Precipitation of Surfactant Salts:
The Effect of Counterion Exchange on Micelles

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The solubility of alkaline earth salts of dodecylsulfate in concentrations exceeding the critical micellar concentration (CMC) of the surfactant have been analyzed. A quantitative description of the precipitation boundary can be obtained by taking into consideration the solubility product and the CMC dependence on the electrolyte content, as well as the counterion exchange on the micelle. The latter was accounted for by the separation factor which was found to be independent of the electrolyte concentration and similar in value for the exchange of all four alkaline earth ions with sodium.

It has been shown that the solubility boundary of salts of ionic surfactants in aqueous solutions is greatly affected by the excess of long chain anions.[1-14] In the absence of micelles, the interpretation of data, based on the solubility product alone (defined in terms of activities of the precipitating ions), is applicable. Above the critical micellar concentration (CMC) the solubility increases appreciably, because a fraction of anions is associated. In addition, the micelles bind a certain amount of counterions further affecting the solubility of the surfactant salt. For these reasons, the precipitation in such systems resembles phenomena observed with inorganic salts when interacting ions form solute complexes. It was shown earlier[8-14] that the solubility boundaries can be explained, in principle, if the counterion binding by micelles is taken into account. In the presence of more than one kind of cation, one of which is the precipitating ion, it is necessary to consider their selective association with the micelles.

This study analyzes the precipitation of alkaline earth salts of dodecylsulfate in the presence of sodium ions. As such, the work represents an extension of the phenomenological approach to micellization, counterion binding, and solid phase formation in surfactant salt systems.[8,14]

Theoretical

The interpretation of precipitation phenomena in solutions of ionic surfactant in the presence of micelles is based on the following relationships.

(1) Solubility product

$$K_s^\circ = a_{M^{2+}} \, a_{DS^-}^2 = y^6 \, c_{M^{2+}} \, c_{DS^-},\tag{1}$$

where $a_{M^{2+}}$ and a_{DS^-} are the activities of alkaline earth cations and dodecylsulfate anion, respectively, and c represents the corresponding concentrations. The activity coefficient y for the monovalent ion is given by

$$-\log y = A \, I^{1/2} / (1 + I^{1/2}).\tag{2}$$

I is the ionic strength and for aqueous solutions at 20 °C, $A = 0.509$. Note that the activity coefficient for divalent ions is y^4.

(2) Critical micellization concentration

The effect of divalent counterions on the CMC obeys the following empirical relationship.[15-17]

$$CMC = \beta \, [M(NO_3)_2]^{-b} = c_{DS^-},\qquad(3)$$

where β and b are constants. Thus, the concentration of DS⁻ ions in solutions containing micelles is equal to the CMC.

(3) Separation factor

If the exchange of sodium for alkaline earth cations at the micelles is approached phenomenologically, the ion exchange equilibrium can be expressed in terms of the separation factor α.[1,9]

$$\alpha = \frac{x}{1-x} \cdot \frac{a_{Na^+}}{a_{M^{2+}}},\qquad(4)$$

where x is the fraction of surfactant ions in the micelle neutralized by alkaline earth counterions.

(4) Mass balances

For the system prepared by mixing NaDS with $M(NO_3)_2$ solutions, the total concentration of NaDS at the solubility boundary is given by:

$$[NaDS] = c_{DS^-} + c_{DS^-,m},\qquad(5)$$

where $c_{DS^-,m}$ is the concentration of the DS⁻ anions in the micellar form. Total concentration of the alkaline earth nitrate is:

$$[M(NO_3)_2] = c_{M^{2+}} + \frac{x}{2} c_{DS^-,m}.\qquad(6)$$

The concentration of sodium ions is calculated from

$$c_{Na^+} = [NaDS] - (1-x) c_{DS^-,m}.\qquad(7)$$

The ionic strength is calculated from the equilibrium concentrations of all free ionic species. A combination of the above expressions yields

258

$$\alpha = xy^3 c_{DS^-}^2 \, \{[NaDS] - (1-x) \\ ([NaDS] - c_{DS^-})\} \, / \, \{K_S^\circ (1-x)\}\qquad(8)$$

where $x = \dfrac{([M(NO_3)_2] - K_S^\circ \, y^{-6} \, c_{DS^-}^{-2})}{[NaDS] - c_{DS^-}}$ and (9)

y and c_{DS^-} are computed from eqs. (2) and (3). The ionic strength is given by

$$I = [M(NO_3)_2] + 2K_S^\circ \, y^{-6} \, c_{DS^-}^{-2} + \tfrac{1}{2} \, \{[NaDS] \\ - (1-x) \, ([NaDS] - c_{DS^-}) + c_{DS^-}\}.\qquad(10)$$

The value of K_S° is computed from the solubility data below the CMC, while constants b and β are attained from the measured CMC as a function of the concentration of $M(NO_3)_2$, eq. (3). For each experimental point corresponding to the solubility boundary above the CMC (i.e., for each pair of $M(NO_3)_2$ and NaDS concentrations), the separation factor, α, is then calculated by the iteration procedure.

