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## Effect of hydroxyl alkyl amines on the solubility behavior of calcium sulphate dihydrate (gypsum) in the aqueous sodium chloride system at 35 °C

Jignesh Shukla & Arvind Kumar\*

Salt and Marine Chemicals Division, CSIR-Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research, GB Marg, Bhavnagar 364 002, India

Email: [arvind@csmcri.org](mailto:arvind@csmcri.org)

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The solubility behavior of calcium sulphate dihydrate (gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) in aqueous NaCl solutions upon addition of hydroxyl alkyl amines, such as, ethanolamine (EA), diethanolamine (DEA), or triethanolamine (TEA) at 35 °C is reported. The addition of hydroxyl alkyl amines alters the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in NaCl solutions significantly. At any equal concentration of hydroxyl alkyl amines in the solution, the order of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  solubility enhancement is found to be: EA < DEA < TEA. A three-fold increase in  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  solubility maximum is observed in the solutions containing 15 wt% TEA. The addition of hydroxyl alkyl amines shifts the solubility maximum of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  towards higher concentration of NaCl in solution. Solution properties such as density ( $\rho$ ) and speed of sound ( $u$ ) data have been measured for the quaternary systems ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{NaCl} + \text{hydroxyl alkyl amines} + \text{H}_2\text{O}$ ). All the measurements have been carried out at 35 °C under atmospheric pressure. Solution isentropic compressibility ( $\kappa_s$ ) values have been derived from  $u$  and  $\rho$  data. Solubility, density, speed of sound, and isentropic compressibility data have been fitted with suitable polynomial equations in these systems.

**Keywords:** Solution chemistry, Solubility, Density, Compressibility, Calcium sulphate, Gypsum, Hydroxyl alkyl amines

Measurements and interpretation of solution behaviour of electrolyte solutions is necessary for processing of recovery of their pure salts from industrial streams or processing these for value added chemicals in industrial applications. Such studies are also fundamentally important for understanding complex ionic interactions and phase behaviour of natural waters.<sup>1,2</sup> Focus of our studies so far has been the saline aqueous solutions containing gypsum (calcium sulphate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  occurs in nature as a mineral or precipitates just before crystallization of common salt (NaCl) during solar evaporation of sea water or

underground saline water. It is non-toxic and widely used material in diverse applications.<sup>3,4</sup> The studies on aqueous solutions of gypsum (calcium sulphate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) are particularly relevant as it forms scale in pipes and other production equipment in desalination plants due to low solubility during the industrial water treatment.<sup>5</sup> Studies on gypsum solutions are also important in development of high purity solar salt (NaCl) production processes from natural brines as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  precipitates in small amounts along with crystallization of NaCl, thus making it impure in terms of contamination of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  content.<sup>6</sup>

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  scaling or contamination in brine streams can be stopped by enhancing its the solubility to prevent the deposition using organic or inorganic additives. Electrolytes effect on dissolution behavior of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous or brine systems has been extensively investigated in past by various researchers as well as by our own research group.<sup>7-24</sup> However, effect of organic solvents/additives on dissolution characteristics of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous or brine systems is rarely studied.<sup>25-29</sup> Organic solvents are generally mixed to adjust hydrate formation or to alter the solubility. Nature of organic additives changes the extent of mineral scaling significantly. Therefore, we have embarked on a systematic study on physicochemical data measurements of aqueous-NaCl solutions saturated with  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in presence of organic solvents. Such investigations will be useful for developing new models for prediction of solubility and other solution properties and also for testing of existing models of solution chemistry of brine and related systems. The studies will also be helpful in understanding the drowning out precipitation of salts from saline systems and producing high purity crystals of desired shape and size.<sup>30-33</sup> In this work we have studied the effect of organic solvents (hydroxyl alkyl amines) on the solubility behavior of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous NaCl solutions in order to test their ability towards alteration of solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . We have also measured thermodynamic solution properties to contribute towards understanding of drowning out precipitation of inorganic salts utilizing organic solvents.

