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# Comprehending The Concepts Of Surfactant System Models, Theories Of Mixing, And Mixed Micelle

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**Abstract-This article delves into the intricacies of surfactant systems, focusing on the comprehensive understanding of models employed to describe their behavior, theories governing mixing phenomena, and the formation of mixed micelles. The study amalgamates theoretical frameworks with practical insights to provide a holistic perspective on surfactant interactions. The exploration begins by elucidating various surfactant system models, ranging from idealized to non-ideal representations. The discussion encompasses key concepts such as regular solution theory, mass action model, and phase separation model. By scrutinizing these models, the research aims to establish a foundational understanding of the surfactant interactions. A pivotal aspect of the study revolves around mixed micelles, exploring their formation, and stability in surfactant systems**

**Keywords- Micellisation, CMC, Surfactant, Mass action model.**

## I.INTRODUCTION

Surfactants, short for surface-active agents, exhibit amphiphilic properties, featuring hydrophilic (water-attracting) and hydrophobic (water-repelling) components. This unique structure allows surfactants to reduce the surface tension of liquids and facilitate the formation of micelles in solution. Micelles are aggregates where hydrophobic tails cluster together to form a core shielded by the hydrophilic heads. are of significant importance in a wide range of applications, encompassing emulsification, detergency, medicines, and increased oil recovery. [1]

### Mixed micelles

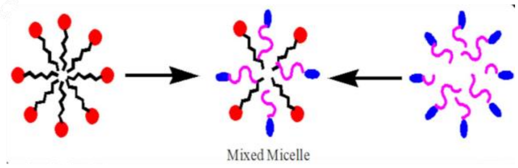

Figure 1: Formation of mixed micelles

The surfactants used in a multitude of industrial products, processes and other practical applications almost always consist of a mixture of surfactants. Therefore, mixed surfactant systems are encountered in nearly all practical applications of surfactant. micelles can have different sources of origin. Often, it could be because of the natural polydispersity of the commercial surfactants or due to the presence of impurities associated with the course of manufacture. These mixtures are less expensive to produce than their isomerically pure counterparts and often exhibit better physicochemical properties than single pure surfactants. Mixed surfactant systems that contain surfactants with different structures are of great theoretical and industrial interest. [2,3]

Mixed micellar systems could also arise due to the deliberate mixing of different surfactant types to exploit synergistic behaviour in mixed systems or to have multiple qualities belonging to individual components in one mixture. Although the incorporation of solubilizates into surfactant micelles also results in the formation of mixed micelles;

generally, the term mixed micelle is used to represent a micelle that is composed of surfactants that are themselves capable of forming micelles.

Mixed surfactants also micellise after critical micelle concentration, like single surfactants. The tendency to aggregate is guided by their synergistic (attractive) and antagonistic (repulsive) interactions, and this is reflected in their CMC values compared to those of their components. Mixed surfactant systems, as is the case with single surfactant systems, exhibit preferential adsorption at interfaces at low concentrations forming mixed monolayers leading to lowering of surface tension. Surfactant monomers undergo co-operative self-association in the bulk at concentrations above CMC to form mixed micelles. Different techniques have been used to collect structural information on mixed micelle formation and to obtain their critical micelle concentration (CMC). [4,5]

Both ideal and nonideal mixing can occur during the formation of mixed micelles. Since the hydrophobic effect, which drives the aggregation process, is not specific to the surfactant head group, the formation of randomly mixed surfactant aggregates will be favoured, leading to the ideal mixing component. But in the case of mixtures comprising different surfactants, the electrostatic repulsion between the head groups leads to nonideal mixing in the aggregate. Mixing of dissimilar surfactants often leads to synergistic behaviour due to the nonideal interactions of the components, and this results in substantially lower CMCs and interfacial tensions than the individual surfactant systems. This has led to both theoretical and practical interest in the understanding of the behaviour of mixed surfactant systems so that they could be exploited in such fields as detergency, enhanced oil recovery, etc.

Mixed micellar systems involving a wide range of surfactant types have been studied, and these include combinations of nonionic, anionic and cationic systems and their binary mixtures with zwitterionic surfactants. [6,7]

## II.POLYMER-SURFACTANT INTERACTION

The wide variety of applications of polymer-surfactant mixed systems in aqueous solutions has thus motivated both chemists and biologist s olutions at a concentration above a critical concentration (CMC), surfactant molecules tend to aggregate and form micelles. In the presence of large polymers, surfactant micelles can form self-assembled complexes [Figure 2]. These complexes play a fundamental role in a broad range of industrial applications, including colloid stabilisation and detergency, and are increasingly found in commercial surfactant formulations such as foods, pharmaceuticals, cosmetics, textiles, polymers, paints, and paper.

