

w cohesive energy difference per molecule between the micellar and singly dispersed state, J/molecule
 z_i valence of species i
 $\beta_{Ca^{2+}}$ fractional counterion binding of Ca^{2+} on a micelle

β_{Na^+} fractional counterion binding of Na^+ on a micelle
 Φ_0 electrical potential at the micelle surface, V

Registry No. SDS, 151-21-3; $CaCl_2$, 10043-52-4; NaCl, 7647-14-5.

Hardness Tolerance of Anionic Surfactant Solutions. 2. Effect of Added Nonionic Surfactant

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Precipitation of anionic surfactant by calcium has been studied in the presence of added nonionic surfactant and added NaCl. A model is developed that can predict the precipitation boundary as a function of surfactant composition and concentration of added NaCl. The model uses a solubility product relationship between anionic surfactant monomer and unbound calcium and a regular solution theory description of monomer-micelle equilibrium and considers counterion binding of divalent and monovalent counterions onto the micelles. The model works well at moderate NaCl concentrations but is less accurate at high NaCl concentrations. Calculations from the model confirm that mixed micelle formation is responsible for increased hardness tolerance in anionic surfactant solutions when nonionic surfactant is added.

Introduction

Hardness tolerance of an anionic surfactant is defined as the minimum concentration of multivalent cation necessary to cause precipitation of the surfactant. In the preceding paper in this issue (part 1 of this series),¹ we discussed the precipitation of anionic surfactant with or without added monovalent electrolyte. A model was developed which could predict hardness tolerance as a function of surfactant concentration and monovalent electrolyte concentration. In an earlier paper,² we discussed salinity tolerance (minimum concentration of a monovalent electrolyte to cause precipitation) of an anionic surfactant in the presence of a nonionic surfactant. The nonionic surfactant was shown to enhance salinity tolerance substantially due to mixed micelle formation. In this paper, we extend these previous two investigations to consider the effect of added nonionic surfactant on the hardness tolerance of an anionic surfactant.

Hardness tolerance is a commonly encountered problem in the utilization of ionic surfactants. Builders (e.g., phosphates) are traditionally added to detergent formulations to prevent anionic surfactant precipitation.³ In enhanced oil recovery by surfactant flooding, alcohols are often added to an injected slug to prevent precipitation.⁴

The addition of nonionic surfactants to anionic surfactants to enhance hardness tolerance in practical applications is receiving increasing attention. Nonbuilt heavy-duty liquid laundry detergents may utilize mixtures of anionic and nonionic surfactants.^{5,6} Mixed surfactant systems employing nonionic surfactant have been proposed for use in enhanced oil recovery.⁷ More generally, surfactant mixtures can have a number of synergistic advantages over the use of a single surfactant type.⁸

In this work, the precipitation phase boundary is measured for an anionic-nonionic surfactant mixture at different NaCl concentrations. Furthermore, a model is developed which can predict this phase boundary.

Experimental Section

The experimental materials and methods are the same as those used in part 1 of this series¹ with the following additions due to the inclusion of nonionic surfactant in these studies.

The nonionic surfactant (NPE) was a polydisperse nonylphenol polyethoxylate with an average of 10 ethylene oxide groups per molecule. The NPE has a trade name of Igepal CO-660 from GAF Corp. and was used as received.

In order to determine if NPE incorporated itself into the precipitated crystals, we filtered the precipitate from the solution, washed it with cold water, and dried it at low heat. The crystals were then dissolved in water, and the concentration of NPE in the solution was determined by using HPLC with UV detection. The precipitate formed from mixed surfactant solutions of various compositions was analyzed and found to contain no detectable nonionic surfactant contaminant (>99.98% pure).

Theory

The model developed here is an extension of the hardness tolerance model developed in part 1 of this series,¹ the main addition being that regular solution theory will be included to account for the equilibrium between sur-

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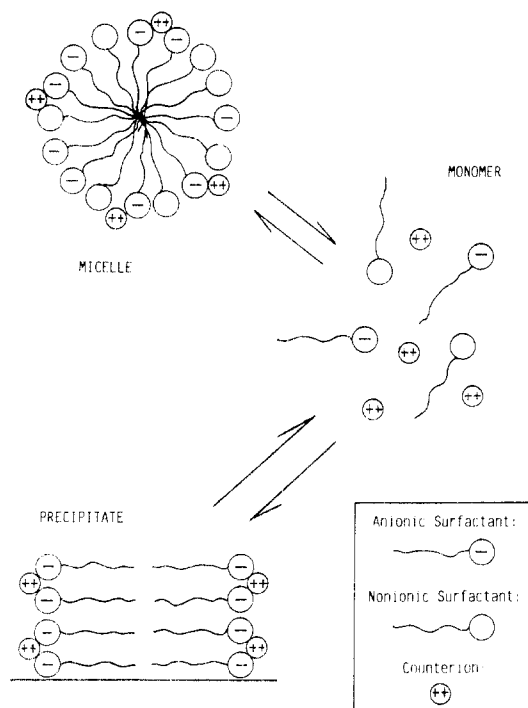
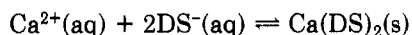


Figure 1. Schematic of equilibrium existing in system.

factant monomer and micelles. Figure 1 is a schematic diagram that represents precipitation in these mixtures when micelles are present. The anionic surfactant is present in three environments: (1) as monomer (unassociated molecules), (2) incorporated in mixed micelles, and (3) as precipitate. Nonionic surfactant is present (1) as monomer and (2) in mixed micelles. Monovalent counterions (not shown in Figure 1 for clarity) and divalent counterions both exist (1) as unbound (unassociated) species and (2) bound onto the micelle surface. In addition, the divalent counterion is present in any precipitate that forms. The anionic surfactant used is sodium dodecyl sulfate (NaDS).

Nonionic surfactant does not participate in the precipitation reaction, which is represented



This can be described by a solubility product relationship between unassociated species:

$$K_{\text{sp}} = [\text{Ca}^{2+}]_{\text{un}}([\text{DS}^{-}]_{\text{mon}})^2 f_{\text{Ca}}(f_{\text{DS}})^2 \quad (1)$$

where K_{sp} is the activity-based solubility product, $[\text{Ca}^{2+}]_{\text{un}}$ is the concentration of unbound calcium, $[\text{DS}^{-}]_{\text{mon}}$ is the monomer concentration of anionic surfactant, and f_{Ca} and f_{DS} represent the activity coefficients of unbound Ca^{2+} and monomeric DS^{-} in solution, respectively.