## Experimental

Analytical grade  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (99.0% by mol) and  $\text{NaCl}$  (>99.9% by mol) were procured from Samir Tech Chem India, Baroda and RANKEM (RFCL Limited, New Delhi) respectively. To remove the moisture content, the salts were dried at 70 °C in an oven. Analytical grade ethanolamine, diethanolamine and triethanolamine with a purity of 99.0 mol% were obtained SD Fine-Chem Limited (Mumbai). Solvents were also dried over 0.4 nm molecular sieves prior to use without any further purification. Solutions with a precision of  $\pm 0.0001$  g were constructed by weight in Millipore grade water using a digital electronic balance (Denver Instrument APX-200). Aqueous  $\text{NaCl}$ -organic solvent stock solutions were prepared by adding known amounts of organic solvent (5-10 wt%) and  $\text{NaCl}$ . Aqueous  $\text{NaCl}$  solutions containing different organic solvents always measured a pH value of higher than 8.5. Solutions saturated with  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  were then prepared by diluting the aqueous  $\text{NaCl}$  stock solutions with an aqueous solution of ethanolamine, diethanolamine or triethanolamine and adding excess  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Temperature of the solutions was kept constant using a thermostatically controlled water bath. To ensure complete dissolution, solutions were stirred continuously with an electrical paddle for about 24 h. The solutions were then kept unstirred for 6-8 h and filtered with Whatman filter paper. No liquid-liquid demixing was observed in the resulting solutions. Samples prepared were analyzed for  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  concentrations volumetrically using standard EDTA or  $\text{AgNO}_3$  respectively, with an error of < 0.2%.  $\text{SO}_4^{2-}$  concentration with an estimated error of < 0.1% was determined gravimetrically using  $\text{BaCl}_2$  as precipitating agent.<sup>17</sup> The overall error in solubility measurement was < 0.005 mol·kg<sup>-1</sup>.

Density ( $\rho$ ) and speed of sound ( $u$ ) of the solutions were measured at 35 °C ( $\pm 0.01$  °C) with an Anton Paar (model DSA 5000M) density and sound velocity meter (resolution:  $5 \times 10^{-2}$  kg m<sup>-3</sup> and 0.01 m·s<sup>-1</sup> respectively). The machine was calibrated with aqueous  $\text{NaCl}$  solutions<sup>34</sup> for  $\rho$  and with water<sup>35</sup> for  $u$  with an accuracy of 0.01%. The speed of sound were measured at a frequency of 3 MHz. The estimated error for  $\rho$  and  $u$  was 0.0005 kg m<sup>-3</sup> and  $\leq \pm 0.1$  m s<sup>-1</sup> respectively for standard solutions. To check the reproducibility, at least three measurements were made. The overall error in density values was < 1% considering the compositional errors of prepared solutions.

## Results and discussion

Solubility ( $s$ ) of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous-hydroxyl alkyl amines- $\text{NaCl}$  solutions and solution properties ( $\rho$  and  $u$ ) at 35 °C are given in Table 1. The dependence of physical properties of solution and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  solubility in the systems ( $\text{NaCl} + \text{H}_2\text{O} + \text{hydroxyl alkyl amines}$ ) as a function of  $\text{NaCl}$  concentration is correlated using a polynomial type equation, Eq. (1),

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

where  $Q$  represents measured physical properties ( $s$ ,  $\rho$  and  $u$ ) or derived parameter (isentropic compressibility,  $\kappa_s$ ) and  $m$  is the  $\text{NaCl}$  concentration (mol·kg<sup>-1</sup>) in different solutions. The method of least squares using non-linear method with all points weighted equally was used to evaluate the parameters  $A_i$ . Table 2 includes the parameters  $A_i$  and standard deviations  $\sigma$ . Solubility patterns of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  with different hydroxyl alkyl amines additives (5-15 wt%) in aqueous-  $\text{NaCl}$  solutions are compared with organic solvent-free system<sup>22</sup> in Figs 1-3. Hydroxyl alkyl amines (TEA and DEA) showed a salting-in effect wherein the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous  $\text{NaCl}$  solutions was found higher as compared to that without any organic additives. In the case of EA, the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous  $\text{NaCl}$  solutions was found to be lower as compared to organic additive free system. However, solutions containing higher amounts of EA showed higher dissolution of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in concentrated  $\text{NaCl}$  regime when compared with organic additive-free system. In general, an increase in solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  was observed with the increase of amount of hydroxyl alkyl amines (5-15 wt%) in the solutions. This is because of increased hydrophilicity of the water on addition of hydroxyl alkyl amines. At a fixed concentration of hydroxyl alkyl amines, the sequence of solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous  $\text{NaCl}$  solutions was: TEA > DEA > EA. The higher solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in the case of TEA containing solutions is because of higher number of hydroxyl groups contributing to the enhanced hydrophilicity of the solution. The solubility maximum of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  shifted towards higher  $\text{NaCl}$  concentration in all the hydroxyl alkyl amine containing systems.