Results

The solubility data for Mg^{2+}, Ca^{2+}, Sr^{2+} salts of dodecylsulfate were used from earlier work.[7] Additional measurements were carried out with the $Ca(NO_3)_2$/NaDS system to extend the solubility boundary to lower concentrations of $Ca(NO_3)_2$, and to gain more data points. The latter improved the accuracy which was necessary to test the validity of formulations.

The upper part of Fig. 1 shows that the separation factor, α, is indeed constant at $Ca(NO_3)_2$ concentrations varied over three orders of magnitude. The squares, calculated from the new measurements, agree well with the previous data but show less scatter. In calculation of α, the values $K_S^\circ = 2.14 \times 10^{-10}$, $b = 0.23$, and $\beta = 8 \times 10^{-4}$ were used.[14] The solid line in the same part of the figure gives x as a function of the $Ca(NO_3)_2$ concentration. Over the solubility range investigated, the fraction of Ca^{2+} bound to micelles shows a small maximum. The average value of this fraction ($\sim 16\%$) is in reasonable agreement with the previous estimate, when x was taken to be invariant. The maximum in x can be understood if one considers the concentration of free Na^+ and Ca^{2+} ions given by dotted lines. At the lowest $Ca(NO_3)_2$ concentrations, the fraction of Ca^{2+} on the micelles is rather small due to the relatively high Na^+ content. As the addition of $Ca(NO_3)_2$ increases, its share in neutralizing the
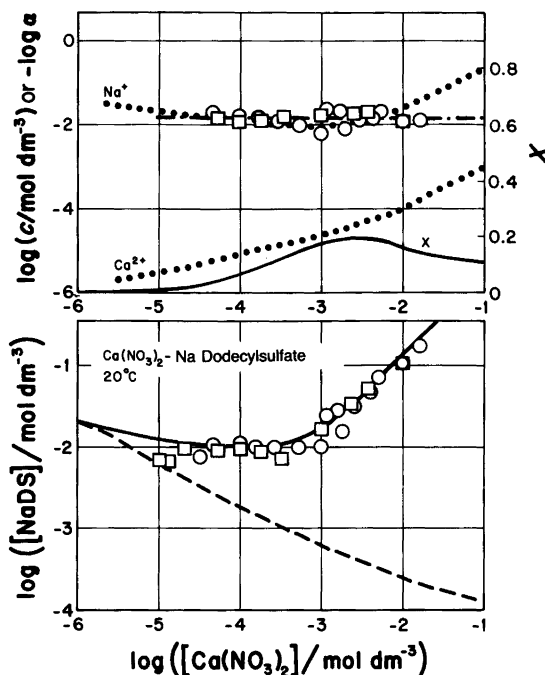
Fig. 1. Lower: precipitation boundary of calcium dodecylsulfate for the system Ca(NO₃)₂/NaDS at 20 °C, above the CMC. Circles were taken from Ref. 7 whereas squares represent newly established data. Solid line was calculated using derived expressions and the values given in Table 1. Dashed line was calculated from the solubility product alone in the absence of any ionic associations.
Upper: circles and squares designate the separation factor α, calculated from the corresponding experimental data. The fraction of micellar charge compensated by Ca^{2+} counterions (x) is shown by the full line. Dotted lines give the concentrations of free Na^+ and Ca^{2+} ions, respectively, all as a function of the total Ca(NO₃)₂ concentration.
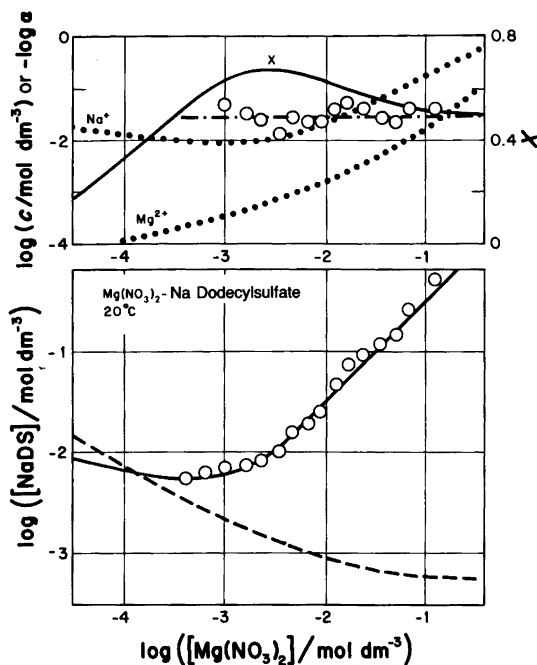

