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Technical Note

Sulfate solubility algorithms for $CaSO_4$–NaCl–H_2O and Na_2SO_4–NaCl–H_2O in chlor alkali brine at 25, 65, 75 and 85 °C

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1. Introduction

Acting as a nonmetallic impurity in brine systems, the sulfate ion SO_4^{2-} forms complexes with numerous possible bonding modes, but normally acts as a spectator ion. Under certain conditions of temperature, concentration, or in the presence of certain nongroup IA cations in a chlorine cell, the sulfate ion can interact indirectly with electrodes, separators, cell bodies and ancillary process equipment. Sulfates can, therefore, have a detrimental effect on the cell performance, operating conditions and overall economics for all three of the current commercial chlor-alkali processes. At critical concentrations, the sulfate anion can effectively alter the kinetics of chlorine evolution at the metaloxide anodes (dimensionally stable anodes, DSA). This can occur by sulfate excluding chloride ions from the diffusion layer (mass transfer layer) at the anode surface and thereby lowering the oxygen overpotential enough to provide more oxygen from water electrolysis and lower surface pH, resulting in much greater anode wear. The sulfate anion can also facilitate the transport of multivalent cations to mercury cathodes and thereby produce mercury butter as an intractable alloy in mercury cells, or form hard crystal lattices within membranes to disrupt separator continuity in membrane cells or plug diaphragms in diaphragm cells. These effects can all be traced back to the solubility and concentration parameters for the sulfate anion in the brine media, thus making the precise knowledge of these parameters of paramount importance for the chlor-alkali process engineer and plant chemist [1–5].

This work provides accurate and correct data and algorithms for the solubility of sodium sulfate and calcium sulfate in a chlor-alkali brine system as a function of temperature and in the proper concentration and temperature ranges of interest to the chlor-alkali producers. The regressed experimental data, presented in the form of graphs and equations, can be used in actual process control and operations, as well as in the laboratory to predict and control the sulfate levels in brine systems. Using a novel experimental system, this work provides requisite data to give a clear explanation of the solubility relations for calcium sulfate and sodium sulfate in brine. The data shows that temperature has less effect on sulfate solubility than the variation in the sodium chloride concentrations of the brine [6–8]. This increased solubility of the calcium sulfate crystals with sodium chloride concentration appears to occur because of the effect of the increased coulomb forces from dissolved Na^+ and Cl^- ions on the $CaSO_4$ crystals as follows:

$$\begin{aligned}&CaSO_4(s) + Na^+(aq) + Cl^-(aq)\\ &\quad \Rightarrow [NaSO_4]^-(aq) + [CaCl]^+(aq)\end{aligned} \tag{1}$$

2. Experimental details

2.1. *Equipment and method*

The laboratory method in these studies employed a novel isothermal solution-filter system to keep all solutions involved in the run at constant temperature at all times, as shown in Figure 1. Actual plant brine was used. At the beginning of each run the sample was blended in a two-litre beaker stationed in position 1 in the electrically heated constant temperature bath and stirred with a mechanical stirrer through an insulated Teflon lid until the solution reached constant temperature. The preheated sample was then moved to position 2 where it was again stirred vigorously for 20 min to ensure constant-temperature dissolution of the sulfate salts in the brine. While still stirring, a 150 ml sample was removed and then immediately put through the jacketed funnel at position 3 and held at constant temperature as the bath by circulation of the bath

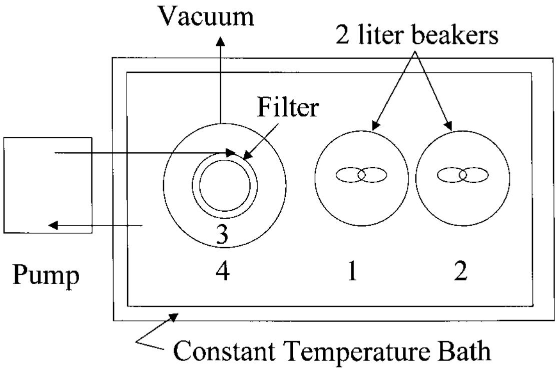

Fig. 1. Top view of isothermal solution system.

