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Phenomena in Mixed Surfactant Systems

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FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

PREFACE

MIXED SURFACTANT SYSTEMS are of scientific interest as well as technological value. Surfactants are used in numerous applications, including detergents, flotation, enhanced oil recovery, surface-wetting modification, foaming control, emulsification, controlled-release, and surfactant-based separation processes. Commercial surfactants are almost always composed of mixtures of surfactants. The production of single-component surfactants is generally expensive, and the properties of monoisomerically pure surfactants are rarely better than the surfactant mixtures. Often, the mixture may exhibit superior behavior compared to the pure surfactant components. It is an enormous challenge to understand the interactions between different surfactant components in the various applications in which surfactants are used.

This book presents chapters that discuss research on surfactant mixture behavior from a variety of active researchers around the world. I am grateful to the organizing committee of the symposium on which this book is based for allowing me to organize and chair sessions on this topic and especially to Josip Kratohvil for organizing the logistics of the program in such an efficient fashion.

I thank departmental staff Polly Dvorak, Sherry Childress, and Rick Wheeler for their efficient help with correspondence associated with the book. Kevin Stellner and Jim Rathman helped me by proofreading the first draft of the manuscripts. Cuong Nguyen provided the figure upon which the drawing on the cover of this book is based. I would also like to thank the authors who participated in this effort and the reviewers who must remain anonymous. Finally, I would like to thank my colleagues and graduate students at the University of Oklahoma for stimulating interactions and for helping to keep my perspective fresh and my interest in surfactants high.

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CONTENTS

MIXED MICELLE FORMATION

MIXED MONOLAYER FORMATION
AT AIR AQUEOUS SOLUTION INTERFACE

STUDIES OF MIXED MICELLES
AND MIXED MONOLAYERS

MIXED SURFACTANT ADSORPTION
ON SOLID SURFACES

FORMATION AND BEHAVIOR
OF OTHER SURFACTANT-AGGREGATE STRUCTURES

FUTURE PERSPECTIVES

An Overview of Phenomena Involving Surfactant Mixtures

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The effect of using mixtures of surfactants on micelle formation, monolayer formation, solubilization, adsorption, precipitation, and cloud point phenomena is discussed. Mechanisms of surfactant interaction and some models useful in describing these phenomena are outlined. The use of surfactant mixtures to solve technological problems is also considered.

Surfactants used in practical applications essentially always consist of a mixture of surface-active compounds. Isomerically pure surfactants are often expensive to produce and generally have only a small potential advantage in performance over the less expensive surfactant mixtures. In many applications, mixtures of dissimilar surfactants can have superior properties to those of the individual surfactant components involved. These synergistic properties of surfactant mixtures have provided impetus for much of the research on interactions between surfactants.

Individual surfactants vary in their tendency to form aggregated structures. Examples of such aggregates are micelles, precipitate, and monolayers. In solutions containing mixtures of surfactants, the tendency to form aggregated structures can be substantially different than in solutions containing only the pure surfactants involved. For example, precipitation may not occur in a surfactant mixture whose components individually precipitate when present as single components. The tendency for components to distribute themselves between the unaggregated state and an aggregate may vary from component to component for mixtures. Therefore, for

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example, the surfactant composition of a micelle may differ greatly from that of the surfactant monomer with which it is in equilibrium. This is important because the processes of interest may depend only on either monomer composition or on aggregate composition. For example, adsorption of surfactant on solids such as minerals depends only on monomer composition and concentration, not micellar properties. On the other hand, solubilization of compounds into micelles depends only on micellar composition.

The surfactant technologist needs to be able to predict and manipulate the tendency for surfactant mixtures to form aggregates, the properties of these aggregates, and the distribution of surfactant components between monomer and aggregate. A central theme of this paper is that mixtures of surfactants can achieve great synergisms in various processes by manipulation of the relative tendency to form various aggregated structures. Often, the formation of a certain aggregate will inhibit the formation of a less desirable aggregate. For example, addition of nonionic surfactants to anionic surfactants enhances the formation of micelles, resulting in a reduced tendency for the anionic surfactant to precipitate.

