

Surfactant Precipitation in Aqueous Solutions Containing Mixtures of Anionic and Nonionic Surfactants

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The salinity tolerance (precipitation phase boundary) is measured for a mixed anionic/nonionic surfactant system above the CMC. For any total surfactant concentration, the salinity tolerance is shown to increase as the percentage of nonionic surfactant in the system is increased. A model is developed which can predict the phase boundaries for the mixed surfactant system from the pure anionic surfactant phase boundary and information about mixed micelle formation. In the model, precipitation is viewed as a solubility product relationship between the anionic surfactant monomer and the total unassociated counterion. The reason that salinity tolerance (or counterion concentration necessary to cause precipitation) increases with addition of nonionic surfactant is that mixed micelle formation reduces the anionic surfactant monomer concentration. For the experimental studies, sodium dodecyl sulfate is the anionic surfactant, a polyethoxylated nonylphenol is the nonionic surfactant, and sodium chloride is the added salt.

The precipitation of ionic surfactants can limit the effectiveness of detergent formulations in a number of applications. This is of special concern in aqueous environments with high salinities and/or high levels of hardness (multivalent ions). For example, builders are often added to household detergents to minimize the effects of hard water. In enhanced oil recovery, surfactant flooding generally cannot be used to effectively recover oil from reservoirs of high salinity or hardness without extensive pre-flushing or other expensive measures.

Salinity and hardness tolerances can be increased for ionic surfactant solutions by the addition of nonionic surfactant. For example, builder can be eliminated from heavy-duty liquid laundry detergent formulations by using mixtures of anionic and nonionic surfactants (1-3). In enhanced oil recovery, mixtures of anionic and nonionic surfactants have been proposed to give the surfactant slug a greater tolerance for both salinity and hardness (4,5).

Despite this great economic and commercial interest in the precipitation behavior of these surfactant mixtures, there has been little published work discussing the underlying reasons for the salinity tolerance enhancement gained by addition of nonionic surfactants to an ionic detergent solution. In this paper, the precipitation phase boundary (salinity tolerance) of a well-defined anionic/nonionic surfactant mixture is measured as a function of surfactant composition. A model is developed which can make a priori predictions of the salinity tolerance for the mixed surfactant system.

EXPERIMENTAL PROCEDURES

Materials. Sodium dodecyl sulfate ($C_{12}SO_4$), Fisher Scientific, was recrystallized twice from a 50/50 mixture of

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water and methanol before drying under vacuum with low heat. The nonionic surfactant [NP(EO)₁₀], trade name Igepal CO-660, GAF Corp., is a polydisperse nonylphenol polyethoxylate with an average of 10 ethylene oxide groups per molecule. The NP(EO)₁₀ was used as received. Both surfactants exhibited the absence of a minima in surface tension curves, and no impurities were observed using High Performance Liquid Chromatography (HPLC) with a conductivity detector for the $C_{12}SO_4$ and a UV detector for the NP(EO)₁₀. The NaCl was Fisher reagent grade and the water was distilled and deionized.

Techniques. A series of solutions, each with the same surfactant concentration and composition, but with varying NaCl concentrations, was prepared in one-liter volumetric flasks to determine salinity tolerance. Experiments showed that these solutions could remain supersaturated for long periods of time; therefore, the solutions were cooled to force precipitation to occur. The solutions were then placed in a water bath kept at 30.0 ± 0.2 C and gently shaken periodically. Crystals in the solutions that were below the precipitation boundary dissolved, so that the lowest concentration of NaCl where crystals remained was taken as a data point on the precipitation phase boundary. Equilibrium was established within seven days for all systems. The presence of precipitate in solutions could be accurately determined visually as the crystals glistened in a high-intensity beam of light.

The composition of the crystals was determined by filtering precipitate from a solution, washing the crystals with cold water and drying them at low heat. These crystals were then dissolved in water and the surfactant concentrations in the resulting solution analyzed using HPLC.

The critical micelle concentration (CMC) for each system of interest was determined from the break in the surface tension vs. $\ln(\text{surfactant concentration})$ curve. A DuNouy ring tensiometer (Central Scientific) with a platinum-iridium ring was used for surface tension measurements. The necessary precautions were taken to maximize accuracy (6). Solutions were allowed to equilibrate at 30 C until the surface tension readings stabilized. Equilibration times ranged from 15 min to 3.5 hr.

THEORY

Consider an aqueous solution containing anionic surfactant, nonionic surfactant, and added monovalent electrolyte. The surfactant concentration is assumed to be above the CMC, as is generally the case in detergency and enhanced oil recovery; therefore, micelles are present. The counterion (cation) contributed by the added electrolyte is assumed to be the same species as that contributed by the anionic surfactant salt upon dissolution. The precipitate that forms is a salt between the anionic surfactant and the counterion. A schematic diagram of this system is shown in Figure 1.