An extended Debye-Hückel equation is used to describe the activity coefficient of the unassociated ions¹

$$\log f_{\text{Ca}} = -0.5139(2)^2(I)^{0.5}/(1 + 1.9782(I)^{0.5}) \quad (2)$$

$$\log f_{\text{DS}} = -0.5139(-1)^2(I)^{0.5}/(1 + 2.3079(I)^{0.5}) \quad (3)$$

$$I = \sum 0.5c_i(z_i)^2 = [\text{NaCl}] + [\text{NaDS}] + 3[\text{CaCl}_2] \quad (4)$$

where I is the ionic strength, c_i is the total concentration of ion i in solution, z_i is the valence of species i , and $[\text{NaCl}]$, $[\text{NaDS}]$, and $[\text{CaCl}_2]$ are the total concentrations of each species represented.

On the precipitation phase boundaries, the amount of anionic surfactant and calcium present as precipitate is infinitesimal. Therefore, a material balance for each surfactant (anionic and nonionic) and counterion (calcium

and sodium) present in solution on this boundary yields

$$[\text{NaDS}] = [\text{DS}^{-}]_{\text{mon}} + [\text{DS}^{-}]_{\text{mic}} \quad (5)$$

$$[\text{NPE}] = [\text{NPE}]_{\text{mon}} + [\text{NPE}]_{\text{mic}} \quad (6)$$

$$[\text{CaCl}_2] = [\text{Ca}^{2+}]_{\text{un}} + [\text{Ca}^{2+}]_{\text{b}} \quad (7)$$

$$[\text{Na}^{+}]_{\text{tot}} = [\text{NaCl}] + [\text{NaDS}] = [\text{Na}^{+}]_{\text{un}} + [\text{Na}^{+}]_{\text{b}} \quad (8)$$

where $[\text{DS}^{-}]_{\text{mic}}$ represents the concentration of DS^{-} present in micelles, $[\text{NPE}]$ is the total NPE concentration in solution, $[\text{NPE}]_{\text{mon}}$ and $[\text{NPE}]_{\text{mic}}$ represent the concentration of NPE present as monomer or in micelles, respectively, $[\text{Ca}^{2+}]_{\text{b}}$ is the concentration of calcium bound onto micelles, and $[\text{Na}^{+}]_{\text{tot}}$, $[\text{Na}^{+}]_{\text{un}}$, and $[\text{Na}^{+}]_{\text{b}}$ represent the total sodium concentration, the unbound sodium concentration, and the concentration of sodium bound onto micelles, respectively. The concentration of each counterion bound onto the micelle is related to its value of fractional counterion binding by

$$\beta_{\text{Ca}} = 2[\text{Ca}^{2+}]_{\text{b}}/[\text{DS}^{-}]_{\text{mic}} \quad (9)$$

$$\beta_{\text{Na}} = [\text{Na}^{+}]_{\text{b}}/[\text{DS}^{-}]_{\text{mic}} \quad (10)$$

where β_{Ca} and β_{Na} are the fraction of micellar charge neutralized by the respective counterion.

Application of regular solution theory to describe monomer-micelle equilibrium^{8,9} yields

$$[\text{DS}^{-}]_{\text{mon}} = X_{\text{DS}}\gamma_{\text{DS}}\text{cmc}_{\text{DS}} \quad (11)$$

$$[\text{NPE}]_{\text{mon}} = X_{\text{NPE}}\gamma_{\text{NPE}}\text{cmc}_{\text{NPE}} \quad (12)$$

$$\ln \gamma_{\text{DS}} = (X_{\text{NPE}})^2 W/RT \quad (13)$$

$$\ln \gamma_{\text{NPE}} = (X_{\text{DS}})^2 W/RT \quad (14)$$

where X_{DS} and X_{NPE} are the micellar mole fraction of the respective surfactants, γ_{DS} and γ_{NPE} represent the activity coefficients of the respective surfactants in the micelle, cmc_{DS} and cmc_{NPE} are the cmc values of the respective pure component surfactants at the same unbound counterion concentrations as present in the system of interest (generally different than the cmc of the pure surfactant without additives), W is the regular solution theory interaction parameter, R is the gas constant, and T is absolute temperature.

Mole fractions used here are on a surfactant-only basis:

$$X_{\text{DS}} = [\text{DS}^{-}]_{\text{mic}}/([\text{DS}^{-}]_{\text{mic}} + [\text{NPE}]_{\text{mic}}) \quad (15)$$

$$X_{\text{DS}} + X_{\text{NPE}} = 1 \quad (16)$$

From eq 11, it is necessary to know cmc_{DS} as a function of unbound electrolyte concentration. The calculation of this can be summarized by the following equations:¹

$$K_2 S^2 = [\text{Na}^{+}]_{\text{un}} P + [\text{Ca}^{2+}]_{\text{un}} P^2 \quad (17)$$

$$\ln \text{cmc}_{\text{DS}} = K_3 + K_g \ln P \quad (18)$$

$$S = [\text{Na}^{+}]_{\text{un}} P(S_{\text{Na}})/(\text{cmc}_{\text{SDS}} P_{\text{SDS}}) + [\text{Ca}^{2+}]_{\text{un}} P^2(S_{\text{Ca}})/(0.5\text{cmc}_{\text{CDS}}(P_{\text{CDS}})^2) \quad (19)$$

$$K_g = [\text{Na}^{+}]_{\text{un}} P(K_{g,\text{Na}})/(\text{cmc}_{\text{SDS}} P_{\text{SDS}}) + [\text{Ca}^{2+}]_{\text{un}} P^2(K_{g,\text{Ca}})/(0.5\text{cmc}_{\text{CDS}}(P_{\text{CDS}})^2) \quad (20)$$

where K_2 , K_3 , and K_g are constants, $K_{g,\text{Na}}$ is the value of K_g when only Na^{+} is present, $K_{g,\text{Ca}}$ is the value of K_g when only Ca^{2+} is present, cmc_{SDS} and cmc_{CDS} are the cmc values of pure sodium dodecyl sulfate and pure calcium dodecyl

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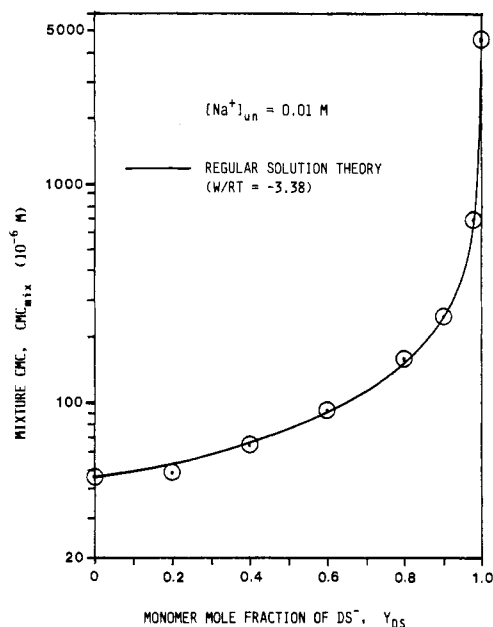


Figure 2. cmc of mixed surfactant system at $[\text{Na}^+]_{\text{un}} = 0.01 \text{ M}$.

sulfate, without added electrolyte, P is a term related to the electrical potential at the micelle surface, P_{SDS} and P_{CDS} are the values of P at cmc_{SDS} and cmc_{CDS} , respectively, S is the surface charge density of the micelle, S_{Na} is the surface charge density of the micelle when Na^+ is the only counterion present in solution, and S_{Ca} is the surface charge density of the micelle when Ca^{2+} is the only counterion present in solution.