This overview will outline surfactant mixture properties and behavior in selected phenomena. Because of space limitations, not all of the many physical processes involving surfactant mixtures can be considered here, but some which are important and illustrative will be discussed: these are micelle formation, monolayer formation, solubilization, surfactant precipitation, surfactant adsorption on solids, and cloud point phenomena. Mechanisms of surfactant interaction will be discussed, as well as mathematical models which have been shown to be useful in describing these systems. Practical applications will be covered as part of the consideration of individual phenomena.

This overview will attempt to outline the state of current knowledge, without much comment on the areas in which further research is needed, the direction the field is taking, and the impact of the other chapters in this book. These are reserved for the Future Perspectives Chapter (last chapter of the book).

Micelle Formation

The structure and thermodynamics of formation of mixed micelles is of great theoretical interest. Micelles are also present and often integrally involved in practical processes. For example, in a small pore volume surfactant flooding process (sometimes called micellar flooding), the solution injected into an oil field generally contains 5-12 weight % surfactant (1) and the surfactant is predominately in micellar form in the reservoir water. In detergency, solubilization can be important (2), so micelles are generally present in the detergent solution. In micellar-enhanced ultrafiltration, a separation technique to remove dissolved organic from water (3), micelles effect the separation.

Monomer-Micelle Equilibria. The distribution of surfactant components between micelles and monomeric state in aqueous solutions depends on surfactant structures as well as on overall solution composition. For example, for a binary system of surfactants A and B in solution, the micelle may contain 50 mole % A/50 % B while the monomer may be 90 % A/10 % B. Since either the monomer or the micelle composition may be crucial to behavior of the system, the ability to predict the relative distribution of surfactant components between monomer and micelle, given the overall solution composition, is an important one.

Except for some anionic/cationic surfactant mixtures which form ion pairs, in a typical surfactant solution, the concentration of the surfactant components as monomeric species is so dilute that no significant interactions between surfactant monomers occur. Therefore, the monomer-micelle equilibria is dictated by the tendency of the surfactant components to form micelles and the interaction between surfactants in the micelle. Prediction of monomer-micelle equilibria reduces to modeling of the thermodynamics of mixed micelle formation.

The behavior of mixed micelles is commonly approximated by using the pseudo-phase separation model (4). This considers the micelles to be a separate thermodynamic phase in equilibrium with the monomer. Monomer-micelle equilibria then becomes analogous to vapor-liquid equilibria; i.e., in both cases a dilute phase with little intermolecular interaction is in equilibrium with a concentrated phase in which intercomponent interaction can be significant. The vast array of solution thermodynamic models developed for mixing in macroscopic phases can be utilized for mixed micelles using the pseudo-phase approach. The pseudo-phase separation model is a good approximation when the micellar aggregation number is greater than about 50 (5), which is commonly the case for surfactants of commercial importance.

Ideal Mixed Micelles. The Critical Micelle Concentration (CMC) is the lowest surfactant concentration at which micelles form; the lower the CMC, the greater the tendency of a system to form micelles. When the total surfactant concentration equals the CMC, an infintesimal fraction of surfactant is present as micelles; therefore, the CMC is equal to the total monomer concentration in equilibrium with the micellar pseudo-phase. The CMC for monomer-micelle equilibrium is analogous to the dew point in vapor-liquid equilibrium.

The total monomer concentration of a binary mixture of two similarly structured surfactants of like charge (an ideal system) lies between the CMC's of the individual surfactants involved for total surfactant concentrations at or above the mixture CMC. Analogously, the vapor pressure of a mixed ideal liquid is intemediate between the vapor pressures of the components of which it is composed, whether there is substantial liquid present or the system is at the dew point (where an infintesimal amount of liquid is present).