As shown in Figure 1, the anionic surfactant is present

SURFACTANT MIXTURE PRECIPITATION

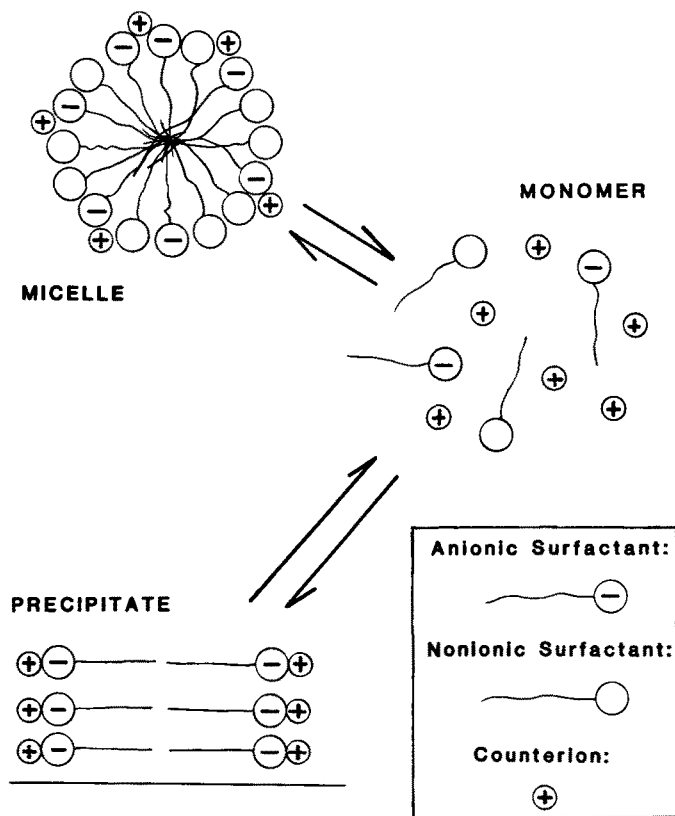


FIG. 1. Schematic diagram of equilibria in system.

in three environments: as monomer (unassociated molecules); incorporated in mixed micelles, and as precipitate. Similarly, the counterion exists as unassociated species; bound onto the micelle surface, and as precipitate. The nonionic surfactant is present both as monomer and in mixed micelles.

The precipitation of the anionic surfactant by association with counterion can be represented by a solubility product relationship involving the free or unassociated species involved:

$$K_{SP} = [A^-]_{mon}[C^+]_u \quad [1]$$

where K_{SP} is the concentration-based solubility product, $[A^-]_{mon}$ is the concentration of the anionic surfactant monomer, and $[C^+]_u$ is the concentration of the unassociated or unbound counterion.

The purpose of the theory is to predict the phase boundary or minimum added electrolyte required to cause the formation of precipitate for a given concentration and composition of surfactant. On the precipitation phase boundary, an infinitesimal amount of the surfactant is present as precipitate. Therefore, for material balance purposes, all of the surfactant is present as micelles or monomer, even though the monomeric surfactant must also satisfy the solubility product in Equation [1]. An overall material balance on the anionic and nonionic surfactant in solution yields:

$$[A^-]_{tot} = [A^-]_{mon} + x_A[M] \quad [2]$$

$$[N]_{tot} = [N]_{mon} + (1 - x_A)[M] \quad [3]$$

where $[A^-]_{tot}$ is the total concentration of anionic surfactant in solution, $[N]_{tot}$ is the total concentration of nonionic surfactant in solution, x_A is the mole fraction of anionic surfactant in the micelle, $[M]$ is the total concentration of surfactant present as micelles, and $[N]_{mon}$ is the concentration of the nonionic surfactant monomer. The micellar mole fraction is on a surfactant-only basis: i.e., x_A is the ratio of moles of anionic surfactant in micellar form to the total moles of surfactant in micellar form.

When the solution composition corresponds to a point on the precipitation phase boundary, a material balance on the counterion yields:

$$[S] + [A^-]_{tot} = [C^+]_u + \beta x_A[M] \quad [4]$$

where $[S]$ is the concentration of added electrolyte, and β is the fractional counterion binding on the micelles. Note that counterion comes from both added salt and the anionic surfactant upon dissolution (left hand side of Equation [4]); the counterion from these two contributions is assumed to be of the same type. The right hand side of Equation [4] accounts for the total counterion in solution as either unassociated species, or bound on micelles. The fractional counterion binding is defined as the ratio of the number of counterions bound on the mixed micelle to the number of anionic surfactant molecules in that mixed micelle.

In order to calculate the concentration of monomeric anionic surfactant, the equilibrium between the mixed micelle and monomers needs to be modeled. In general, the relative amounts of the anionic and nonionic surfactant in the micelles will be different from that in the monomer. Also, the total monomer concentration will be a function of micelle composition. Regular solution theory has been widely used to model the monomer-micelle equilibrium for ionic/nonionic surfactant systems (7-14) and will be used here. From a definition of surfactant component activity coefficients in micelles, and applying regular solution theory (7):

$$[A^-]_{mon} = x_A \gamma_A CMC_A \quad [5]$$

$$[N]_{mon} = (1 - x_A) \gamma_N CMC_N \quad [6]$$

$$\ln \gamma_A = (1 - x_A)^2 W/RT \quad [7]$$

$$\ln \gamma_N = x_A^2 W/RT \quad [8]$$

where γ_A and γ_N are the activity coefficients of the anionic and nonionic surfactant in the micelles, respectively, and CMC_A and CMC_N are the CMC values for the pure anionic surfactant and the pure nonionic surfactant in a solution of the same electrolyte concentration as the mixed system being studied, respectively, W is the interaction parameter, R is the ideal gas constant, and T is the absolute temperature.

The CMC of the pure nonionic surfactant was found to be fairly independent of the salinity over the range of interest in this work, as will be shown. However, the CMC of the anionic surfactant varies substantially with salinity variations as described by (15):

$$\ln(CMC_A) = a - b \ln([C^+]_u) \quad [9]$$

where a and b are constants.

