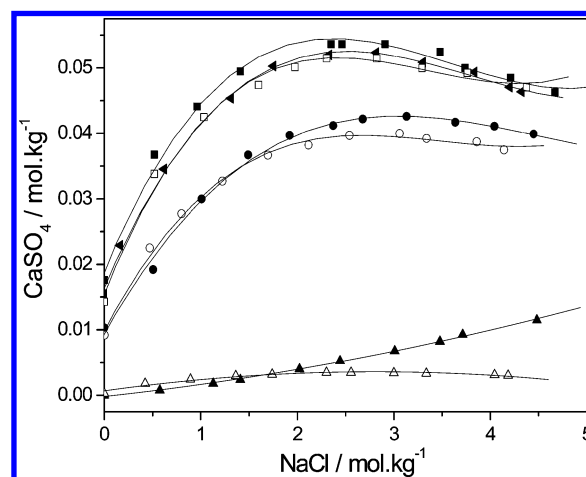
Figure 1. Comparison of solubility of $CaSO_4 \cdot 2H_2O$ at 35 °C in aqueous NaCl solutions containing organic solvents (10 wt %): ■, EA; ◀, no organic additive; □, GLY; ●, IPA; ○, DMF; ▲, OA and △, PA. Lines are a polynomial fit to the experimental data.

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Figure 2. Density of aqueous−NaCl−organic solvent (10 wt %) solutions saturated with $CaSO_4 \cdot 2H_2O$ at 35 °C. ●, EA; ○, GLY; ▲, IPA; ▼, DMF; △, OA and ◄, PA. Lines are linear fits to the experimental data.

Figure 3. Speed of sound in aqueous−NaCl−organic solvent (10 wt %) solutions saturated with $CaSO_4 \cdot 2H_2O$ at 35 °C. ●, EA; ○, GLY; ▲, IPA; ▼, DMF; △, OA and ◄, PA. Lines are linear fits to the experimental data.

Figure 4. Isentropic compressibility of aqueous−NaCl−organic solvent (10 wt %) solutions saturated with $CaSO_4 \cdot 2H_2O$ at 35 °C. ●, EA; ○, GLY; ▲, IPA; ▼, DMF; △, OA and ◄, PA. Lines are polynomial fits to the experimental data.

organic solvent−NaCl solutions at 35 °C are given in Table 1. The dependence of $CaSO_4 \cdot 2H_2O$ solubility and other solution properties in NaCl + H_2O + organic solvent systems as a function of NaCl concentration has been correlated by means of a polynomial type equation,

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

where Q represents a general measured property (solubility, density, 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 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 $CaSO_4 \cdot 2H_2O$ with different organic solvent additives (10 wt %) in aqueous−NaCl solutions is shown in Figure 1. EA or GLY did not show an antisolvent effect, and the solubility of $CaSO_4 \cdot 2H_2O$ in aqueous−EA−NaCl or aqueous−GLY−NaCl remained almost same as that in aqueous−NaCl solution. EA showed a slight salting-in effect wherein we observed a somewhat higher dissolution of $CaSO_4 \cdot 2H_2O$ as compared to organic solvent free system. IPA and DMF showed a significant but comparable antisolvent effect. The solubility maximum of $CaSO_4 \cdot 2H_2O$ decreased about 18 % and 23 % in IPA and DMF containing solutions, respectively. Also, when compared to the organic solvent free system, the solubility maximum of $CaSO_4 \cdot 2H_2O$ appeared at higher NaCl concentrations in IPA containing solution, whereas the maximum appeared at slightly lower NaCl concentration in DMF containing solution. OA and PA containing solutions made of $CaSO_4 \cdot 2H_2O$ almost insoluble. OA containing solutions were highly acidic (pH = 2.0), and formation of low solubility calcium oxalate results in the lowering of $CaSO_4 \cdot 2H_2O$ solubility to a highly reduced level. PA containing solutions were highly basic (pH = 10.0) and probably resulted in lowering of $CaSO_4 \cdot 2H_2O$ solubility. Only a small maximum in solubility of $CaSO_4 \cdot 2H_2O$, that too at considerable lower NaCl concentrations, appeared in OA containing solutions. However, a distinct pattern of $CaSO_4 \cdot 2H_2O$ solubility, wherein it continued to increase with the increase of NaCl concentration, was observed in PA containing solutions. The antisolvent effect shown by the ethylene glycol derivatives (10 wt %)[28] is almost similar to that demonstrated by IPA and DMF, and the solubility of $CaSO_4 \cdot 2H_2O$ decreases to a significant level in all of these cases.