Table 1 – Solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous hydroxyl alkyl amines-NaCl solutions, solution density ( $\rho$ ) and speed of sound ( $u$ ).  
 [Temp.: 35 °C; Expt pressure  $p = 0.1$  MPa]

NaCl (mol·kg <sup>-1</sup> )	CaSO <sub>4</sub> (mol·kg <sup>-1</sup> )	$\rho$ (kg·m <sup>-3</sup> )	$u$ (m·s <sup>-1</sup> )	NaCl (mol·kg <sup>-1</sup> )	CaSO <sub>4</sub> (mol·kg <sup>-1</sup> )	$\rho$ (kg·m <sup>-3</sup> )	$u$ (m·s <sup>-1</sup> )
5% Ethanolamine (EA)				10% Ethanolamine (EA)			
0	0.0113	1005.12	1545.7	0	0.0150	1014.8	1560.7
0.6211	0.0250	1030.77	1580.8	0.9099	0.0322	1043.9	1615.8
1.0519	0.0307	1042.91	1603.2	1.6628	0.0427	1073.1	1650.2
1.6027	0.0388	1065.89	1630.7	2.1436	0.0480	1091.9	1675.7
2.2038	0.0428	1087.31	1660.5	2.5844	0.0504	1108.7	1695.5
2.5545	0.0447	1101.45	1681.4	2.9650	0.0527	1122.0	1716.4
3.1555	0.0464	1120.76	1709.8	3.5661	0.0532	1141.0	1744.8
3.5060	0.0466	1134.57	1727.2	3.9868	0.0533	1158.9	1762.2
4.0068	0.0455	1152.74	1751.3	4.2931	0.0528	1168.1	1786.3
4.6078	0.0437	1173.48	1779.2	4.6063	0.0512	1178.9	1806.3
4.9083	0.0420	1184.12	1799.5	4.9452	0.0503	1189.6	1834.5
15% Ethanolamine (EA)				5% Diethanolamine (DEA)			
0	0.0188	1020.6	1578.0	0	0.0188	1002.7	1546.0
0.48683	0.0295	1036.6	1606.0	0.6411	0.0357	1027.0	1581.1
0.95562	0.0366	1053.4	1630.4	1.0818	0.0467	1045.0	1603.9
1.33427	0.0425	1067.4	1650.8	1.5802	0.0526	1062.9	1633.8
2.2065	0.0535	1100.2	1693.8	2.1036	0.0558	1082.6	1658.5
2.66854	0.0559	1116.3	1714.2	2.6044	0.0571	1100.2	1684.5
3.10127	0.0561	1131.9	1743.3	3.0853	0.0570	1119.3	1710.9
3.33567	0.0561	1139.5	1754.8	3.5260	0.0565	1133.7	1730.8
3.87659	0.0552	1158	1785.1	4.0469	0.0549	1149.3	1757.0
4.46257	0.0546	1179.2	1820.6	4.6078	0.0517	1168.5	1779.4
4.96261	0.0536	1196.5	1847.9	4.7557	0.0500	1186.1	1799.9
10% Diethanolamine (DEA)				15% Diethanolamine (DEA)			
0	0.0218	1007.2	1557.5	0	0.0253	1013.2	1580.2
0.4936	0.0341	1030.9	1590.2	0.7820	0.0398	1032.8	1617.8
0.9112	0.0419	1048.0	1612.9	1.2628	0.0470	1049.5	1640.9
1.4237	0.0486	1067.5	1640.7	1.7016	0.0528	1066.7	1666.2
1.8224	0.0531	1084.7	1662.8	2.1236	0.0562	1085.9	1694.4
2.3919	0.0587	1104.1	1691.9	2.6032	0.0593	1101.6	1717.0
2.7341	0.0608	1123.5	1711.7	3.1246	0.0625	1116.5	1750.0
3.2651	0.0606	1134.2	1732.8	3.8279	0.0627	1142.4	1781.3
3.6827	0.0598	1149.1	1755.8	4.2283	0.0621	1150.7	1800.0
4.3830	0.0568	1162.8	1790.2	4.4473	0.0611	1172.6	1815.8
4.6998	0.0547	1186.1	1811.3	4.7690	0.0600	1179.2	1829.2
5% Triethanolamine (TEA)				10% Triethanolamine (TEA)			
0	0.0193	1005.1	1535.07	0	0.0245	1011.5	1550.39
0.9556	0.0554	1030.8	1588.04	0.5305	0.0556	1034.3	1580.61
1.3343	0.0635	1042.9	1610.47	1.0017	0.0698	1054.8	1609.32
1.8391	0.0699	1065.9	1638.17	1.5040	0.0828	1073.1	1637.87
2.2358	0.0753	1087.3	1660.58	1.9639	0.0914	1090.4	1662.37
2.6685	0.0754	1101.5	1682.07	2.4041	0.0996	1110.4	1687.47
3.1013	0.0749	1120.8	1703.56	2.9543	0.1072	1127.2	1718.52
3.3357	0.0729	1134.6	1715.53	3.4397	0.1076	1143.9	1740.32
3.8766	0.0685	1152.7	1749.02	3.9080	0.1079	1163.5	1762.77
4.4626	0.0634	1173.5	1777.71	4.3567	0.1048	1178.9	1785.75
4.8012	0.0563	1184.1	1795.43	5.0085	0.0983	1192.6	1815.64