For a binary system of surfactants A and B, the mixed micelle formation can be modeled by assuming that the thermodynamics of mixing in the micelle obeys ideal solution theory. When monomer and micelles are in equilibrium in the system, this results in:

$$C_M = CMC_A CMC_B / (y_A CMC_B + y_B CMC_A) \quad (1)$$

$$x_A = y_A C_M / CMC_A \quad (2)$$

where C_M is the total monomer concentration, CMC_A or CMC_B are the CMC values for the individual components, y_A or y_B are the monomer mole fractions of A or B, respectively, and x_A or x_B are the micellar mole fractions of A or B, respectively. The mole fractions are on a surfactant-only basis: i.e., y_A is the moles of A in monomer/ total moles of surfactant monomer. Therefore, $y_A + y_B = 1$ and $x_A + x_B = 1$. The values of CMC_A and CMC_B are needed at the same added electrolyte concentration as the mixture. If the total surfactant concentration in the mixed system is at the CMC (infintesimal number of micelles present), then C_M from Equation 1 is equal to the mixture CMC.

The mixture CMC is plotted as a function of monomer composition in Figure 1 for an ideal system. Equation 1 can be seen to provide an excellent description of the mixture CMC (equal to C_M for this case). Ideal solution theory as described here has been widely used for ideal surfactant systems (4,6-18). Equation 2 can be used to predict the micellar surfactant composition at any monomer surfactant composition, as illustrated in Figure 2. This relation has been experimentally confirmed (15-18). As seen in Figure 2, for an ideal system, if the ratio $x_A/y_A < 1$ at any composition, it will be so over the entire composition range. In classical phase equilibrium thermodynamic terms, the distribution coefficient between the micellar and monomer phases is independent of composition.

Equations 1 and 2 provide the ability to make a priori predictions of mixed micellar behavior for binary systems of similar surfactants (easily extended to more than 2 components(10)). No mixture data is necessary to use these equations. If the overall concentration of the individual surfactants in solution are known, Equations 1 and 2 can be combined with a material balance to