The purpose of the equations presented here is to predict the minimum calcium concentration required to cause precipitation at any surfactant concentration. The independent variables include the total concentration of each surfactant and the concentration of added sodium chloride. Therefore, when $[\text{NaDS}]$, $[\text{NPE}]$, and $[\text{NaCl}]$ are set, the dependent variable of interest is $[\text{CaCl}_2]$. If K_{sp} , β_{Ca} , β_{Na} , K_2 , K_3 , $K_{\text{g,Na}}$, S_{Na} , cmc_{SDS} , P_{SDS} , $K_{\text{g,Ca}}$, S_{Ca} , cmc_{CDS} , P_{CDS} , W/RT , and cmc_{NPE} are known, eq 1-20 can be solved simultaneously to obtain $[\text{CaCl}_2]$, $[\text{Ca}^{2+}]_{\text{un}}$, $[\text{Ca}^{2+}]_{\text{b}}$, $[\text{DS}^-]_{\text{mon}}$, $[\text{DS}^-]_{\text{mic}}$, $[\text{NPE}]_{\text{mon}}$, $[\text{NPE}]_{\text{mic}}$, $[\text{Na}^+]_{\text{un}}$, $[\text{Na}^+]_{\text{b}}$, I , f_{Ca} , f_{DS} , X_{DS} , X_{NPE} , γ_{DS} , γ_{NPE} , P , cmc_{CDS} , S , and K_{g} . Therefore, from the theory presented here, it is possible to predict hardness tolerance ($[\text{CaCl}_2]$) for any surfactant concentration with any anionic-nonionic surfactant composition and for any amount of added salt.

Results and Discussion

Determination of Parameters in Model. The values of K_{sp} , K_2 , K_3 , $K_{\text{g,Na}}$, S_{Na} , cmc_{SDS} , P_{SDS} , $K_{\text{g,Ca}}$, S_{Ca} , cmc_{CDS} , and P_{CDS} have been obtained for this system in part 1 of this series.¹ It is now necessary to obtain values for cmc_{NPE} , W/RT , β_{Ca} , and β_{Na} .

cmc_{NPE} was found to be approximately constant over the entire range of electrolyte concentrations of interest in this study at a value of $4.2 \times 10^{-5} \text{ M}$.

Counterion binding on mixed anionic-nonionic micelles has been shown^{10,11} to be a function of the micelle mole fraction of anionic surfactant, X_{DS} . Similarly, binding in mixed (monovalent and divalent) counterion systems is a function of the monovalent/divalent concentration ratio.¹ Currently, there is no known work that has measured counterion binding in systems containing both mixed

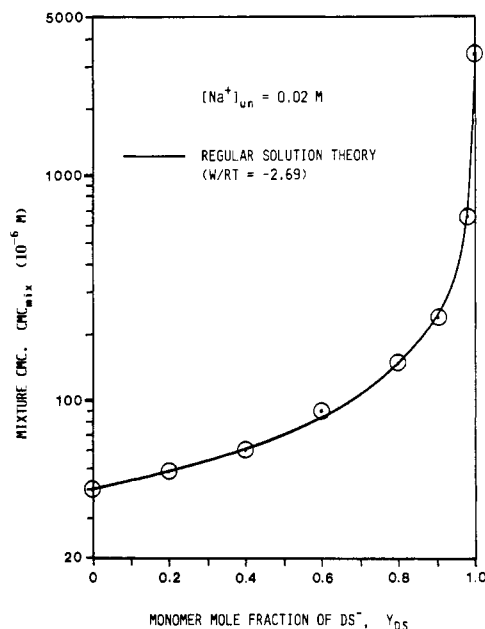


Figure 3. cmc of mixed surfactant system at $[\text{Na}^+]_{\text{un}} = 0.02 \text{ M}$.

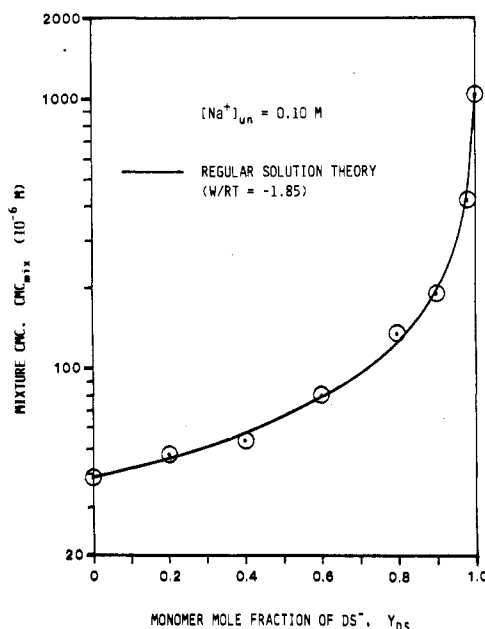


Figure 4. cmc of mixed surfactant system at $[\text{Na}^+]_{\text{un}} = 0.10 \text{ M}$.

surfactant and mixed counterions. Fortunately, the overall mole fraction of NPE (i.e., $[\text{NPE}]/([\text{NaDS}] + [\text{NPE}])$) in the mixtures studied here does not exceed 0.1, so micellar mole fractions of DS^- are high. At high X_{DS} , values for counterion binding (β_{Na} and β_{Ca}) are approximately equal^{10,11} to the values of counterion binding on a pure anionic micelle¹ ($\beta_{\text{Na}}^{\circ} = 0.20$ and $\beta_{\text{Ca}}^{\circ} = 0.45$).