(Contd)

Table 1 – Solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous hydroxyl alkyl amines-NaCl solutions, solution density ( $\rho$ ) and speed of sound ( $u$ ).  
[Temp.: 35 °C; Expt pressure  $p = 0.1$  MPa]. (Contd.)

NaCl (mol·kg <sup>-1</sup> )	CaSO <sub>4</sub> (mol·kg <sup>-1</sup> )	$\rho$ (kg·m <sup>-3</sup> )	$u$ (m·s <sup>-1</sup> )	NaCl (mol·kg <sup>-1</sup> )	CaSO <sub>4</sub> (mol·kg <sup>-1</sup> )	$\rho$ (kg·m <sup>-3</sup> )	$u$ (m·s <sup>-1</sup> )
15% Triethanolamine (TEA)				No additives (Data from Ref. 22)			
0	0.0314	1018.4	1567.39	0	0.0151	996.1	1521.4
0.4233	0.0574	1038.4	1590.61	0.1796	0.0250	1004.4	1532.6
0.9029	0.0744	1056.6	1619.32	0.3184	0.0295	1010.5	1541.1
1.4425	0.0931	1077.6	1647.87	0.4777	0.0351	1017.4	1550.4
1.8231	0.1002	1093.3	1672.37	0.7754	0.0410	1030.1	1568.0
2.3039	0.1089	1110.9	1696.47	1.1295	0.0462	1042.3	1585.3
2.8048	0.1156	1127.1	1723.52	1.4890	0.0491	1054.4	1603.7
3.2055	0.1204	1145.0	1745.32	2.0024	0.0520	1076.6	1634.1
3.7275	0.1204	1163.0	1772.77	2.5153	0.0529	1094.2	1660.4
4.2068	0.1203	1173.4	1795.75	3.0303	0.0529	1114.2	1688.1
4.6078	0.1192	1191.9	1815.64	3.4906	0.0510	1127.8	1711.3

Table 2 – Parameters ( $A_i$ ) and standard deviations ( $\sigma$ ) of Eq. (1) for the system  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ -NaCl-Water-hydroxyl alkyl amines.  
[Temp.: 35 °C; Expt pressure  $p = 0.1$  MPa]