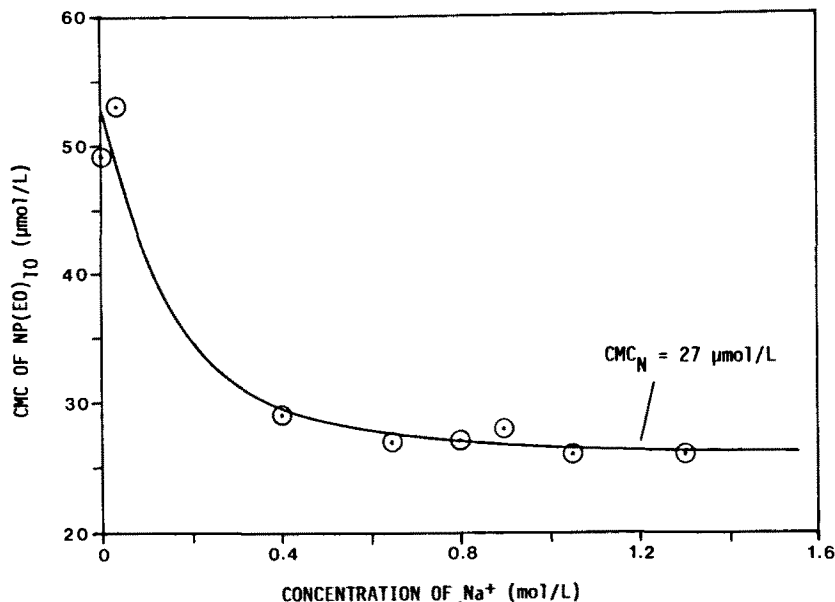


FIG. 2. Effect of counterion concentration on the CMC of NP(EO)₁₀.

The values of a , b , CMC_N , W , and β can all be obtained from independent experiments not requiring any precipitation measurements, as will be described and tabulated for the system studied here.

When a salinity tolerance is determined experimentally, the total concentrations of anionic and nonionic surfactant in solution ($[A^-]_{tot}$ and $[N]_{tot}$) are independent variables. The dependent variable is the minimum added electrolyte or salt concentration ($[S]$) which is required to precipitate any surfactant. If K_{sp} is known, then for any arbitrary anionic and nonionic surfactant concentrations in solution, Equations [1-9] can be solved simultaneously for $[S]$, $[A^-]_{mon}$, $[C^*]_w$, $[N]_{mon}$, x_A , $[M]$, CMC_A , γ_A and γ_N . Therefore, the precipitation phase boundaries for any arbitrary surfactant mixture composition or concentration above the CMC can, in theory, be predicted from the above equations.

RESULTS AND DISCUSSION

Micelle formation. The parameters CMC_N , a , b , W , and β are related to micelle formation and counterion binding on micelles in the mixed surfactant system.

The CMC of the NP(EO)₁₀ is shown as a function of counterion concentration (from added salt) in Figure 2. The Na⁺ concentration which will be covered in phase boundary measurements in this study varies from 0.9 M to 1.55 M. From Figure 2, CMC_N is constant within experimental error over this range and is equal to 27 μ M.

The CMC of C₁₂SO₄ is shown in Figure 3 as a function of total counterion concentration for counterion concentrations below those at which precipitation occurs. Because at the CMC all of the surfactant is present as monomer, the total sodium concentration in Figure 3 is also equal to the unassociated counterion concentration ($[C^*]_w$). Applying Equation [9] to the data in Figure 3 results in $a = -8.52$ and $b = 0.696$, where all concentrations are in M.

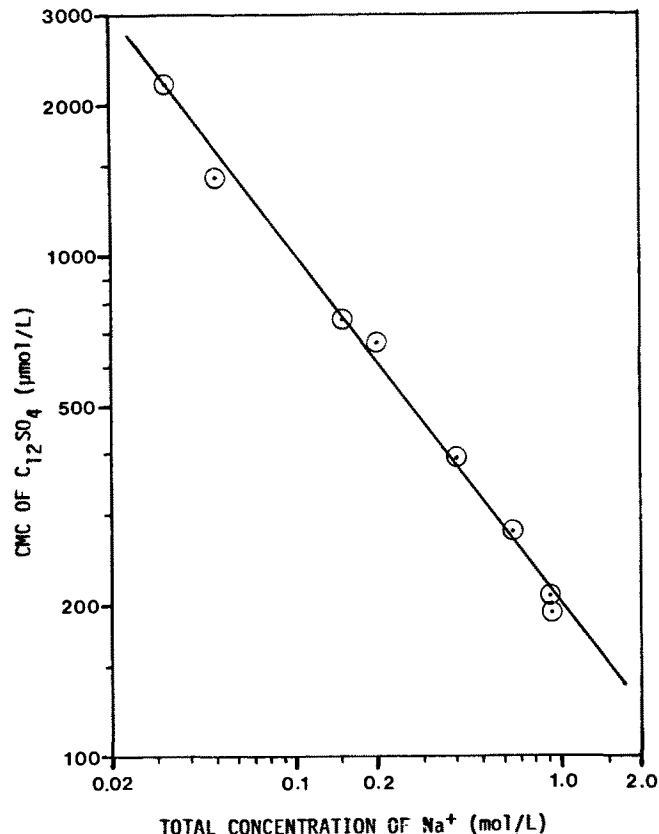


FIG. 3. Effect of total counterion concentration on the CMC of C₁₂SO₄.

In applying regular solution theory to mixed micelles, it is convenient to define:

$$CMC_M = [A^-]_{mon} + [N]_{mon} \quad [10]$$

$$y_A = [A^-]_{mon} / ([A^-]_{mon} + [N]_{mon}) \quad [11]$$

SURFACTANT MIXTURE PRECIPITATION

where CMC_M is the CMC in the mixed surfactant system, and y_A is the surfactant-only based monomer mole fraction of the anionic surfactant. Substituting Equations [10] and [11] into Equations [5] and [6] results in:

$$y_A CMC_M = x_A y_A CMC_A \quad [12]$$

$$(1 - y_A) CMC_M = (1 - x_A) y_N CMC_N \quad [13]$$

The relative mole fraction of each surfactant was held constant in solution and the surface tension measured as a function of total surfactant concentration. The CMC values (CMC_M) determined from these experiments as a function of y_A are shown in Figures 4-7 for the $C_{12}SO_4/NP(EO)_{10}$ system at four different Na^+ concentrations. Equations [7], [8], [12] and [13] can be solved simultaneously for a given value of W to predict the CMC curves from regular solution theory. The curves shown in Figures 4-7 were determined from the best fit value of W at each salinity. Regular solution theory fits the CMC data very well. The resulting values of W are shown in Figure 8 as a function of Na^+ concentration. The decrease in the absolute value of W with increasing electrolyte concentration shown in Figure 8 is commonly observed (7,9). The value of W cannot be determined directly at the counterion concentrations studied in phase boundary determinations. Therefore, it must be extrapolated from that at lower Na^+ concentrations, as shown in Figure 8. The predicted precipitation phase boundaries are not highly sensitive to the value of W for this system,