The following equations define the relationship between the mixture cmc (cmc_{mix}) and the monomer mole fraction of anionic surfactant (Y_{DS}) at the cmc of the mixture:

$$Y_{\text{DS}}\text{cmc}_{\text{mix}} = [\text{DS}^-]_{\text{mon}} \quad (21)$$

$$(1 - Y_{\text{DS}})\text{cmc}_{\text{mix}} = [\text{NPE}]_{\text{mon}} \quad (22)$$

The final parameter needed in the model is W/RT . Using eq 11-14, 16, 21, and 22, we can use cmc_{mix} data as a function of Y_{DS} to obtain a best-fit value of W/RT at a specific added electrolyte concentration and temperature. The curves shown in Figures 2-4 are the results of such analysis at different unbound Na^+ concentrations, and

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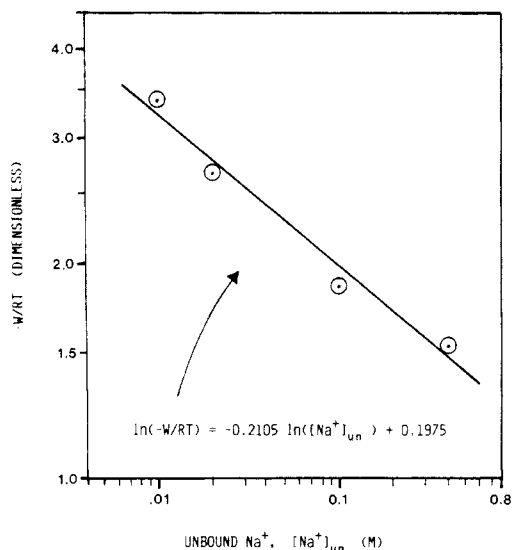


Figure 5. Effect of unbound Na^+ concentration on W/RT .

regular solution theory can be seen to fit cmc_{mix} data very well. Only at the cmc is the unbound Na^+ concentration equal to the total Na^+ concentration. As shown in Figure 5, the resultant values of W/RT decrease as $[\text{Na}^+]_{\text{un}}$ increases. This is due to the fact that as electrolyte concentration increases the electrical potential at the micelle surface decreases, which implies a reduction in electrostatic repulsion between ionic groups in the micelle. This means that the synergistic effect of adding nonionic surfactant (which also reduces surface electrical potential^{10,11}) is decreased as electrolyte concentration increases. The data in Figure 5 can be described by the relationship

$$\ln(-W/RT) = -0.2105 \ln[\text{Na}^+]_{\text{un}} + 0.1975 \quad (23)$$

Obviously, unbound Ca^{2+} will also affect the value of W/RT . To account for this, it is assumed that the mixture of Ca^{2+} and Na^+ can be translated into an "equivalent" Na^+ concentration. For any value of $[\text{Ca}^{2+}]_{\text{un}}$ and $[\text{Na}^+]_{\text{un}}$, cmc_{DS} can be calculated from eq 17–20. There is a corresponding unbound Na^+ concentration, $[\text{Na}^+]_{\text{eq}}$ that gives the same value of cmc_{DS} in a $\text{NaDS} + \text{NaCl}$ solution (without added divalent counterion). Assuming the same electrostatic effects for W/RT in the Na^+ – Ca^{2+} mixture and the Na^+ -only system (at the same value of cmc_{DS}), W/RT for the Na^+ – Ca^{2+} mixture can be calculated from eq 23 by using $[\text{Na}^+]_{\text{eq}}$ in the place of $[\text{Na}^+]_{\text{un}}$. When cmc_{DS} is known for given values of $[\text{Na}^+]_{\text{un}}$ and $[\text{Ca}^{2+}]_{\text{un}}$, the equivalent Na^+ concentration can be calculated by

$$\ln \text{cmc}_{\text{DS}} = -0.69832 \ln[\text{Na}^+]_{\text{eq}} - 8.5134 \quad (24)$$

Divalent magnesium is similar to divalent calcium in its effect on the cmc of anionic surfactants, yet it has a much higher K_{sp} , so micellization can be studied over a much wider range. Therefore, we will present effects of Mg^{2+} on cmc with the understanding that this is equivalent to the effect of Ca^{2+} on the cmc . For example, Figure 6 gives cmc_{mix} data for $[\text{Na}^+]_{\text{un}} = 0.01175 \text{ M}$ and $[\text{Mg}^{2+}]_{\text{un}} = 0.001 \text{ M}$. For anionic surfactant only ($Y_{\text{DS}} = 1$), the value of cmc_{DS} is equal to $1.750 \times 10^{-3} \text{ M}$. From eq 24, the unbound Na^+ concentration (without added divalent cation) required to give the same cmc_{DS} is $[\text{Na}^+]_{\text{eq}} = 0.0450 \text{ M}$. When this value is used in eq 24 for $[\text{Na}^+]_{\text{un}}$, it results in a calculated value of $W/RT = -2.34$. The actual value of W/RT determined experimentally in Figure 6 is $W/RT = -2.15$. It will be shown that the predictions of precipitation boundaries are not highly sensitive to the value of

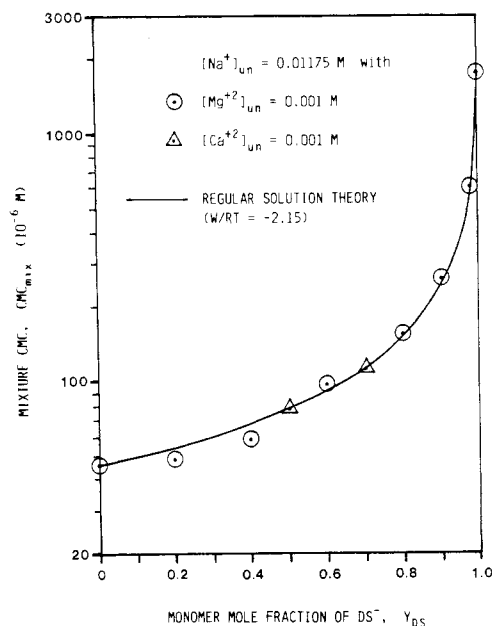


Figure 6. cmc of mixed surfactant system with mixed electrolytes present.

Table I. Summary of Parameters Used in Model

parameter	value	source
K_{sp}	$5.02 \times 10^{-10} \text{ M}^3$	ref 1
β_{Ca}	0.20	this paper
β_{Na}	0.45	this paper
K_2	$2.8724 \times 10^5 \text{ M m}^4 \text{ C}^{-2}$	ref 1
K_3	-10.5396	ref 1
$K_{\text{g,Na}}$	0.69832	ref 1
S_{Na}	$7.960 \times 10^{-3} \text{ C m}^{-2}$	ref 1
cmc_{NPE}	$4.2 \times 10^{-5} \text{ M}$	this paper
cmc_{SDDS}	$6.652 \times 10^{-3} \text{ M}$	ref 1
P_{SDDS}	2736.32	ref 1
$K_{\text{g,Ca}}$	0.895	ref 1
S_{Ca}	$6.816 \times 10^{-2} \text{ C m}^{-2}$	ref 1
cmc_{CDS}	$1.900 \times 10^{-3} \text{ M}$	ref 1
P_{CDS}	118.52	ref 1
W/RT	from eq 23 or 25	this paper

W/RT . Calculation of W/RT can be simplified by combining eq 23 and 24 to give

$$\ln(-W/RT) = 0.3014 \ln \text{cmc}_{\text{DS}} + 2.765 \quad (25)$$

Precipitation Boundary Predictions from Model.