Organic solvent	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma$
Solubility (mol·kg <sup>-1</sup> )					
5% EA	0.0126	0.0201	-0.0029	-	0.0008
10% EA	0.0153	0.0210	-0.0029	-	0.0005
15% EA	0.0195	0.0210	-0.0029	-	0.0010
5% DEA	0.0099	0.0282	-0.0085	0.0008	0.0007
10% DEA	-0.0002	0.0016	0.0002	-	0.0002
15% DEA	0.0007	0.0021	-0.0004	-	0.0002
5% TEA	0.0226	0.0371	-0.0064	-	0.0020
10% TEA	0.0290	0.0447	-0.0062	-	0.0020
15% TEA	0.0356	0.0470	-0.0064	-	0.0019
Density, $\rho$ (kg·m <sup>-3</sup> )					
5% EA	1001.53	32.74	-	-	2.67
10% EA	1014.11	35.87	-	-	1.05
15% EA	1020.17	35.70	-	-	0.48
5% DEA	1003.94	36.88	-	-	1.91
10% DEA	1017.73	35.40	-	-	3.55
15% DEA	1008.04	35.42	-	-	2.60
5% TEA	997.29	39.46	-	-	2.91
10% TEA	1016.70	36.82	-	-	2.30
15% TEA	1023.00	37.04	-	-	1.72
Speed of sound, $u$ (m·s <sup>-1</sup> )					
5% EA	1521.7	55.8	-	-	4.5
10% EA	1561.6	52.8	-	-	3.8
15% EA	1577.4	53.8	-	-	1.8
5% DEA	1548.6	51.8	-	-	2.1
10% DEA	1583.4	48.4	-	-	5.7
15% DEA	1579.7	49.9	-	-	4.1
5% TEA	1535.5	55.2	-	-	3.7
10% TEA	1568.2	50.8	-	-	3.4
15% TEA	1570.0	54.1	-	-	1.4
Isentropic compressibility $10^{12} \times \kappa_s$ (Pa <sup>-1</sup> )					
5% EA	414.98	-42.05	2.23	-	0.9
10% EA	419.39	-33.97	0.52	-	1.8
15% EA	387.84	-35.39	1.82	-	2.0
5% DEA	416.34	-43.15	2.35	-	1.6
10% DEA	402.48	-46.88	3.61	-	2.4
15% DEA	394.10	-34.17	1.09	-	3.0
5% TEA	421.47	-41.81	1.64	-	3.4
10% TEA	405.41	-45.77	3.16	-	0.8
15% TEA	398.96	-43.85	2.76	-	0.6

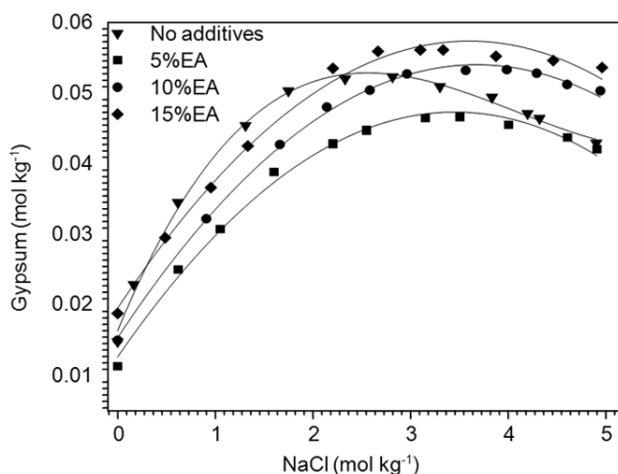


Fig. 1 – Comparison of solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 308.15 K in aqueous NaCl-solutions containing ( $\blacktriangledown$ ) 0, ( $\blacksquare$ ) 5%, ( $\bullet$ ) 10% and ( $\blacklozenge$ ) 15% ethanolamine (EA). [Lines are polynomial fit to the experimental data. Data for no additives is plotted from Ref. 22].

The density ( $\rho$ ) and speed of sound ( $u$ ) values for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{NaCl} + \text{H}_2\text{O} + \text{hydroxyl alkyl amines}$  systems at 35 °C as a function of NaCl concentration are plotted in Fig. 4. Both,  $\rho$  and  $u$  increase linearly with increase in electrolyte concentration in the solution. The nature of aqueous-hydroxyl alkyl amine medium also influenced the physical properties. The solutions containing hydroxyl alkyl amine were found denser than water at any given NaCl concentration and the solutions became denser with the increase of organic solvent concentration. The density of the solutions was in the order: TEA > DEA > EA. This is according to the concentration of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in the corresponding solutions and also due to the nature of the organic solvent. The speed of sound ( $u$ ) was found maximum in TEA containing solutions, and least in EA containing solutions. With increase in electrolyte concentration in the solutions,  $u$  increased almost linearly. The composition dependence of  $\rho$  and  $u$  has been fitted to Eq. 2. The parameters  $A_i$  along with the standard deviations  $\sigma$  are given in Table 2.