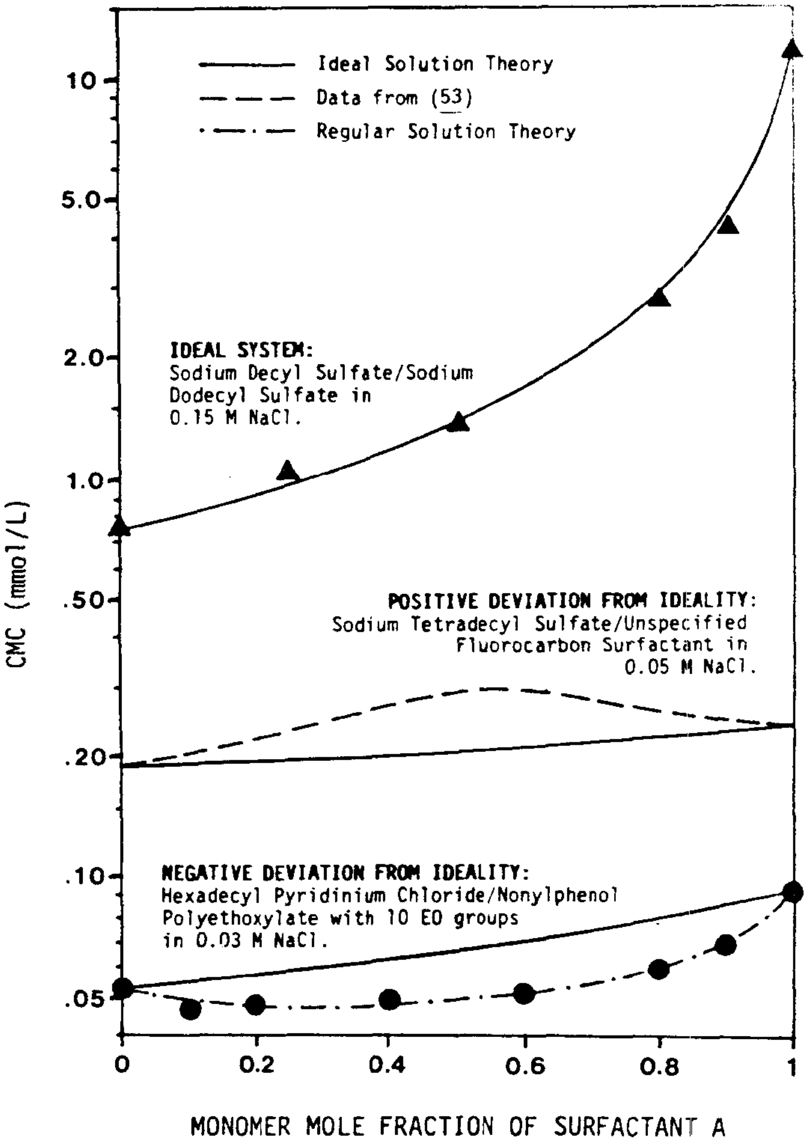

Figure 1. Mixed surfactant CMC values at 30°C (fir
surfactant listed is surfactant A).

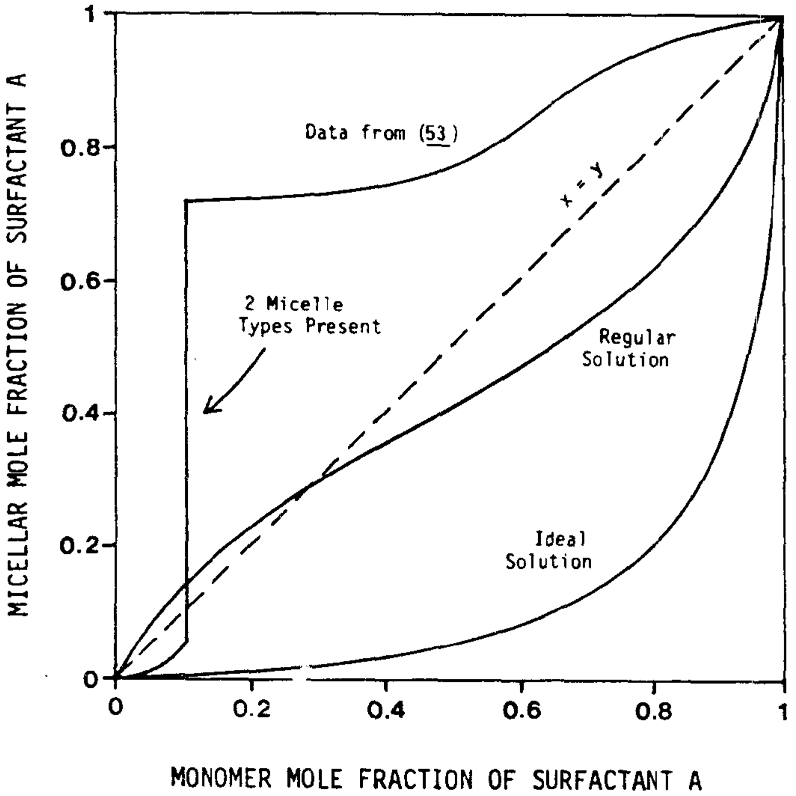

Figure 2. Monomer-micelle equilibrium for systems in Figure 1.

calculate the concentration of each surfactant in monomeric form and micellar form. This predictive capability is a powerful tool.

Mixed Micelles Showing Negative Deviation from Ideality. In an aqueous solution containing a mixture of [1] an ionic surfactant and a nonionic surfactant, or [2] an anionic surfactant and a cationic surfactant, or [3] a zwitterionic surfactant and an anionic surfactant, the CMC of the mixed surfactant system exhibits a CMC which is substantially less than that predicted by Equation 1 (9,12,18-37). This means that the mixed micelle formation is enhanced and that the mixing process in the micelle shows negative deviation from ideality. This is demonstrated for a cationic/nonionic system in Figure 1.