At this point, all the parameters that are required to predict precipitation boundaries have been obtained as shown in Table I. With these values, eq 1–20 with eq 25 must be solved simultaneously to predict the hardness tolerance of an anionic–nonionic surfactant mixture with both monovalent and divalent counterions present.

Figure 7 shows the experimental and predicted precipitation boundary for the anionic–nonionic surfactant mixture containing 10% nonionic surfactant (i.e., $[\text{NPE}]/([\text{NaDS}] + [\text{NPE}]) = 0.10$), with no added NaCl . The precipitation phase boundary¹ for NaDS only has also been included in Figure 7 to show the benefit of adding nonionic surfactant. It can be seen that by adding 10% NPE the minimum hardness tolerance for the $\text{NaDS} + \text{CaCl}_2$ system increases approximately 850%. This serves to demonstrate the tremendous potential of using anionic–nonionic mixtures in applications where the sensitivity of anionic surfactants to hard ions must be reduced. It is possible to understand why hardness tolerance increases with added nonionic surfactant by considering Figures 2–4 and 6. When a small amount of nonionic surfactant is added to anionic surfactant, cmc_{mix} decreases rapidly due

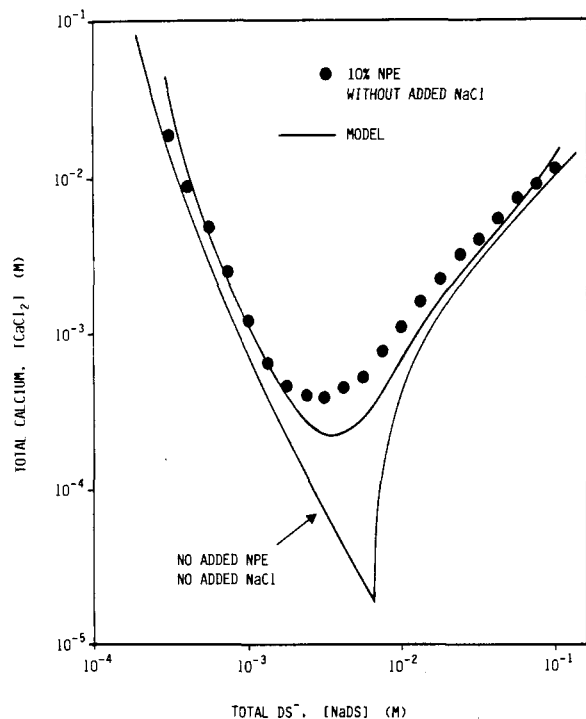


Figure 7. Precipitation phase boundary without added NaCl and with and without added nonionic surfactant.

to a reduction of electrostatic repulsion in the micelles. From eq 21, as cmc_{mix} decreases, the monomer concentration of anionic surfactant, $[DS^-]_{mon}$, also decreases. Therefore, a higher concentration of unbound Ca^{2+} is required to cause precipitation to occur (eq 1). The curve in Figure 7 is a true prediction, without adjustable parameters.

One advantage of the model presented here is that, without additional data, it can predict the precipitation boundary of the NaDS + $CaCl_2$ system for any amount of added nonionic surfactant and any concentration of added NaCl. Figure 8 gives predictions for 10% added NPE with 0.02 M added NaCl. The predictions for this system show excellent agreement with the experimentally determined precipitation boundary except at very high $CaCl_2$ concentrations. Figure 9 gives results for 10% added NPE with 0.10 M added NaCl. The curve labeled $K_{g,Ca} = 0.895$ and $cmc_{CDS} = 1.9 \times 10^{-3}$ M is the a prior predictive model, and it can be seen that the predictions for this system are not as accurate at these high salinities. The experimentally determined increase in minimum hardness tolerance is 1400% for the 0.02 M NaCl system and 5000% for the 0.10 M NaCl system, both compared to the NaDS-only system without added NaCl.

From Figure 9, it seems that the model has difficulty in giving good predictions at high $CaCl_2$ concentrations. This corresponds to high NaCl concentrations, under which conditions hardness tolerance is increased ($CaCl_2$ concentrations on the phase boundary are increased.) The main reason for this is that the model is sensitive to the value of cmc_{DS} calculated from eq 17–20. An accurate value for cmc_{DS} is important because it greatly affects the monomer concentration of DS^- that is obtained from eq 11. If $[DS^-]_{mon}$ has significant error, then the calculated value of $[Ca^{2+}]_{un}$ will be greatly in error (eq 1). The parameters used in eq 17–20 must be obtained from data taken at low divalent counterion concentrations. The probable cause of the deviation between predictions and experimental data at high $CaCl_2$ concentrations is the required extrapolation of these values. The values of cmc_{CDS}

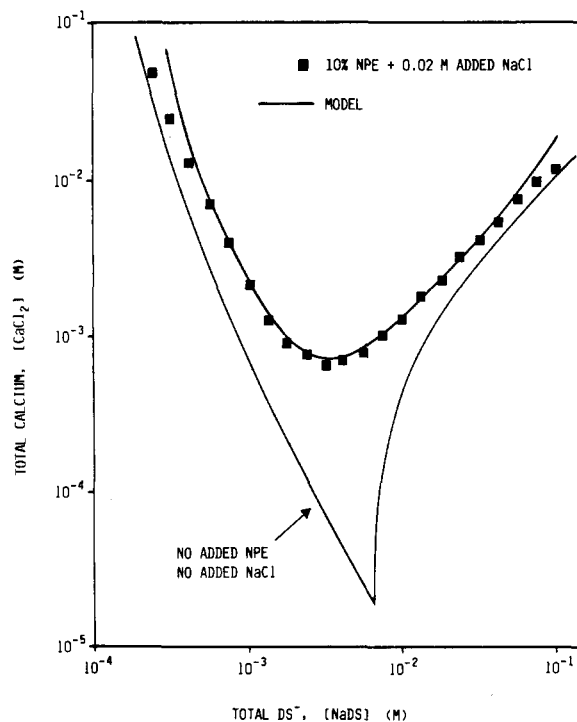


Figure 8. Precipitation phase boundary with nonionic surfactant and 0.02 M added NaCl and without added nonionic surfactant or added NaCl.