Fig. 2. The same plots as in Fig. 1 for the system Mg(NO₃)₂/NaDS.

The same analysis was carried out for systems containing Mg^{2+}, Sr^{2+}, and Ba^{2+} ions instead of Ca^{2+}. Only data for the Mg(NO₃)₂/NaDS system are reproduced in Fig. 2 which represents analogous plots to Fig. 1. The value of α is again constant within experimental error at concentrations of Mg(NO₃)₂ between 10^{-3} and 10^{-1} mol dm^{-3}.

The fraction of the charge of the micelle compensated by the Mg^{2+} counterion (x) is ~55 %

surfactant charge on the micelles rises. At the highest contents of both cations, the activity coefficient effects cause x to decrease again.

The lower part of Fig. 1 shows the old and new solubility data in the presence of micelles, while the solid line is calculated using the mean value of α, and all other constants given above. The dashed line represents the solubility boundary below the CMC. At [Ca(NO₃)₂] > 10^{-3} mol dm^{-3} the slope of the solid line is equal to unity while below this concentration the solubility remains essentially constant.

Table 1. Quantities for the precipitation, micellization, and ion exchange of alkaline earth/sodium ions in the system M(NO₃)₂/NaDS.

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$-\log K_s^\circ$	8.51	9.67	9.79	11.47
β	8×10^{-4}	8×10^{-4}	8×10^{-4}	(8×10^{-4})
b	0.23	0.23	0.23	(0.23)
$\log \alpha$	1.5	1.8	1.4	≈ 2

Values for K_s°, β, and b are from Ref. 14. The value of α for Ba^{2+} was estimated, since the values of β and b were not known with certainty.

259

over the precipitation range investigated. The x dependence on $[Mg(NO_3)_2]$ again shows a maximum which can be interpreted in terms of Na^+ and Mg^{2+} concentrations in the solution bulk.

The summary of the constants, characteristic of the four alkaline earth dodecylsulfate salts in the presence of sodium ions, is given in Table 1.

Discussion

Unusual solubility phenomena of metal salts of surfactants have been interpreted in terms of micelle formation, either by taking a phenomenological approach[8,14] or by applying a thermodynamic model.[18] Systems of alkaline earth/sodium dodecylsulfate can be reasonably well explained when counterion binding by micelles is taken into consideration.

In this study, the understanding of the solid phase formation in the presence of micelles has been further advanced by introducing the counterion separation factor in the exchange of the sodium for alkaline earth ions, that are involved in the neutralization of the micellar charge. Previously,[8] the interpretation was based on the evaluation of the fraction of the micellar charge compensated by the divalent counterions (x). The value of this quantity depends greatly on the system; e.g., in the sparingly soluble $Ba(DS)_2$, $x \approx 0.02$ due to the low Ba^{2+} concentration. In contrast, in the case of the more soluble $Mg(DS)_2$, $x = 0.56$. It is also recognized that x is not a constant quantity over the entire precipitation boundary.

The separation factor, α, takes into account the difference in the affinity of Na^+ and alkaline earth ions for the surfactant micelles, and as such, is a parameter which characterizes the ion exchange properties of the system. Although theoretically, α is not necessarily a constant,[19] in the systems studied the values were independent of the concentration parameters. Obviously, α is a meaningful quantity for the elucidation of precipitation effects of surfactant salts in the presence of micelles. It is likely that similar values of α would apply to other surfactants with the same type of head groups. In the absence of specific interactions, α should also be independent of counterions, as long as the charge is the same as was the case in the investigated systems.

This analysis of precipitation boundaries of surfactant salts shows that the rather complex phenomena can now be understood if sufficiently detailed account of micellar interactions with counterions, for a system of a given solubility, is taken into consideration. In principle, it is now possible to predict reasonably well the precipitation domain of a surfactant salt from the solubility ionic product and the CMC assuming that α is known for a given counterion pair.

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