If the interactions between surfactants in the mixed micelle can be described by regular solution theory, the following equations apply for a binary system:

$$1 = \frac{y_A x_B CMC_B \exp[W(x_A^2 - x_B^2)/RT]}{y_B x_A CMC_A} \qquad (3)$$

$$C_M = x_B CMC_B \exp[W x_A^2/RT])/y_B \qquad (4)$$

where W is the interaction parameter, R is the gas constant, and T is the absolute temperature. Once again, C_M from Equations 3 and 4 is equivalent to the mixture CMC when the total surfactant concentration is at the CMC.

Solution of Equation 3 at a given monomer composition (y_A, y_B) result in predictions of values of the the micellar composition (x_A, x_B). Then, solution of Equation 4 predicts the value of the total monomer concentration (C_M). However, this model does not give *a priori* predictions. The adjustable parameter W is needed. If a mixed CMC value is available, Equations 3 and 4 can be used to determine W by substituting the measured CMC values for C_M. Then the model can predict monomer-micelle equilibrium at any other system composition. In fact, if multiple mixed CMC values are available, a regression analysis is normally done to determine the best value of W over the entire range of measurements. Equations 3 and 4 have been widely used to model CMC data for mixed surfactant systems showing negative deviations from ideality (12,25-36). Equations 3 and 4 have been used to model the mixed cationic/nonionic system in Figure 1. The model can be seen to describe the data very well. The model can be extended to include more than two surfactant components (12). The predicted micellar compositions from Equations 3 (as illustrated in Figure 2) have also been experimentally confirmed (25,34).

The more negative the value of W (or W/RT which is dimensionless), the greater the degree of nonideality of the system. When W = 0, the system is ideal and

Equations 3 and 4 reduce to Equations 1 and 2. From tabulations of literature values of W/RT, some general conclusions about degree of interactions between dissimilar surfactants can be reached (31-34):

1. The deviation from ideality for binary pairs of surfactants increases in the order cationic/nonionic, anionic/nonionic, anionic/cationic.

2. The deviation from ideality decreases as added electrolyte concentration increases.

3. For an ionic/nonionic system, where the nonionic is a polyethoxylate, the greater the degree of polymerization of the polyoxyethylene hydrophilic group, the greater the deviation from ideality.

4. The deviation from ideality of a zwitterionic/anionic system can vary widely, from a value typical of a cationic/nonionic system to nearly that of a anionic/cationic system.

5. The deviation from ideality decreases as temperature increases for ionic/nonionic systems.

Average values of W/RT from tabulated literature (33) at approximately room temperature and with no added electrolyte are −2.7 for cationic/nonionic systems; −3.4 for anionic/nonionic systems; and −19 for anionic/cationic systems.

In order to illustrate the effect of micellar nonidealities of mixing on total surfactant monomer concentrations and micelle compositions in a system at the CMC, consider a hypothetical binary surfactant pair, A and B. Assume CMC_A = 1 mM and CMC_B = 2 mM. For a equimolar mixture of A and B as monomer, the values of C_M and micelle compositions are tabulated in Table I at various values of W/RT.

Table I. Total Monomer Concentrations and Micellar Compositions for a Binary Surfactant System at Various Deviations from Ideality

W/RT	C_M (mM)	x_A
0 (ideal system)	1.33	0.667
−2	0.83	0.586
−5	0.40	0.550
−25	0.0027	0.513

As seen in Table I, for the ideal system, the values of C_M are between the CMC values of the two pure surfactant components. However, the systems showing negative deviations from ideality could have mixture monomer concentration values lower than either pure surfactant. In fact, for a W/RT of −25 (possible for an anionic/cationic mixture), the total surfactant monomer concentration is less than 1% of that of either pure component. Enormous monomer concentration depressions are possible in these systems exhibiting negative deviations from ideality. When it is desirable to minimize monomer concentrations, these mixture effects can be useful.