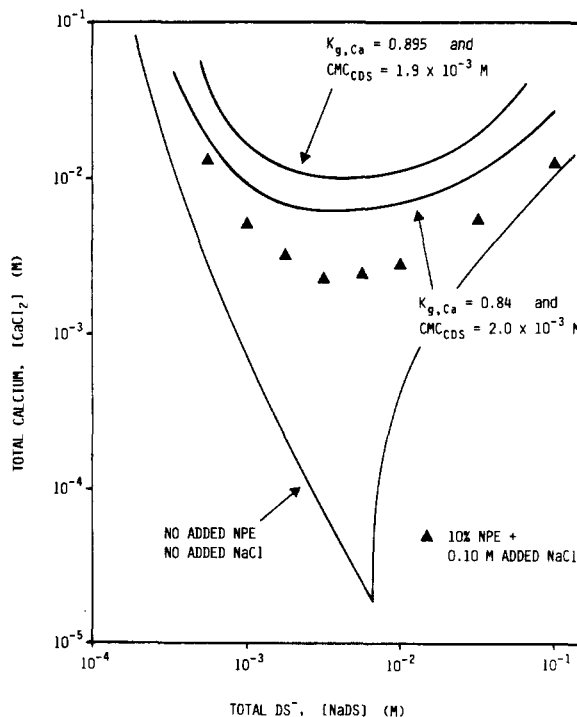


Figure 9. Precipitation phase boundary with nonionic surfactant and 0.10 M added NaCl and without added nonionic surfactant or added NaCl.

and $K_{g,Ca}$ were obtained from experimental cmc_{DS} data.¹ If these values are changed, such that $cmc_{CDS} = 2.00 \times 10^{-3}$ M and $K_{g,Ca} = 0.84$, the calculations from the model improve substantially at high $CaCl_2$ concentrations, as shown in Figure 9 for the 10% NPE + 0.10 M NaCl system. Table II gives a comparison between calculated and experimental values of cmc_{DS} using $cmc_{CDS} = 2.00 \times 10^{-3}$ M and $K_{g,Ca} = 0.84$. The only other parameters in Table I that are changed by changing the values of cmc_{CDS} and $K_{g,Ca}$ are S_{Ca} and P_{CDS} . The use of these values still gives

Table II. Comparison between Calculated and Experimental Values of cmc_{DS} with Added NaCl and MgCl_2^a

[NaCl]	$[\text{Mg}^{2+}]_{\text{un}}^b$	$[\text{Na}^+]_{\text{un}}^c$	calcd ^d cmc_{DS}	exptl cmc_{DS}	error, %
0.0	0.100	4.5762	4.5762	4.450	+2.8
0.0	0.300	3.1445	3.1445	2.800	+12.3
0.0	1.000	1.9659	1.9659	1.930	+1.9
10.0	1.000	11.807	1.8071	1.750	+3.3
20.0	0.500	22.046	2.0464	1.900	+7.7
20.0	3.000	21.143	1.1425	1.150	-0.7
100.0	0.600 ^e	101.01	1.0070	0.965	+4.4

^a All concentrations in mM. $K_{s,\text{Ca}} = 0.84$, $\text{cmc}_{\text{DS}} = 2.0 \times 10^{-3}$ M. ^b $[\text{Mg}^{2+}]_{\text{un}} = [\text{MgCl}_2]$. ^c $[\text{Na}^+]_{\text{un}} = [\text{NaCl}] + [\text{NaDS}]$. ^d Calculated from eq 17-20. ^e This point is for CaCl_2 , not MgCl_2 .

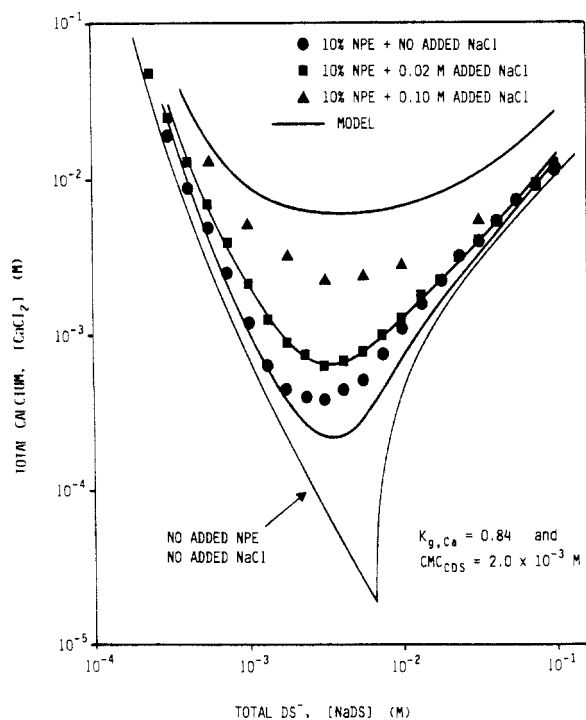


Figure 10. Comparison of precipitation phase boundaries with predictions using modified model parameters.

excellent prediction of cmc values (Table II) while substantially improving the prediction of the precipitation phase boundaries. Results of this work serve to emphasize the need to fully investigate the effect of monovalent-divalent counterion mixtures on the cmc of anionic surfactants.

For the NaDS-only solutions presented in ref 1, the cmc corresponded to the calculated minimum CaCl_2 concentration for each precipitation boundary. In Figure 10, however, it is not possible to identify a cmc along any of the precipitation boundaries because micelles are present at all NaDS concentrations shown. At the CMC for an anionic-nonionic mixture, all surfactant is present as monomer, so the monomer mole fraction, Y_{DS} , is equal to the overall mole fraction. For a mixture containing 10% NPE, therefore, $Y_{\text{DS}} = 0.9$. This corresponds to a low cmc_{mix} in Figures 2-4 and 6, which implies a low DS^- monomer concentration. As the total surfactant concentration increases to a point far above the cmc , virtually all surfactant is present as micelles, so the micellar mole fraction, X_{DS} , is equal to the overall mole fraction (0.90 in this case). At this point, essentially all nonionic surfactant is present in the mixed micelles, and the value of Y_{DS} is much higher than 0.9. This means (from Figures 2-4 and 6) that as the total surfactant concentration in-

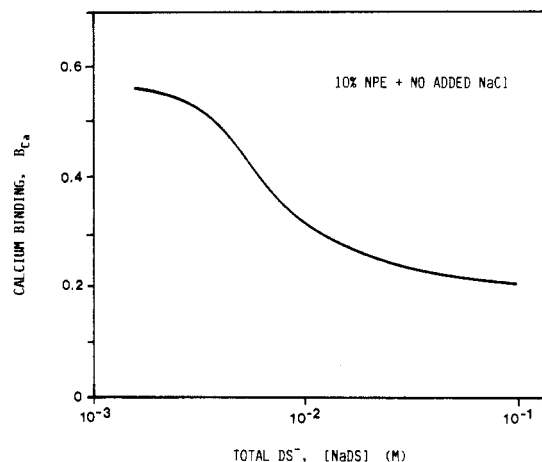


Figure 11. Values of fractional counterion binding of calcium required to describe system with nonionic surfactant and no added NaCl.

creases, the corresponding value of $[\text{DS}^-]_{\text{mon}}$ increases. As $[\text{DS}^-]_{\text{mon}}$ increases, $[\text{Ca}^{2+}]_{\text{un}}$ must decrease as dictated by the solubility product (eq 1). Therefore, the curves in Figure 10 are at high $[\text{CaCl}_2]$ values at low total surfactant concentration but drop as total surfactant concentration increases.