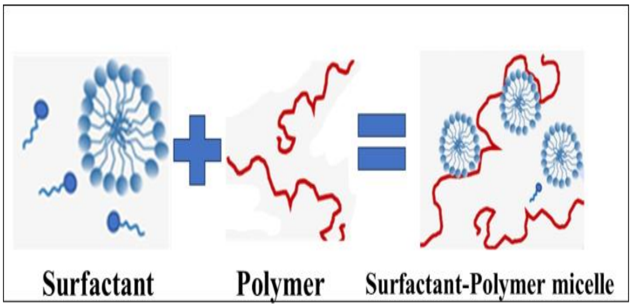

Figure 2: Formation of mixed micelles

Water-soluble polymers are often included in commercial surfactant formulations. They modify both the surface behaviour and the rheology of the bulk solution. These effects may become very large when the polymer/surfactant interaction is sufficiently strong. The most common pattern of behaviour for uncharged polymers and surfactants is for the surfactant to form micelles on the polymer chain at a concentration below the critical micelle concentration of the surfactant on its own. This changes the conformation of the polymer chain in solution by a significant amount if the surfactant is charged because it endows the polymer with polyelectrolyte qualities.

This alone will cause major changes to the rheological properties. The surfactant micelles may also cross-link the polymer molecules, and the resulting gel-like structure makes the solution very viscous. The aggregation in the bulk solution has been relatively well studied by various techniques, including small-angle neutron scattering. However, the behaviour of polymer/surfactant mixtures at interfaces has hardly been studied, mainly because of a lack of experimental techniques. The interaction between polyelectrolytes and surfactants has been studied extensively due to various applications of these systems, ranging from personal care products and pharmaceuticals to industrial usages. [8,9]

## III.SURFACTANT MIXING THEORIES

### Ideal mixing theory

Clint [10] has proposed an ideal mixing theory using a phase separation model to describe the phenomenon of mixed micelle formation. This model treats the micelles as a separate phase from that of dissolved surfactant unimers and proposed that the mixed micelle is an ideal solution of two surfactants. It predicts the mixture cmc, micelle composition, and unimer concentration.

The cmc values for the mixed surfactant system ($c_{12}$) can be calculated theoretically using Clint's equation. [11]

$$\frac{1}{C_{12}} = \frac{\alpha_1}{C_1} + \frac{(1-\alpha_1)}{C_2}$$

Where $C_{12}$, $C_1$ and $C_2$ are the cmc values of the mixture, surfactant 1 and surfactant 2 respectively. $\alpha_1$ is the mole fraction of surfactant 1 and $\alpha_2$ (i.e $1 - \alpha_1$) is the mole fraction of surfactant 2 in solution, respectively. Although it provides the description of nearly ideal mixing, it fails to predict either the cmc or monomer concentrations of surfactant mixtures differing in head groups, where nonideal mixing is more common.

### Nonideal mixing theory

When the two surfactants forming the mixed micelle have different head group, the CMC cannot be predicted by ideal theory. Rubingh [12] has predicted the CMC of mixed micelle using regular solution theory is approach provides a way to ideal enthalipic as well as entropic factors on mixed micelle formation. A comparison of the prediction of the theory with experimental data reveals that the nonideal mixed micelle theory provides a much better description than the ideal mixing theory.

This observation regarding interaction among surfactant monomers is quantified in terms of interaction parameters ($\beta^m$) accordingly when

(i) $\beta^m = 0$, the two surfactants form an ideal mixture,

(ii) $\beta^m$ = negative, the interactions to be strongly attractive and mixed micelles are stabilised electrostatically.

(iii) $\beta^m$ = positive, indicates non-compatibility of constituent surfactant species and is thus a measure of antagonistic behaviour of surfactant mixture.

According to this theory, the molecular interactions between two surfactants in micelles or at an interface are commonly measured by the so-called β parameters, which are conveniently obtained from critical micelle concentration data or from a surface (or interfacial tension). The micellar interaction parameter is obtained by use of the following equations.

$$\frac{(X_1)^2 \ln[(\alpha_1 C_{12} / X_1 C_1)]}{(1-X_1)^2 \ln[(1-\alpha_1)C_{12} / (1-X_1)C_2]} = 1 \qquad \text{(A)}$$

$$\beta^m = \frac{\ln[(\alpha_1 C_{12} / X_1 C_1)]}{(1-X_1)^2} \qquad \text{(B)}$$

Where $X_1$ is the mole fraction of surfactant 1 in the total surfactant in the mixed micelle and $C_1^M$, $C_2^M$ and $C_{12}^M$ are the critical micelle concentrations (cmcs) for surfactant 1, surfactant 2 and their mixture, respectively at the solution mole fraction $\alpha_1$. Equation A is solved iteratively using a computer program for $X_1$, which is then substituted into Equation B to evaluate $\beta^m$.