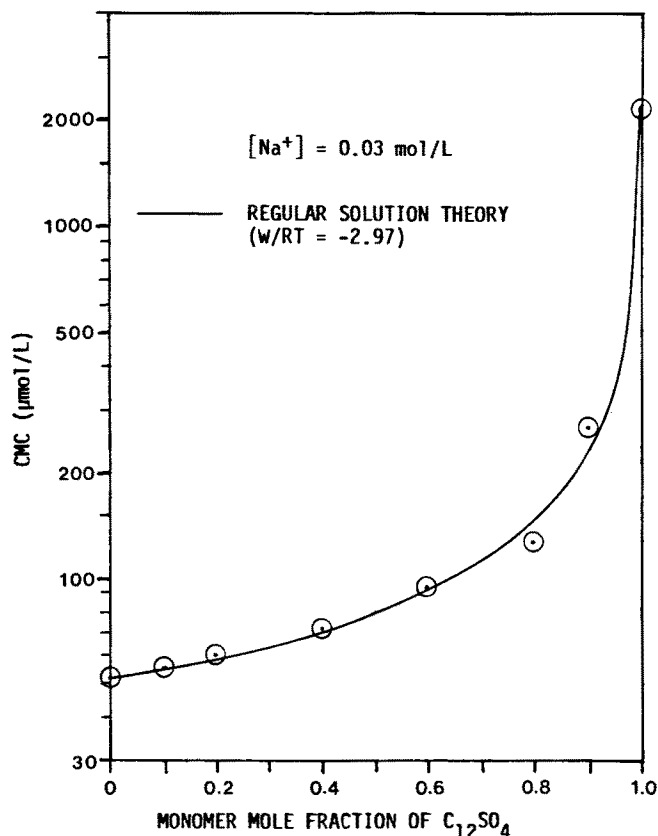


FIG. 4. Effect of monomer composition on CMC of $C_{12}SO_4/NP(EO)_{10}$ mixtures, $[Na^+] = 0.03$ M.

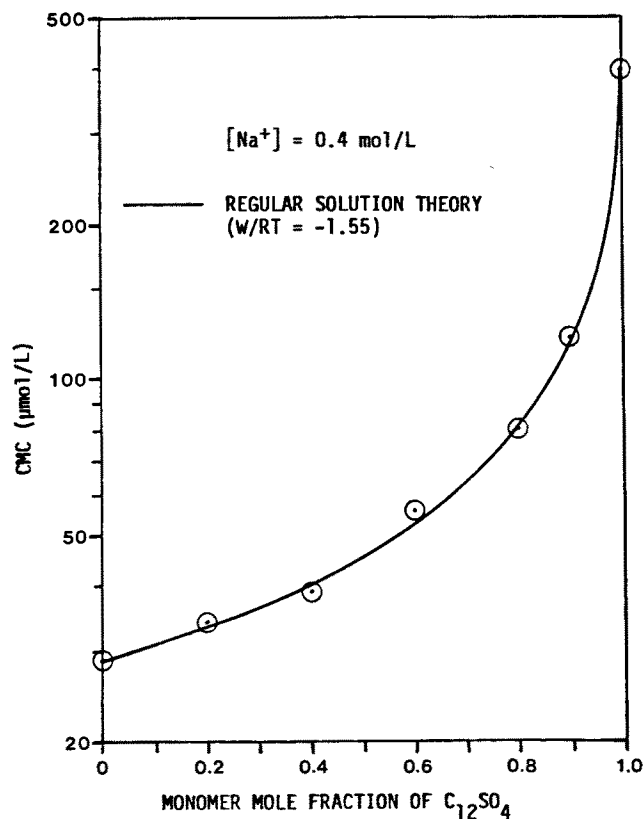


FIG. 5. Effect of monomer composition on CMC of $C_{12}SO_4/NP(EO)_{10}$ mixtures, $[Na^+] = 0.40$ M.

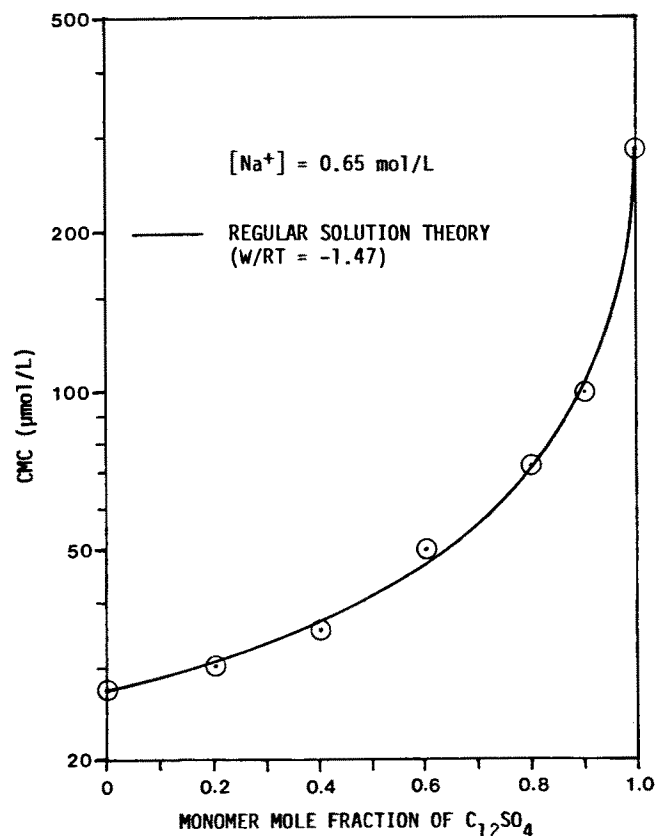


FIG. 6. Effect of monomer composition on CMC of $C_{12}SO_4/NP(EO)_{10}$ mixtures, $[Na^+] = 0.65$ M.