The higher the concentration of micelles in solution, the higher the concentration of bound Ca^{2+} . Hence, a higher total Ca^{2+} concentration is necessary for the unbound calcium concentration to permit the solubility product to be exceeded. The minima in Figure 10 occur at the points where the amount of Ca^{2+} bound on micelles begins to account for a significant percentage of the total Ca^{2+} present in solution. At still higher surfactant concentrations, binding dominates, so that virtually all of the Ca^{2+} in the mixture is bound onto the micelles and the hardness tolerance becomes proportional to the total surfactant concentration.

The precipitation boundary for 10% NPE without added NaCl (Figure 8) describes the data well at low NaDS concentrations. In this region, there are so few micelles in solution that binding is insignificant. Therefore, hardness tolerance depends entirely on the value of $[\text{DS}^-]_{\text{mon}}$ calculated by regular solution theory. The agreement between predictions and experiments in this region implies that regular solution theory does an adequate job of calculating monomer-micelle equilibrium, a conclusion reached in other work.^{8,12}

Discrepancies between calculated and experimental values occur around the minimum point in the precipitation boundary, i.e., where the amount of Ca^{2+} bound on micelles becomes an important quantity. For the model to fit the data, a higher value of Ca^{2+} counterion binding (β_{Ca}) would be necessary in this region. However, as NaDS concentration continues to increase, the actual binding approaches the value of β_{Ca} (0.20) which was used in the model. Figure 11 shows the values of β_{Ca} that are required to fit the experimental precipitation data. Binding in mixed electrolyte systems is a complicated process, and presently there are no theories available to describe these results. It has been shown, however, that binding depends on the $\text{Ca}^{2+}/\text{Na}^+$ ratio in solution.^{13,14} It is not surprising, then, that a higher value for β_{Ca} is observed around the minimum of the boundary without added NaCl, since there

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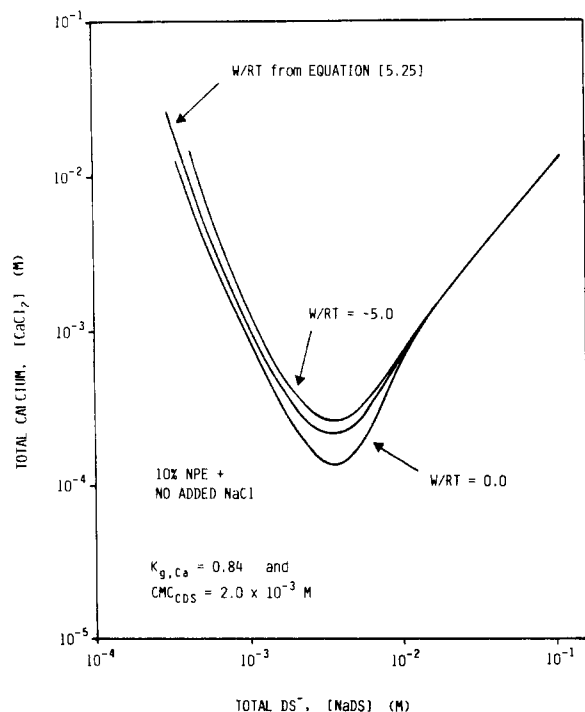


Figure 12. Effect of W/RT on predicted precipitation phase boundaries.

is a relatively high Ca^{2+}/Na^{+} ratio at this point. At the same time, a value of $\beta_{Ca} = 0.20$ predicts the precipitation boundary with 0.02 M added NaCl very well. This is probably due to a lower Ca^{2+}/Na^{+} ratio (because of added NaCl) in the region where binding becomes important.

In order to test the sensitivity of the model to the value of W/RT , Figure 12 compares calculations from the model using $W/RT = -5.00$, $W/RT = 0.0$ (ideal solution), and W/RT obtained from eq 23. This figure shows it is not possible to assume the micelles behave ideally under these conditions because significant errors result. Interestingly, even with an unreasonably low value of $W/RT = -5.0$, the calculated boundary does not agree with experimental results around the minimum. This seems to confirm the fact that the error in this region is the result of using too low a value for calcium binding, β_{Ca} , not of deficiencies in regular solution theory to model mixed micelle formation.

The precipitation boundaries obtained from the model were not sensitive to the value of cmc_{NPE} used. There was essentially no change in calculated quantities in the range $cmc_{NPE} = 30 \times 10^{-6}$ to 55×10^{-6} M. Therefore, for the precipitation boundary without added NaCl, an inadequate description of counterion binding is responsible for the error in the predictions obtained from the model.

Relationship to Previous Work. Fan et al.¹⁵ used a similar approach to that taken here to describe the effect of nonionic surfactant on precipitation of SDS by calcium and magnesium. In that work, several concentrations of added nonionic surfactant were used, whereas we only studied one nonionic surfactant concentration. However, no added monovalent electrolyte was added to those systems, and the monomeric anionic surfactant concentration above the cmc was assumed to be affected only by the added divalent cation (not the monovalent cation).

Nishikido et al.¹⁶ found that the Krafft temperatures of divalent metal dodecyl sulfates was lowered when nonionic

surfactant was added, which corresponds to an increase in hardness tolerance.

Gerbacia¹⁷ measured hardness tolerance in the same four-component system presented here (with a different nonionic surfactant) and demonstrated that hardness tolerance increased as ionic strength was increased, which is the same result given in this study. In that work, the counterion binding of Ca^{2+} was shown to decrease as the Na^{+}/Ca^{2+} ratio increased, consistent with this work.

Noik et al.¹⁸ has presented the entire precipitation boundary for a four-component mixture, but they include butanol rather than nonionic surfactant. In that work, the increase in hardness tolerance, with added butanol, is attributed to a decrease in anionic surfactant monomer concentration.

Shah et al.¹⁹ reported the influence of ethoxylated sulfonates on the hardness tolerance of an anionic surfactant and demonstrated that hardness tolerance increases as the percent of ethoxylated sulfonate increases. Interestingly, they mention that precipitation boundaries merge to follow the same curve at high anionic surfactant concentrations (the same result seen in this study).

The general phenomena of reduction of surfactant monomer concentrations upon mixed micelle formation has been discussed in literature review articles.^{8,20} Several authors^{15,21,22} have identified that mixed micelle formation is the mechanism by which hardness tolerance is increased when nonionic surfactant is added.