### Synergism or Negative Synergism

The efficiency of surface tension reduction by a surfactant has been defined as the solution phase surfactant concentration required producing a given surface tension (reduction). Synergism in this respect is present in an aqueous system containing two surfactants when a given surface tension can be attained at a total mixed surfactant concentration lower than that required of either surfactant itself. Negative synergism is present when it is attained as a higher mixed surfactant concentration than that required of either surfactant by itself.

Synergism in this respect is present when the CMC in an aqueous medium of any mixture of two surfactants is smaller than that of either of the individual surfactants. Negative synergism is present when cmc of the mixture is larger than the CMC of either surfactant of the mixture. According to Rubingh's approach, [12] the micellar interaction parameter $\beta^m$ should be constant over an entire range of composition behaviour has been found to be valid in the case of anionic/nonionic surfactant mixtures of NaOL/$C_{10}(EO)_6$ and SDS/$C_9PhE_{10}$.[13] Rubingh's regular solution theory is helpful due to its simplicity and application to other phenomena. This nonideal solution treatment has been used by many researchers all over the world for the analysis of binary surfactant mixtures. [14 – 16]

Although Rubingh's treatment has been extensively used, it has a few drawbacks,

- The interaction parameter $\beta^m$ is considered to be independent of temperature and micellar composition, but it has been found to be substantially temperature and composition-dependent.
- Meaningful values of $\beta^m$ have not been realised for some anionic/cationic surfactant mixtures. Contrary to expectations, positive $\beta^m$ values have been obtained at all mole fractions of the anionic/cationic surfactant combination.
- This theory cannot uniquely account for the interactional features of surfactants in the mixed micelles.
- If the regular solution theory applies to ionic/nonionic mixed micelles, the effective degree of counterion binding must be proportional to the micelle's mole fraction of ionic surfactant, but this is contrary to the experimental observations. [17,18]

The micellar interaction parameter evaluated using Rubingh's theory accounts well for the headgroup/headgroup interactions.

Maeda [19] suggested that besides the electrostatic interactions, the chain/chain interaction is also important and suggested a relationship by which chain/chain interaction can be computed. This chain/chain interaction becomes important in the mixed micelles when the hydrophobic group chain lengths are different. Maeda extracted a contribution, $B_1$, which accounts for the standard free energy change when an ionic monomer replaces a nonionic pure micelle; in addition to another interaction parameter, $B_2$ (an analogue of the familiar interaction parameter 'β' in the regular solution approach) for mixed micelles. According to this approach, the thermodynamic stability ($\Delta G_m$) is defined as a function of mole fraction of ionic component ($X_2$) by

$$\frac{G_{mic}}{RT} = B_0 + B_1X_1 + B_2X_1^2 \qquad \text{(C)}$$

$$B_0 = \ln C_1 \qquad \text{(D)}$$

($C_1$ is the cmc of the nonionic surfactant)

$$B_1 + B_2 = \ln\left(\frac{C_2}{C_1}\right) \qquad \text{(E)}$$

($C_2$ is the cmc of the ionic surfactant)

$$B_2 = -\beta^m \qquad \text{(F)}$$

Where all the quantities are on the unitary scale, one can evaluate $B_1$ from the above expressions and hence $\Delta G_m$.

## IV.SURFACTANT SYSTEM MODELS

### 1.Mass action model

In this model, the micelle and monomeric species are considered to be in association-dissociation equilibrium, and the law of mass action can be applied. According to this model, the micellisation is considered as a stepwise process, and the micelles are not monodisperse, but there is a distribution of aggregation numbers of micelles or micelles that are polydisperse. In the application of the mass-action model, it is essential to know every association constant over the whole stepwise association from monomer to micelle, which is almost impossible experimentally. Therefore, this model has limitations in that it considers only one species of micelle, i.e. it assumes monodispersity of micelle size. This model was originally applied mainly to ionic surfactants, but later on, Corkill et al. [20] used it to nonionic surfactants too.

According to this principle, the concentrations of monomer and micelle above CMC are interdependent. An increase in monomer concentration increases micellar concentration and vice-versa in accordance with the following equilibrium

$$n\,(S^- \text{ or } S^+ \text{ or } S) \overset{K_M}{\rightleftharpoons} (S_n^- \text{or } S_n^+ \text{or } S_n) \qquad \text{(G)}$$

where $S^-$ or $S^+$ or S = micelle; n = aggregation number, and

$K_M$ = micellisation constant with the free energy of micellisation $\Delta G_M^o = RT \ln K_M$.