The solution isentropic compressibility  $\kappa_S$  has been derived from the  $u$  and  $\rho$  values, assuming negligible ultrasonic absorption under the experimental conditions by using the Newton-Laplace equation.

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

Figure 5 shows the comparison of  $\kappa_S$  of the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{NaCl} + \text{H}_2\text{O} + \text{hydroxyl alkyl amine}$

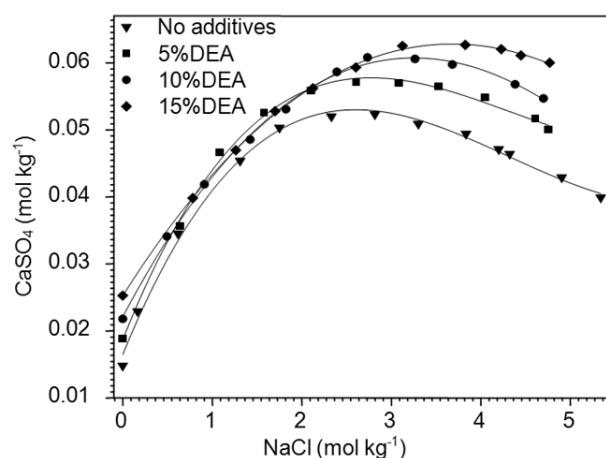


Fig. 2 – Comparison of solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 308.15 K in aqueous NaCl-solutions containing ( $\blacktriangledown$ ) 0, ( $\blacksquare$ ) 5%, ( $\bullet$ ) 10% and ( $\blacklozenge$ ) 15% diethanolamine (DEA). [Lines are polynomial fit to the experimental data. Data for no additives is plotted from Ref. 22].

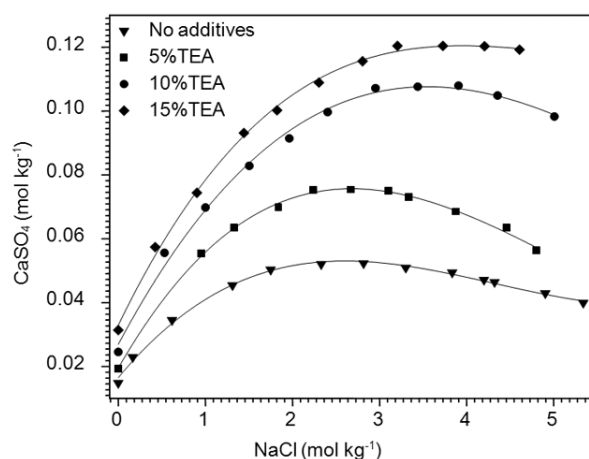


Fig. 3 – Comparison of solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 308.15 K in aqueous NaCl-solutions containing ( $\blacktriangledown$ ) 0, ( $\blacksquare$ ) 5%, ( $\bullet$ ) 10% and ( $\blacklozenge$ ) 15% triethanolamine (TEA). [Lines are polynomial fit to the experimental data. Solubility data in absence of additives is plotted from Ref. 22].

systems. The composition dependence of  $\kappa_S$  has been fitted to Eq. 2, and the parameters and standard deviations are provided in Table 2. The solution compressibility was found to decrease with the addition of hydroxyl alkyl amines and followed the order: TEA < DEA < EA. Decrease in solution compressibility is normally due to breaking of the network structure of water which results in a more compact solution state. Packing efficiency of unlike molecules as a consequence of specific geometries and nature of hydrogen bonding of hydroxyl alkyl