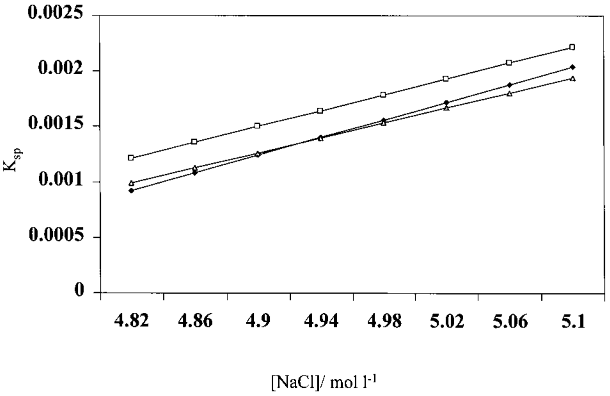

Fig. 2. Calcium sulfate solubility product. Temperature: (●) 25, (□) 75 and (△) 85 °C.

solution through the funnel. The sample was finally collected in the one litre collection vacuum flask in position 4 after filtration. All dissolved material that is soluble and in solution at that temperature and concentration passes through the no. 40 filter paper as well as the coarse fritted glass funnel and is collected in the flask.

2.2. *Analytical procedure*

During the analytical procedure, the samples in 100 ml aliquots were taken from the vacuum flask (4 in Figure 1) diluted immediately with 400 ml of deionized water to prevent precipitation of solids prior to analysis. The metals were then determined in the solution using inductively coupled plasma spectrometry and the sulfate determined by wet gravimetric analysis with barium chloride.

3. Results and discussion

The present studies provide critical solubility data for sodium and calcium sulfate in brine versus temperature and concentration. The sodium sulfate is very soluble in brine and will displace a portion of the sodium chloride from solution, while the calcium sulfate is only slightly soluble in the brine, with a maximum in the range of 5.5 g l^{-1}. Calcium sulfate has an equilibrium constant called the solubility product constant, K_{sp}, which is defined as

$$[Ca^{2+}][SO_4^{2-}] = kK_{ma} = K_{sp} \tag{2}$$

In this equation $[Ca^{2+}]$ and $[SO_4^{2-}]$ represent the molar concentrations of calcium and sulfate ions in solution, with CaSO4(s) the solid phase is given an activity of one.

Exploring the solubility product constant from the data in Table 1, as plotted in Figure 2, we acquire the data to establish the relation ship needed to connect these two variables at three different temperatures, with $[Ca^{2+}]$ and $[SO_4^{2-}]$ given in mol l^{-1}, as follows:

At 25 °C with $R^2 = 99.4\%$

$$[Ca^{2+}] = 0.000\,249\ [SO_4^{2-}]^{-2.579} \tag{3}$$

At 75 °C with $R^2 = 98\%$

$$[Ca^{2+}] = 0.000\,276\ [SO_4^{2-}]^{-2.444} \tag{4}$$

Table 1. Calcium sulfate solubility product in brine at 25, 75, and 85 °C

Run at 25 °C		Run at 75 °C		Run at 85 °C	
[NaCl]/mol l^{-1}	K_{sp}	[NaCl]/mol l^{-1}	K_{sp}	[NaCl]/mol l^{-1}	K_{sp}
4.99	0.00177	4.97	0.00177	5.1	0.00182
4.86	0.00162	4.88	0.00158	4.93	0.00165
4.89	0.00145	4.83	0.00143	4.99	0.00151
4.82	0.0013	4.87	0.00126	4.94	0.0016
4.87	0.00115	4.82	0.00114	4.95	0.00127
4.86	0.0011	4.85	0.00116	4.97	0.00114
4.84	0.00102	4.77	0.00094	4.88	0.00097
4.82	0.0009	4.75	0.00092	4.84	0.00097