At CMC, by conceptual approximation, the free energy of micellisation expressed per mole of monomer unit $\Delta G_m^o = \Delta G_M^o / n$

is given by the relation,

$$\Delta G_m^o = RT \ln CMC \qquad \text{(H)}$$

Considering counterion binding to ionic micelles, equation (H) is modified to

$$\Delta G_m^o = (1+f)RT\ln CMC \quad \text{(I)}$$

where f = fraction of counterion bound to a micelle, For nonionic surfactants, f = 0 and equation (I) is reduced to equation (H).

$\Delta G_m^\circ$ is the measure of the standard free energy change for the transfer of one mole of surfactant from solution to micellar phase.

### 2.Phase separation model

This model considers the micelle as a separate phase. The monomer concentration at and above cmc remains nonvariant; with increasing surfactant concentration above cmc, micelles are only formed. This is like the solubility of a substance where, above the solubility limit, the excess amount separates out as the insoluble phase. The micellar pseudophase, on the other hand, remains in solution. Based on the phase equilibrium,

$$\text{monomer} \rightleftharpoons \text{micelle} \quad \text{(J)}$$

at a constant temperature, the chemical potential of the surfactant monomer in solution ($\mu_m$) is equal to the chemical potential of the monomer in the pseudomicellar phase ($\mu_M$) thus,

$$\mu_m \rightleftharpoons \mu_M \quad \text{(K)}$$

Explicitly,

$$\mu_m^o + RT\ln a_m = \mu_M^o + RT\ln a_M \quad \text{(L)}$$

Wherefrom we again get

$$\Delta G_m^o = RT\ln CMC \quad \text{(M)}$$

for nonionic micelle, and

$$\Delta G_m^o = (1+f)RT\ln CMC \quad \text{(N)}$$

For ionic micelle, The $\mu_m^o$ and $\mu_M^o$ are the standard chemical potentials of monomer and micelle respectively and $a_m$ $a_M$ are their corresponding activities ($a_M$ =1, for micellar pseudo phase is taken to be a pure phase). It is noted that in the above thermodynamic treatments, at the CMC, the equilibrium concentration of free monomer is considered equivalent to CMC.

The equations for the free energy of micellisation by phase separation and mass action model are similar, but the two equations differ slightly because of differences in the way in which the mole fractions are calculated. In the phase separation model, the total number of moles present at cmc is equal to the sum of the number of moles of water and surfactants, whereas the total number of moles in the mass action model is equal to the moles of water, surfactant ions, micelles and free counterions. Unfortunately, the interpretation of mixed micellisation based on the mass action model does not agree well with the experimental CMC values, possibly due to the difference in the physicochemical properties of mixed micelles from those of micelles of individual components. Due to the number of parameters required and the complexity of the mass action model compared to the phase separation model, the former has only been applied in modelling a few systems.

The numerical values $\Delta G_m^\circ$ differ because the mole fractions are calculated differently. In the phase-separation approach, the total number of moles is that of water plus monomer. In the mass-action approach, micelles and free counterions are also included. At cmc, the two totals are approximately equal, and both models yield similar results. [21]

The corresponding entropy of micellisation $\Delta S_m^\circ$ and standard enthalpy $\Delta H_m^\circ$ per mole of the monomer can be computed from the slope and intercept, respectively, of linear $\Delta G_m^\circ$ vs Temperature plots or also by using the following well-known thermodynamic relations,

$$\Delta H_m^\circ = -RT^2\frac{d\ln CMC}{dT} \quad \text{(O)}$$

$$\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ \quad \text{(P)}$$

The enthalpy change represents the net change in intermolecular forces upon micelle formation. The entropy change includes a change in the degrees of freedom of both solvent and surfactant molecules.

In the computation of $\Delta G_m^\circ$ ionic surfactants, apart from the transfer of surfactant molecules from the aqueous phase to the micellar phase, the transfer of $(2-\alpha)$ moles of counterions is also to be considered and hence $\Delta G_m^\circ$ of ionic surfactant is defined as,

$$\Delta G_m^{\circ} = (2-\alpha)RT \ln X_{cmc} \qquad \text{(Q)}$$

where $\alpha$ is the degree of ionisation of micelle; and is often computed from the ratio of the slopes of post micellar region to that of premicellization region of conductance – concentration profile. The relation given in equation I and N are same to equation Q. The fraction of counterion bound to micelle $'f' = 1-\alpha$, where $'\alpha'$ is the degree of ionisation of the micelle.

## IV.CONCLUSIONS

In the pursuit of comprehending surfactant system models, theories of mixing, and the formation of mixed micelles, our exploration has traversed the intricate landscape of interfacial science. This comprehensive study aimed to bridge the theoretical underpinnings with practical applications, shedding light on the dynamic behaviour of surfactants in diverse environments. The exploration of mixed surfactant systems uncovered a realm of possibilities where synergistic effects and unique phase behaviours redefine the boundaries of surfactant applications.

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