so any inaccuracy in the extrapolation shown in Figure 8 has little effect on the final predictions from the theory.

The fractional counterion binding on mixed ionic/non-ionic micelles has been measured and a model developed to describe this phenomena by Rathman and Scamehorn (16). The fractional counterion binding of the $C_{12}SO_4/NP(EO)_{10}$ system has been measured and the ap-

propriate parameters for the model determined (17). The predicted value of β for all of the micellar compositions and salinities studied here is 0.65.

Determination of K_{SP} . If no nonionic surfactant is present in the system, Equations [2], [4] and [5] become:

$$[A^-]_{tot} = [A^-]_{mon} + [M] \quad [14]$$

$$[S] + [A^-]_{tot} = [C^+]_u + \beta[M] \quad [15]$$

$$[A^-]_{mon} = CMC_A \quad [16]$$

Above the CMC, the experimentally determined value of $[S]$ can be used in the simultaneous solution of Equations [1], [9] and [14-16] to calculate K_{SP} .

The precipitation phase boundary for the $C_{12}SO_4$ system is shown in Figure 9 for surfactant concentrations above the CMC. The resulting values of K_{SP} are also shown in Figure 9 for the different surfactant concentrations. The value of K_{SP} can be seen to be essentially independent of surfactant or counterion concentration, and the average value of $1.937 \times 10^{-4} M^2$ will be used in this work.

In the application of this model, the value of K_{SP} will be assumed to be independent of surfactant composition and concentration and salinity. The appropriateness of this assumption will be discussed later in the paper.

Precipitation phase boundaries in mixed surfactant systems. All the parameters needed to solve Equations [1-9] can be obtained from CMC data, counterion bindings and a salinity tolerance for the pure anionic surfactant above the CMC as just described for the $C_{12}SO_4/NP(EO)_{10}$ studied here. The theory then allows a priori predictions of mixed surfactant system precipitation phase boundaries. These predictions will be compared to experimental measurements here.

The salinity tolerance, with NaCl as the added salt, of two systems with constant concentrations of anionic surfactant is shown in Figures 10 and 11 as a function of nonionic surfactant mole fraction. As the percentage of

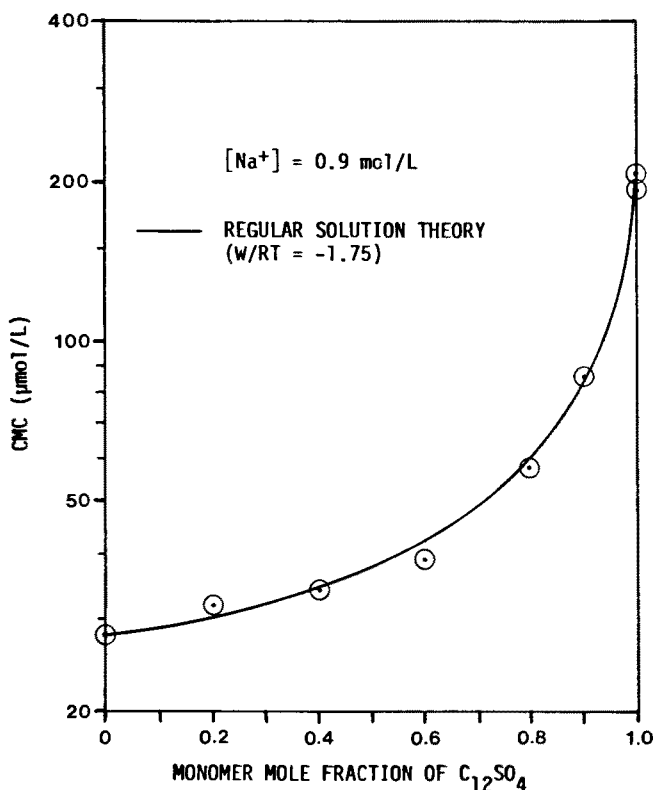


FIG. 7. Effect of monomer composition on CMC of $C_{12}SO_4/NP(EO)_{10}$ mixtures, $[Na^+] = 0.90 M$.

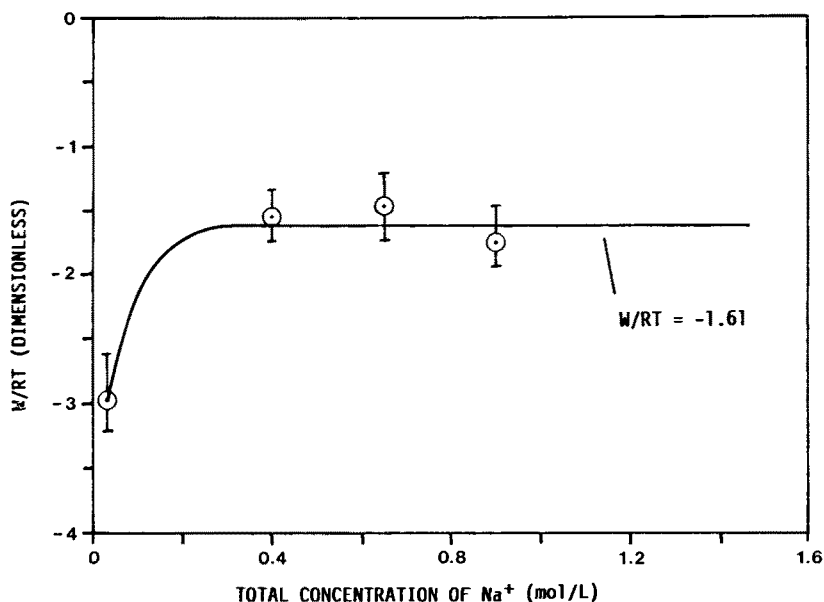


FIG. 8. Effect of total counterion concentration on regular solution theory interaction parameter.