Table 2. Sodium sulfate to augusta brine against temperature

Run at 25 °C		Run at 65 °C		Run at 75 °C		Run at 85 °C	
NaCl /g l^{-1}	Na_2SO_4 /g l^{-1}	NaCl /g l^{-1}	Na_2SO_4 /g l^{-1}	NaCl /g l^{-1}	Na_2SO_4 /g l^{-1}	NaCl /g l^{-1}	Na_2SO_4 /g l^{-1}
298	27.5	290.8	27.5	287.8	27.7	295.3	18.9
300	37.1	285.9	36.7	296.7	39.0	309.5	26.9
297	48.5	289.9	48.1	293.4	49.1	307.8	33.5
295	52.4	278.6	55.8	285.9	58.2	302.2	40.5
295	54.2	285.8	62.3	284.5	63.2	297.0	38.5
291	55.2	284.2	63.8	285.6	63.4	293.7	40.4
294	57.5	285.9	64.0	284.6	62.4	292.4	41.8
291	70.9	280.3	64.2	285.2	61.4	290.1	41.1
283	87.7						
282	93.6						

At 85 °C with $R^2 = 85\%$

$$[Ca^{2+}] = 0.0108 - 0.01948\,[SO_4^{2-}] \tag{5}$$

The solubility product can now be determined from the data in Table 1 for each different value of salt concentration in the brine, with NaCl concentrations in mol l^{-1}:

At 25 °C with $R^2 = 56\%$

$$K_{sp} = -0.01836 + 0.004\,[NaCl] \tag{6}$$

At 65 °C with $R^2 = 69\%$

$$K_{sp} = -0.01614 + 0.0036\,[NaCl] \tag{7}$$

At 85 °C with $R^2 = 86\%$

$$K_{sp} = -0.0154 + 0.0034\,[NaCl] \tag{8}$$

When the K_{sp} values for calcium sulfate in brine (Equations 6, 7, and 8), are set equal to zero, and then solved for [NaCl], the average value is 4.534 mol l^{-1} (265.24 g l^{-1}) in [NaCl] in all three cases. This provides a limiting case in [NaCl] for the brine system. Operating above 4.534 mol l^{-1} in sodium chloride concentration avoids precipitating $CaSO_4$ in the brine system when sufficient calcium and sulfate are available, shown in Table 1, and graphically in a linear format in Figure 2.

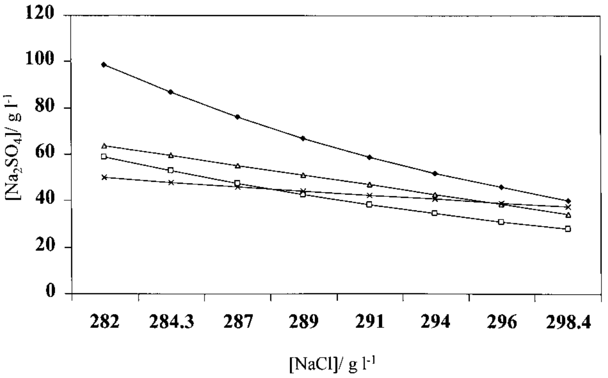

Fig. 3. Sodium sulfate in brine against temperature. Temperature: (♦) 25, (□) 65, (△) 75 and (×) 85 °C.

The data defining the relationship between sodium chloride and sodium sulfate concentrations at various temperatures are shown in Table 2 and Figure 3 for temperatures 25, 65, 75 and 85 °C. Equations 9–11 and 12 define the temperature concentration profiles for the sodium sulfate sodium chloride brine, with (Na_2SO_4) and (NaCl) concentrations given in g l^{-1}:

At 25 °C with $R^2 = 98.7\%$

$$(Na_2SO_4) = 940 - 3\,(NaCl) \tag{9}$$

At 65 °C with $R^2 = 60.4\%$

$$(Na_2SO_4) = 728 - 2.4\,(NaCl) \tag{10}$$

At 75 °C with $R^2 = 53\%$

$$(Na_2SO_4) = 649 - 2.1(NaCl) \tag{11}$$

At 85 °C with $R^2 = 65\%$

$$(Na_2SO_4) = 231 - 0.65\,(NaCl) \tag{12}$$

Thus the present studies provide critical solubility data against concentration and temperature for calcium sulfate and sodium sulfate in brine against temperature.

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