Sulfonate Precipitation-Redissolution-Reprecipitation

In Inorganic Electrolytes

EXTENDED ABSTRACT
\[(C_{Ca}^{++} - x)(C_{R}^- - 2x)^2 = K_{sp} \]  

(1)

where \(K_{sp}\) is the solubility product of the calcium disulfonate, \(C_{Ca}^{++}\) and \(C_{R}^-\) represent the initial concentration of \(Ca^{++}\) and \(Ca_R\) sulfonate in the system and \(x\) is the number of kilomoles of \(CaR_2\) formed per m\(^3\).

A maximum in precipitation is obtained at all \(CaCl_2\) levels at sulfonate concentrations corresponding to the CMC of the system (Figures 1 and 2).

Since the onset of redissolution corresponds to CMC, difference between the sulfonate concentrations corresponding to the complete redissolution and those corresponding to the onset of redissolution \((C_{CR} - C_{OR})\) is proportional to the concentration of micelles in solution and the amount of precipitates redissolved is proportional to this concentration of micelles.

On the basis of the premise that precipitation is due to the formation of calcium disulfonate and redissolution is due to micellar redissolution the dependence of the precipitation as a function of the residual sulfonate concentration was calculated using the experimentally determined values for the solubility products, CMC and sulfonate concentrations for complete redissolution. The results obtained from the sulfonate and calcium analysis are in good agreement with the predicted
values supporting the proposed mechanism of the precipitation-redissolution phenomenon. (See Figures 1 and 2.

The effect of NaCl on precipitation-redissolution of sodium dodecylbenzenesulfonate and sodium dodecylsulfonate with CaCl₂ was also studied in a wide range of NaCl concentrations (up to 2 kmol/m³) at different surfactant and CaCl₂ levels. It was found that addition of NaCl up to 0.5 kmol/m³ to NaDDBS/CaCl₂ system and up to 1.0 kmol/m³ to NaDDS/CaCl₂ system increased redissolution. (See Figures 3 and 4.)

This effect is explained on the basis of the proposed mechanism. If the redissolution is due to micellar solubilization then the addition of NaCl, which lowers CMC, should cause the redissolution of the precipitates in the micelles formed now at a lower residual concentration of sulfonate. It might be noted that there is some redissolution of the calcium precipitates at even lower concentrations than CMC in apparent contradiction with the micellar solubilization mechanism. This can however be resolved by taking into account the effect of the increased ionic strength of the medium on the activities of the species in the system.

If activities are substituted for concentrations in the solubility product equation, we obtain

\[ C_{\text{Ca}^{++}} \cdot C_R \gamma_{\text{Ca}^{++}} \gamma_{R^-}^2 = \frac{K_{\text{sp}}}{\gamma_{\text{Ca}^{++}} \gamma_{R^-}} \] (2)
where \( a_{\text{Ca}^{++}} \) and \( a_{\text{R}} \) are activities, \( \gamma_{\text{Ca}^{++}} \) and \( \gamma_{\text{R}} \) are activity coefficients and \( C_{\text{Ca}^{++}} \) and \( C_{\text{R}} \) are residual concentrations of the respective species. When NaCl is added to the system, activity coefficients decrease due to the increase in the ionic strength. According to equation 2) this results in an increase of the calcium disulfonate concentration product and, consequently, in an apparent redissolution of the precipitates at residual sulfonate concentration lower than CMC. If activities, instead of the residual concentrations, are plotted as a function of NaCl concentrations the apparent discrepancy in the redissolution of the calcium disulfonate below CMC is eliminated (6).

At higher NaCl concentrations (above 0.5 kmol/m\(^3\) in NaDDBS/CaCl\(_2\) and above 1.0 kmol/m\(^3\) in NaDDS/CaCl\(_2\) systems) reprecipitation occurs with little dependence on the concentration CaCl\(_2\) in the system. Another interesting feature of this phenomenon is that in the reprecipitation region there is no measurable depletion of calcium from the solution even up to 2 kmol/m\(^3\) NaCl (Figure 5).

**CONCLUSIONS**

The precipitation-redissolution-reprecipitation phenomenon in CaCl\(_2\)/NaCl sulfonate systems was studied in detail as a function of CaCl\(_2\) and NaCl employing various techniques.
Precipitation of Na-dodecylbenzenesulfonate and Na-dodecylsulfonate was monitored by light transmission measurements and the equilibrium sulfonate and Ca\(^{++}\) concentrations were determined by chemical analysis. Critical micelle concentrations of the sulfonate solutions determined as a function of ionic strength were correlated with the precipitation/redissolution data in order to elucidate the role of solubilization by micelles in causing precipitate-redissolution.

Analysis of the data obtained during this study suggests the precipitation to be due to the formation of calcium disulfonate and redissolution to be due to micellar solubilization of the precipitates. The observed effect of the increase in ionic strength on redissolution supports the above mechanism.

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REFERENCES


Figure 1. Comparison of theoretical and experimental results for NaDDS precipitation.
Figure 2. Diagram illustrating precipitation/redissolution of NaDDBS at various CaCl₂ levels.
Figure 3. Effect of NaCl additions on calcium dodecylsulfonate precipitate redissolution.
Figure 4. Effect of NaCl additions on calcium dodecylbenzenesulfonate precipitate redissolution at different CaCl$_2$ levels.
Figure 5. Residual sulfonate and calcium concentrations in NaDDBS/CaCl$_2$/NaCl system.