Density (ρ) and speed of sound (u) values for the $CaSO_4 \cdot 2H_2O$ + NaCl + H_2O + organic solvent systems at 35 °C as a function of NaCl concentration are reported in Table 1, and the data are plotted in Figures 2 and 3, respectively. Both ρ and u were found to increase linearly with an increase in electrolyte concentration in the solution and also depended upon the nature of aqueous−organic solvent medium. At any given NaCl concentration, the solutions containing GLY were found most dense, and solutions containing PA or IPA were least dense. u was found at a maximum in DMF containing solutions, whereas it was least in OA containing solutions. u increased with the highest slope in EA containing solutions. The composition dependence of ρ and u has been 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 solution isentropic
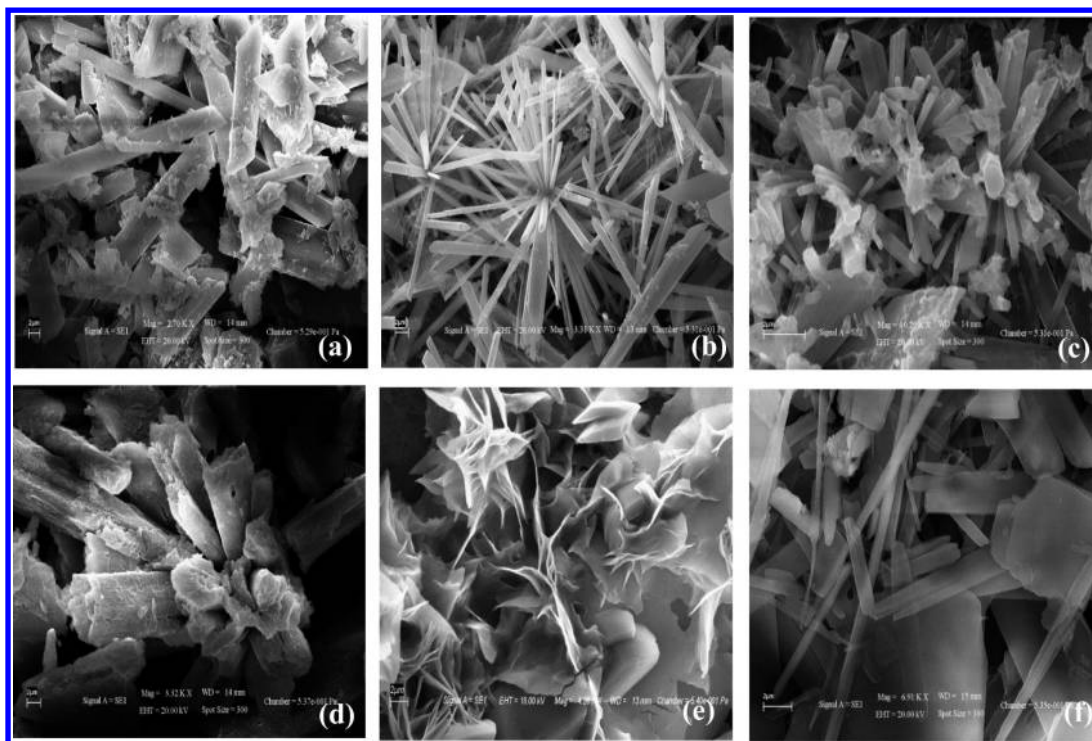
Figure 5. SEM image of CaSO$_4$·2H$_2$O crystallized from aqueous−organic solvent (10 wt %) solutions saturated with CaSO$_4$·2H$_2$O at 35 °C. (a) EA; (b) GLY; (c) IPA; (d) DMF; (e) OA (no gypsum is visible); and (f) PA.
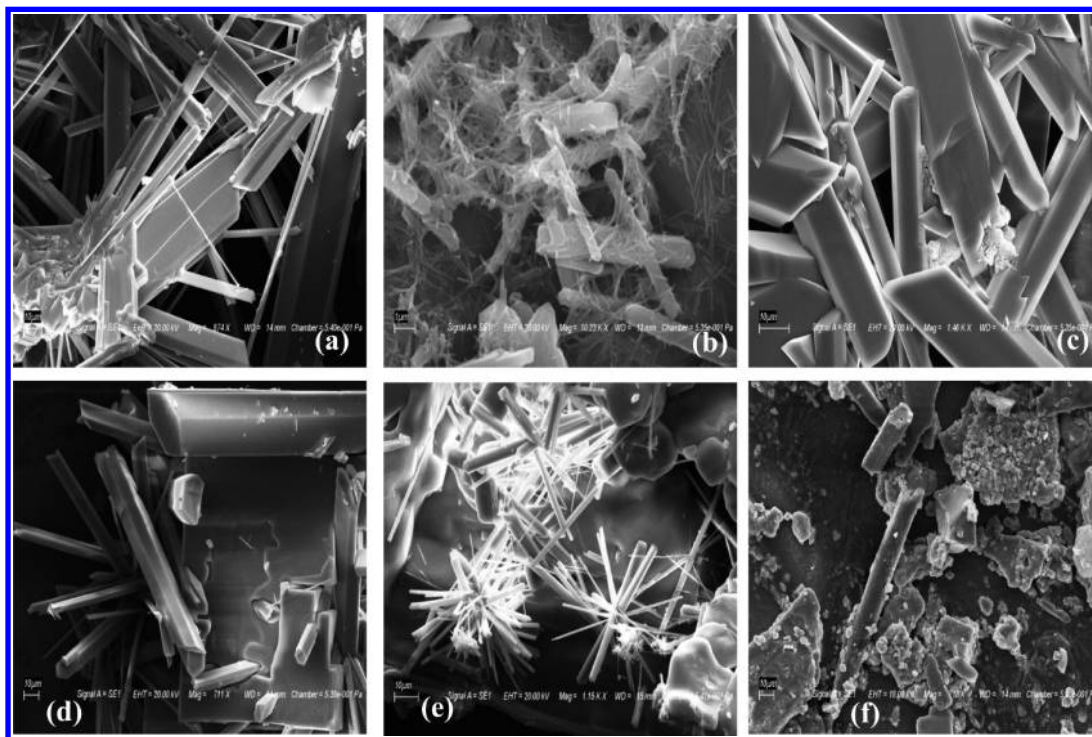
Figure 6. SEM image of CaSO$_4$·2H$_2$O crystallized from aqueous−NaCl−organic solvent (10 wt %) solutions saturated with CaSO$_4$·2H$_2$O at 35 °C. (a) EA; (b) GLY; (c) IPA; (d) DMF; (e) OA; and (f) PA.