SURFACTANT MIXTURE PRECIPITATION

nonionic surfactant increases, salinity tolerance increases, indicating the beneficial effect of using the anionic/nonionic surfactant mixtures. The predicted phase boundary for the mixed surfactant system is also shown in Figures 10 and 11. The theory agrees very well with the experimental data, particularly in light of the fact that it has no adjustable parameters and is truly a predictive model.

The data in Figures 10 and 11 correspond to different proportions of anionic and nonionic surfactant in the mixture. In order to clarify this relation, salinity tolerance is shown in Figure 12 for different ratios of anionic to nonionic surfactant as a function of total surfactant con-

centration. Figure 12 includes some of the data in Figures 10 and 11 and some additional data. From Figure 12, increasing the proportion of nonionic surfactant in the system increases the salinity tolerance at any surfactant concentration. For the mixed systems, the salinity tolerance increases as the total surfactant concentration decreases due to the changing composition of mixed micelles and monomer as the monomer contains an increasing proportion of total surfactant in the system.

The nonionic surfactant increases the salinity tolerance of the system by affecting mixed micelle formation thermodynamics, resulting in a reduced anionic surfactant monomer concentration and a higher counterion concen-

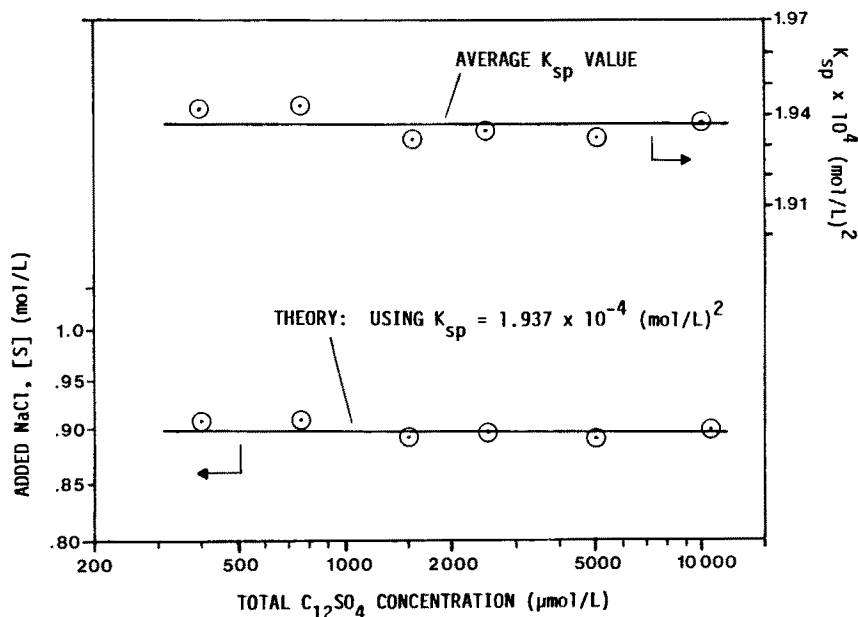


FIG. 9. Determination of K_{SP} from $C_{12}SO_4$ phase boundary.

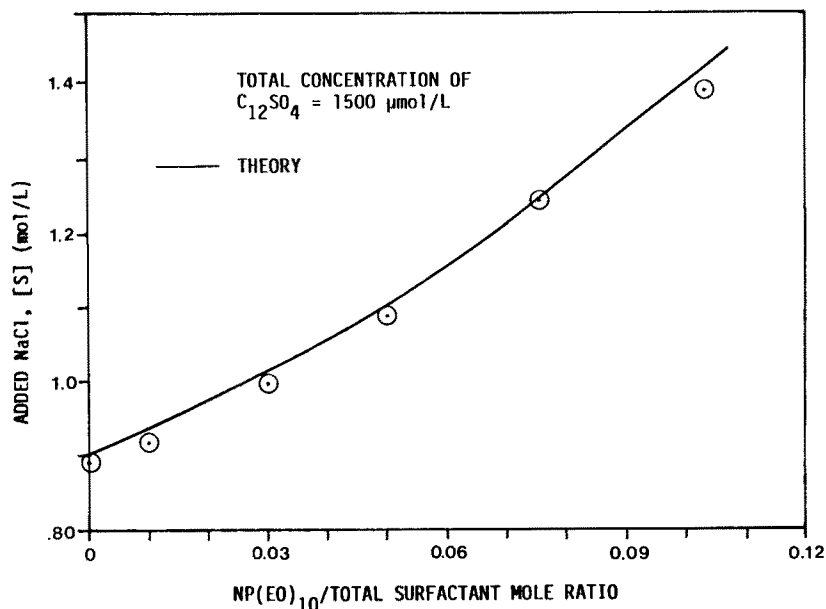


FIG. 10. Effect of surfactant composition on salinity tolerance of $C_{12}SO_4/NP(EO)_{10}$ system, $[C_{12}SO_4] = 1500 \mu M$.

tration required to exceed the solubility product. The negative value of the interaction parameter indicates a negative deviation from ideality in these mixed micelles; i.e., the mixed micelle formation is enhanced relative to pure anionic micelle formation. This effect is illustrated in Figure 13, where the anionic surfactant monomer and added salt concentrations corresponding to the precipitation phase boundary are plotted against nonionic/total surfactant ratio in the system at constant anionic surfactant concentration. As the ratio of nonionic surfactant increases, the anionic surfactant monomer concentration decreases, resulting in increased salinity tolerance in the system.