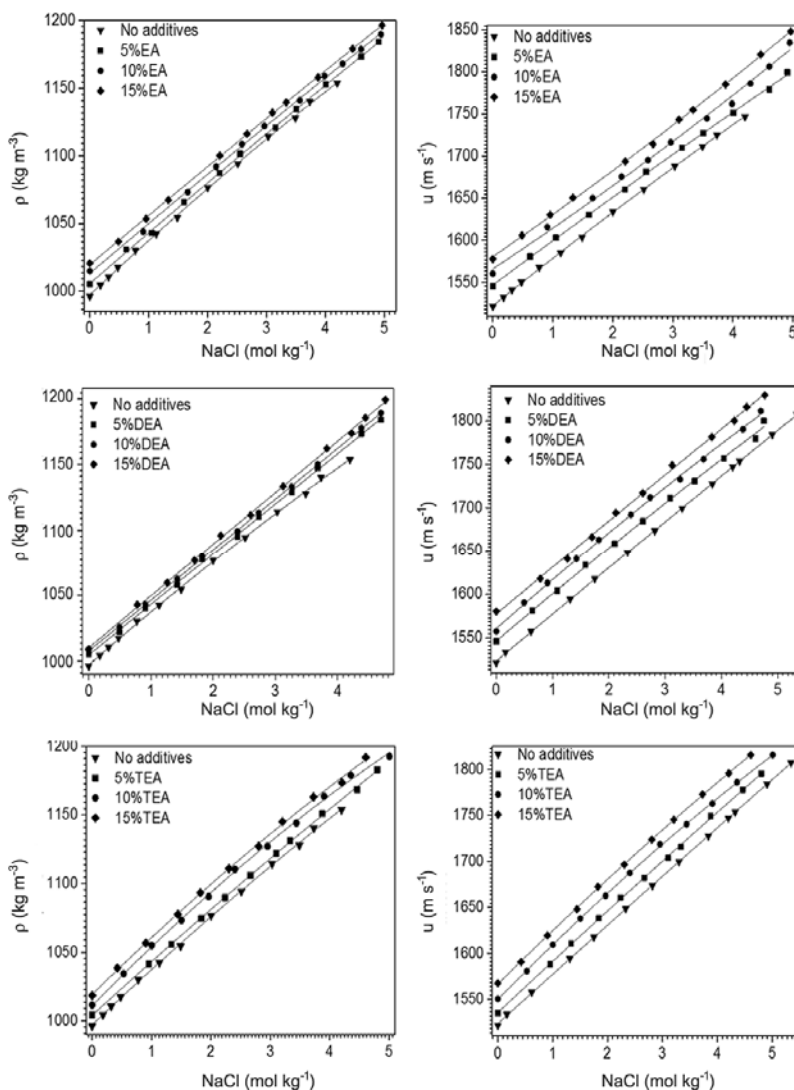


Fig. 4 – Density (left) and speed of sound (right) data of aqueous-NaCl solutions saturated with  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and containing (■) 5%, (●) 10% and (▲) 15% ethanolamine (EA), diethanolamine (DEA) and triethanolamine (TEA) at 308.15 K. [Lines are linear fit to the experimental data. Density data in absence of additives is plotted from Ref. 22].

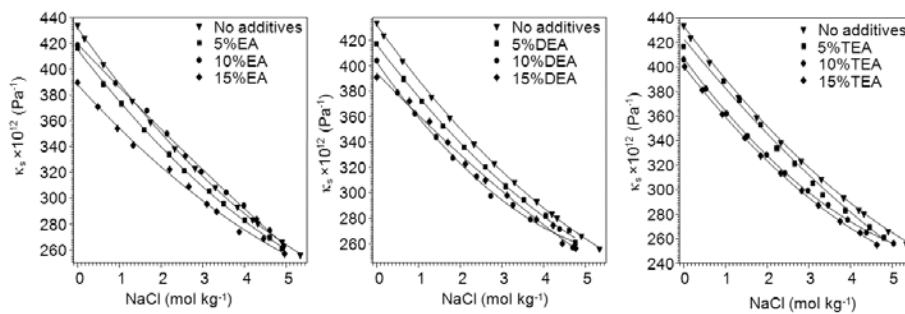


Fig. 5 – Isentropic compressibility of aqueous NaCl solutions saturated with  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  having ethanolamine (EA), diethanolamine (DEA) and triethanolamine (TEA) at 308.15 K. [Lines are polynomial fit to the experimental data. Isentropic compressibility data in absence of additives is plotted from Ref. 22].

amines with water also contributes to the changes in solution compressibility. Further, the compressibility of solutions containing electrolytes comprises configurational and vibrational effects where the configurational effect plays a major role in dilute solutions.<sup>36</sup> Compression of the hydration shell of the ions largely contributes to the isentropic compressibility in the concentrated solutions.

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