As also seen in Table I, the micellar composition can be affected substantially by nonideality. In fact, azeotropic behavior in the monomer-micelle equilibrium is possible for these nonideal systems; i.e., as the monomer composition varies from pure A to pure B, the micelle can vary from $x_A > y_A$ to $x_A = y_A$ (azeotrope) to $x_A < y_A$. This azeotrope formation is illustrated for the cationic/nonionic system in Figure 2, where an azeotrope forms at $x_A = y_A = 0.3$. The minimum CMC for a mixture corresponds to the azeotropic composition if an azeotrope is present (32,37). For an ideal system, azeotropic behavior is not observed.

Systems with low monomer concentrations are of value when micelles are participating in useful processes directly (e.g., solubilization), where monomer is "wasted" surfactant. However, often the monomer composition as well as total monomer concentration is important, when the monomer is participating in important processes and each component interacts differently (e.g., adsorption). The surfactant combinations discussed here can result in low monomer concentrations and the model outlined can predict the monomer concentration of each surfactant species.

Mechanisms of Nonideality. Similarly structured surfactants mix ideally because the environments for the hydrophobic and the hydrophilic groups in the mixed micelle are similar to those in the pure component micelle. When a nonionic surfactant is inserted into a micelle composed of ionic surfactant, the nonionic hydrophilic group separates charged ionic hydrophilic groups from each other, reducing the electrical repulsion in the Stern layer of the micelle (18-20,23,29,31,38,39). In other words, the charge density at the micelle surface is reduced, which reduces the absolute value of the electrical potential there (40). It requires less work to insert a ionic surfactant into this mixed micelle than into a pure ionic micelle because of this reduced electrical repulsion. This charge separation effect causes the mixed micelle to form more easily than an ideal mixed micelle and so the CMC is less than that of an ideal mixed micelle.

In addition to electrostatic forces, another contribution to nonideality is due to the formation of oxonium salts in the hydrophilic group of the nonionic polyethoxylated surfactant (21,23). These result from the association of cations (e.g., H^+ or Na^+) from solution with the negatively polarized ether oxygen atoms. The resulting net positive charge of the nonionic surfactant can also contribute to the stabilization of anionic/nonionic mixed micelles. This is the probable explanation for the generally greater nonideality of the anionic/nonionic systems over the cationic/nonionic systems. However, the number of oxonium ions formed is probably small, as evidenced by the similarity of W/RT for these two types of systems. If an ionic surfactant has a benzene ring in its hydrophobic group, the polyethoxylate group in a nonionic surfactant can interact with the aromatic ring in ionic/nonionic mixed micelles, resulting in an additional stabilizing force for these mixed micelles (41,42). Electrostatic stabilization via the charge separation effect is the main cause of mixed ionic/nonionic surfactant deviations from ideality, with oxonium ion formation and benzene/ethylene oxide group interactions being a secondary effect. The anionic/cationic systems exhibit the ultimate in electrostatically induced nonidealities, with the oppositely charged surfactants combining to form extremely stable micelles.

In a mixed micelle composed of a polyethoxylated nonionic and an anionic surfactant, solubilization results (to be discussed in a later section) indicate that for short polyoxyethylene chains, the nonionic hydophobic groups are less compact than in a pure nonionic micelle because of the space taken up by the anionic hydrophilic group. That is, the volume per ethylene oxide group is greater in the region outside the palisade layer in the mixed case. However, for longer polyoxyethylene chains, the mixed micelle is more compact than a pure nonionic micelle. This latter effect is probably due to the specific interactions between the anionic head group and the oxonium ion of the polyethoxylate chain reducing the extension of the long polyethoxylate chain into solution, which overcomes the steric effect of the space occupied by the anionic hydrophilic groups. As a result, a higher fraction of the ethylene oxide groups is in close proximity to the anionic head group (perhaps wrapped around it), causing the area per total hydrophilic groups in this region to be potentially higher in the mixed case than for either pure surfactant micelle. If the micelle shape did not change drastically, this would result in a lower aggregation number than calculated by a mole fraction weighted average of the pure component values. Anionic/nonionic mixed micelles have been reported to have an aggregation number intermediate between or less than the two pure component micelles (43,44), consistent with this interpretation.

Cationic/nonionic mixed micelles do not seem to show this compaction effect (at least as readily) as