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Nomenclature

c_i	concentration of ion i in solution, $kmol/m^3$
$[CaCl_2]$	total concentration of $CaCl_2$ in solution, $kmol/m^3$
$[Ca^{2+}]_b$	concentration of Ca^{2+} bound on micelles, $kmol/m^3$
$[Ca^{2+}]_{un}$	concentration of unbound Ca^{2+} in solution, $kmol/m^3$
cmc	critical micelle concentration, $kmol/m^3$
cmc_{CDS}	cmc of pure $Ca(DS)_2$, $kmol/m^3$
cmc_{DS}	cmc of SDS under various conditions, $kmol/m^3$
cmc_{mix}	measured mixture cmc values, $kmol/m^3$
cmc_{NPE}	cmc of pure NPE, $kmol/m^3$
cmc_{SDS}	cmc of pure NaDS, $kmol/m^3$
$[DS^-]_{mic}$	concentration of DS^- present in micelles, $kmol/m^3$
$[DS^-]_{mon}$	concentration of DS^- present as monomer, $kmol/m^3$
f_{Ca}	activity coefficient of unbound Ca^{2+} in solution
f_{DS}	activity coefficient of monomeric DS^- in solution
I	ionic strength, $kmol/m^3$

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K_3, K_g	constants	P_{SDS}	value of P at the cmc of pure NaDS
K_2	constant, $M^4 C^{-2}$	R	gas constant, 1.987 kcal/(kmol K)
$K_{g,Ca}$	value of K_g when Ca^{2+} is the only counterion present in solution	S	surface charge density of micelle, $C m^{-2}$
$K_{g,Na}$	value of K_g when Na^+ is the only counterion present in solution	S_{Ca}	surface charge density of micelle when Ca^{2+} is the only counterion present in solution, $C m^{-2}$
K_{sp}	solubility product, M^3	S_{Na}	surface charge density of micelle when Na^+ is the only counterion present in solution, $C m^{-2}$
$[Na^+]_b$	concentration of Na^+ bound on micelles, $kmol/m^3$	T	absolute temperature, K
$[Na^+]_{eq}$	concentration of Na^+ in solution which would have the same effect on the cmc of the anionic surfactant as the actual mixture of counterions in solution, $kmol/m^3$	W	regular solution theory interaction parameter, kcal/kmol
$[Na^+]_{tot}$	total concentration of Na^+ ions in solution, $kmol/m^3$	X_{DS}	mole fraction of DS^- in the micelle
$[Na^+]_{un}$	concentration of unbound Na^+ in solution, $kmol/m^3$	X_{NPE}	mole fraction of NPE in the micelle
$[NaCl]$	total concentration of NaCl in solution, $kmol/m^3$	Y_{DS}	mole fraction of DS^- in the monomer
$[NaDS]$	total concentration of NaDS in solution, $kmol/m^3$	z_i	valence of species i in solution
$[NPE]$	total concentration of NPE in solution, $kmol/m^3$	β_{Ca}	fractional counterion binding of Ca^{2+} on mixed surfactant micelle
$[NPE]_{mic}$	concentration of NPE present in micelles, $kmol/m^3$	β_{Na}	fractional counterion binding of Na^+ on mixed surfactant micelle
$[NPE]_{mon}$	concentration of NPE present as monomer, $kmol/m^3$	β_{Ca}°	fractional counterion binding of Ca^{2+} on micelle in absence of nonionic surfactant
P	term related to Φ_0	β_{Na}°	fractional counterion binding of Na^+ on micelle in absence of nonionic surfactant
P_{CDS}	value of P at the cmc of pure $Ca(DS)_2$	γ_{DS}	activity coefficient of DS^- in the micelle
		γ_{NPE}	activity coefficient of NPE in the micelle

Registry No. SDS, 151-21-3; NPE, 9016-45-9; $CaCl_2$, 10043-52-4; NaCl, 7647-14-5.

Formation of Metal-Oxygen Surface Compounds on Copper, Silver, and Gold Electrodes via Electrochemical Oxidation of Hydroxide Ion and Autoxidation in Acetonitrile

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The oxidation of hydroxide ion in acetonitrile at copper, silver, gold, and glassy carbon electrodes has been characterized by cyclic voltammetry. In the absence of bases the metal electrodes are oxidized to their respective cations (Cu^+ , Ag^+ , and Au^+) at potentials that range from -0.2 V vs SCE for Cu to $+1.3$ V for Au. At glassy carbon OH^- is oxidized to $O^{\cdot-}$ ($+0.35$ V vs SCE) and then to $\cdot O$ by an ECE mechanism. In contrast, with freshly polished metal electrodes the oxidation of OH^- to $O^{\cdot-}$ and $\cdot O$ is facilitated via formation of metal-s/oxygen-p covalent bonds to give a series of surface compounds (MOH, (MO) $^-$, MOM, and MOOM). The shift to less positive oxidation potentials has been used to obtain an estimate of the metal-oxygen covalent bond energies (about 40–60 kcal). On the basis of the redox thermodynamics and the substrate reactions we conclude that the oxygen in these metal-oxygen surface compounds is essentially neutral (atomic $\cdot O$) and stabilized via covalent s-p bonds with neutral-charge metal atoms. Concurrent reduction of Cu^+ plus O_2 , and of Ag^+ plus O_2 , yields a series of surface compounds (MOM, MOOM, and (MO) $^-$) that parallel those that result from OH^- oxidation at the metal surfaces.

In aprotic solvents the electrochemical oxidation of hydroxide ion to hydroxyl radical ($\cdot OH$) and its anion ($O^{\cdot-}$) is facilitated by lower solvation energy (the $\cdot OH/OH^-$ couple has a standard reduction potential of $+1.65$ V vs SCE in water and $+0.68$ V in acetonitrile).¹ In the presence of transition-metal ions OH^- is oxidized at significantly less positive potentials because the product species are stabilized via the formation of metal-oxygen covalent bonds (unpaired d-electron with unpaired p-electron of $\cdot OH$ and $O^{\cdot-}$). For MeCN solutions with Mn-

(OPPh₃)₄²⁺, Fe(OPPh₃)₄²⁺, and Co(OPPh₃)₄²⁺, the respective shifts (ΔE) in the oxidation potential for OH^- are -1.08 , -0.70 , and -0.71 V.¹

Because the coinage metals (Cu, Ag, and Au) have a $d^{10}s^1$ valence shell, electrochemical oxidation of OH^- at their surfaces should be facilitated via covalent bond formation with $\cdot OH$ and/or $O^{\cdot-}$. These metals are used as oxygen activation catalysts for several industrial processes (e.g., Ag/O_2 for the production of ethylene oxide),²⁻¹⁰ and their

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