A nonionic/total surfactant ratio of greater than 0.1 could not be studied with this system because phase separation, similar to that observed above the cloud point of pure nonionic surfactant systems (18), occurred. This range can be extended with proper selection of surfactants and is not a general restriction.

Concentration-based K_{sp} is not necessarily independent of system composition; an activity-based solubility product should be used for this assumption to be valid. However, this requires the use of activity coefficients for both unassociated counterion and anionic surfactant monomer. In pure ionic surfactant micellar solutions, determination of these is very complex (19). No correla-

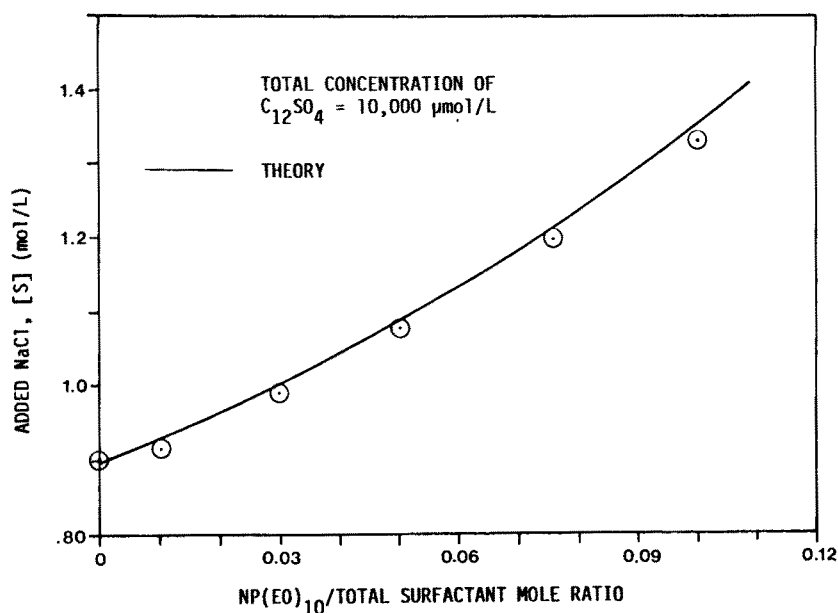


FIG. 11. Effect of surfactant composition on salinity tolerance of $C_{12}SO_4$ /NP(EO)₁₀ system, $[C_{12}SO_4] = 10,000 \mu M$.

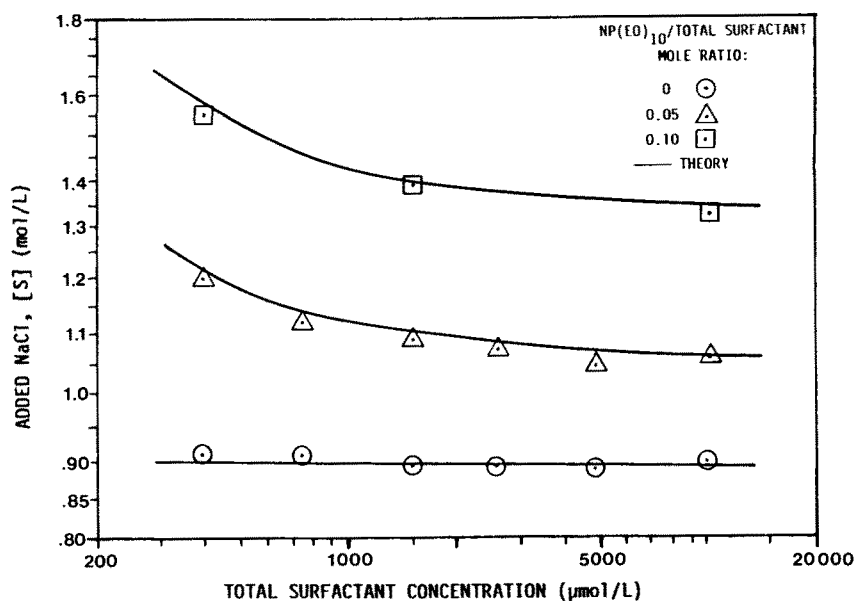


FIG. 12. Effect of surfactant concentration on salinity tolerance of $C_{12}SO_4$ /NP(EO)₁₀ system.

SURFACTANT MIXTURE PRECIPITATION

tion is available for micellar systems containing ionic and nonionic surfactants as well as added electrolyte. The excellent fit of the theory to experimental data in Figures 10–12 implies that K_{SP} is fairly independent of composition for this system over the range of conditions studied, justifying the use of a concentration-based solubility product in this case.

In this work, the value of the K_{SP} was determined from the phase boundary for the pure anionic surfactant above the CMC, rather than from the precipitation phase boundary below the CMC. This has several advantages. The phase boundary is easier to determine experimentally in this region. Also, if K_{SP} were dependent on the system composition, it is reasonable that the true K_{SP} for the mixed system at high surfactant concentrations would be closer to that of the anionic surfactant at similarly high concentrations, rather than to that of the anionic surfactant at low concentrations.

Under the conditions studied here, the unassociated counterion was present in much higher proportion than the counterion bound to micelles. Neglecting the bound counterion would have had very little effect on predicted phase boundaries. In other words, the second term on the right hand side of Equation [4] is much smaller than the first term. In this case, the value of β would not be needed to predict salinity tolerances. Only CMC values and pure anionic surfactant phase boundaries would be necessary to predict mixed system phase boundaries. In practical situations, for a mixture designed to be salinity or hardness tolerant, this would also generally be the case, eliminating the need for the value of the counterion binding on the mixed micelle to apply the theory developed here.