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 CaSO$_4$·2H$_2$O + NaCl + H$_2$O + organic solvent systems. The composition depend-

ence of κ_S has been fitted to eq 1, and the parameters and standard deviations are provided in Table 2. The addition of organic solvents in water decreased the solution compressibility in general and followed the order: GLY < DMF < PA < IPA < EA < OA. However, at higher NaCl concentrations in the solution, the EA containing solutions were found less

compressible than OA containing solutions. Breaking of the network structure of water results in a more compact and hence less compressible state. 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.[34] At higher concentrations the isentropic compressibility is largely determined by the compression of the hydration shell of the ions. The extent of hydrogen bonding of organic solvents with water and packing effect of unlike molecules as a consequence of specific geometries also affects the compressibility.

Figure 5a−f shows the SEM images of $CaSO_4 \cdot 2H_2O$ precipitated from aqueous−organic (10 wt %) solutions. SEM images showed that $CaSO_4 \cdot 2H_2O$ crystals grew with different morphologies from different solutions. Crystals in the form of rod of thickness (2 to 5) μm grow from aqueous−EA solutions. Fine needles of 1 μm thickness which grew in a flower-like arrangement were obtained from the aqueous−GLY solutions. Small-sized needles which stacked in the form of rods grew from aqueous−IPA solutions. Very thick ~10 μm size tubular crystals with a rough surface were obtained from DMF containing solutions. Crystals obtained from OA solutions look flaky or flowery and do not contain any gypsum because of negligible solubility as a consequence of formation of low solubility calcium oxalate. A mixture of long thin needles (< 0.5 μm thickness) and wide sheets were obtained from PA containing solutions. It seems that thin wide sheets are comprised of thin needles. The effect of salinity (16 wt % NaCl) on crystal morphology precipitated from aqueous−organic (10 wt %) solutions was also examined (Figure 6a−f). $CaSO_4 \cdot 2H_2O$ grown from aqueous−NaCl−EA solutions crystallizes in the form of long thin needles and thick sheets. From aqueous−NaCl−GLY solutions, a mixture of nano and micrometer $CaSO_4 \cdot 2H_2O$ sized needles were obtained. Only thick rods of $CaSO_4 \cdot 2H_2O$ were crystallized from aqueous−NaCl−IPA solutions. Micron-sized thick hexagonal rods of $CaSO_4 \cdot 2H_2O$ were grown from aqueous−NaCl−DMF solutions, whereas the flower-like morphology consisting of micrometer-sized rods was obtained from aqueous−NaCl−OA solutions. A few needle-shaped $CaSO_4 \cdot 2H_2O$ rods decorated with NaCl were grown from aqueous−NaCl−PA solutions. Therefore, it is seen that $CaSO_4 \cdot 2H_2O$ can be grown in different morphologies and sizes depending upon nature of organic solvent or salinity of the solution. GLY in particular in saline solutions can produce nanosized $CaSO_4 \cdot 2H_2O$.

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Notes
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