Precipitate composition. The theory developed here assumes that the precipitate is composed only of anionic surfactant and counterion: i.e., no nonionic surfactant is incorporated in the crystal structure. In this work, the precipitate from mixed surfactant solutions of various

compositions was analyzed and found to contain no detectable nonionic surfactant contaminant (>99.98% pure). Other authors have also found that precipitate formed from solutions of mixed dissimilar surfactants contain only one surfactant species (20,21).

Relationship to previous work. Several authors (22–25) have measured phase boundaries for surfactant systems containing only ionic surfactants and developed models to describe this phenomena. In fact, the model developed here is, in large part, an extension to mixed anionic/nonionic systems of the model developed by Peacock and Matijevic (22) for anionic surfactants.

Gerbacia (26) observed that addition of nonionic surfactants increases the hardness tolerance of solutions of anionic surfactants. Nishikido et al. (27) showed that the Krafft temperature of solutions of anionic and nonionic surfactants was lower than that of solutions of anionic surfactant only. This is equivalent to an increase in salinity tolerance. In this work, the increased salinity tolerance in these systems is not only observed, but is quantified in terms of mixed micelle formation.

Only salinity tolerance was studied here. The same basic mechanisms discussed are also responsible for increased hardness tolerance in nonionic/anionic surfactant systems. The model presented here can easily be modified to consider multivalent counterions; current work is focused on this extension.

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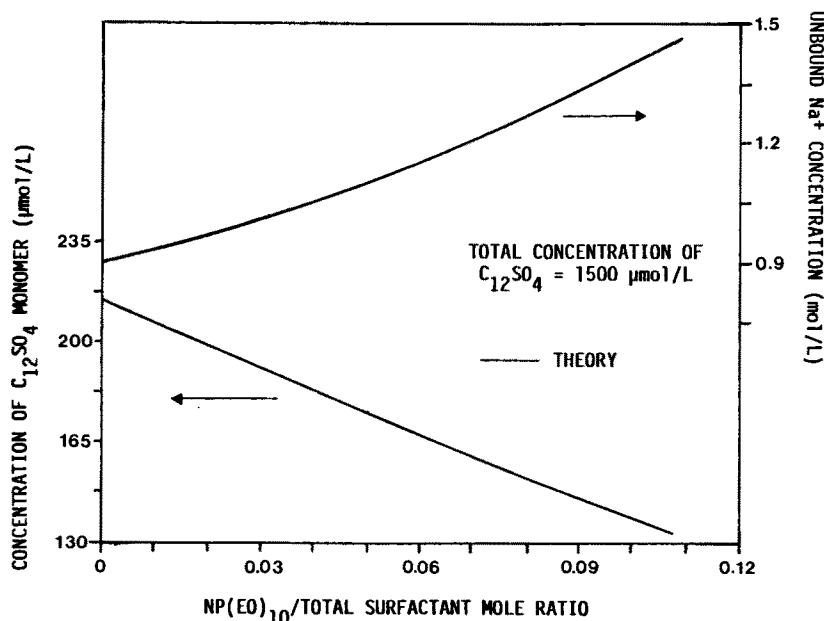


FIG. 13. Monomeric $C_{12}SO_4$ and unbound Na^+ concentrations along the precipitation phase boundary.

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Effect of Protein Cationicity on Inhibition of in vitro Epidermis Curling by Alkylbenzene Sulfonate

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Dilute solutions of linear alkylbenzene sulfonate (LAS), an anionic detergent, caused strips of epidermis to twist and curl. Four commercially available protein hydrolysate mixtures and a synthetic peptide, when added to the LAS solution, countered this to varying degrees, from the epidermis being as distorted as the LAS control to as flat as the water control. A study to determine the contribution of these materials' positive charge (isoionic point) to in vitro epidermis flatness demonstrated a direct linear relationship, i.e., the more positive the charge the flatter the epidermis. This effect was even discernible in a 1 to 30 ratio of a highly cationic protein to detergent. One of the protein mixtures, which was then fractionated according to charge, showed a linear regression correlation coefficient of 0.86 for this relationship. Because the twisting and curling of epidermis has been demonstrated to be related to human skin irritation, these results suggest that positively charged proteins might increase the mildness of solutions containing anionic detergents.

Surface active agents have been employed in household formulations in order to obtain efficient cleansing.

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Some of these agents have the potential to cause skin irritation (1-4), but progress has been made to overcome this (5,6). The study by Eigen and Weiss (5) showed that addition of partially degraded protein mixtures to a dishwashing liquid composition containing anionic surfactants protects the skin from irritation. The nature of the active components in these protein mixtures, however, was not known. It was the purpose of the present study to determine their nature.

This research focused on investigating the contribution of protein charge on ameliorating the skin damaging effect of linear alkylbenzene sulfonate (LAS). An in vitro test method in which detergents caused human epidermis to twist and curl served as the model for in vivo human skin irritation (7). The results demonstrated a sizable effect of protein charge.

EXPERIMENTAL

Materials. Spectrapor 6 dialysis bags, (Spectrum Medical Industries, Los Angeles, California) AG-1-X2 acetate ion exchange resin, (Bio-Rad, Rockville Center, New York) Amberlite MB-1AR mixed bed ion exchange resin, (Rohm and Haas, Philadelphia, Pennsylvania) Glycylarginine, (Vega Biochemicals, Tucson, Arizona) Protein mixtures I, II, III, IV; Linear alkylbenzenesulfonate (LAS), Continental Oil Co., Houston, Texas.