

Chapter 1 : Introduction

[A] Micelles and Mixed Micelles Chemistry

- an Overview

(I) Micelle^[1]

Surfactant or surface-active agent is a species that is active at the interface between two phases , such as the interface between hydrophilic and hydrophobic phases . In order to avoid contact of the hydrophobic moieties with water , the individual surfactant molecules self-associate to form a variety of aggregate structure , known as *micelles* . In the micelles , the apolar groups tend to pack together away from the polar solvent , and the polar or ionic head groups tend to be at the surface of the micelle where they interact with the solvent .

Micellization depends upon a balance between hydrophobic and van der Waals interactions which bring monomers together and repulsions between the polar or ionic head groups . But repulsions between ionic head groups will be offset by attraction of the counterions to the micellar surface .

As the concentrations of surfactants in an aqueous solution are increased , many of the physical and chemical properties of the solution change rather abruptly (but continuously) over a characteristic narrow concentration range , termed the *critical micelle concentration* (CMC) . Affected properties include the refractive index , conductivity , viscosity , surface tension , turbidity , capacity to solubilize hydrocarbons and dyes . (Figure 1-01)

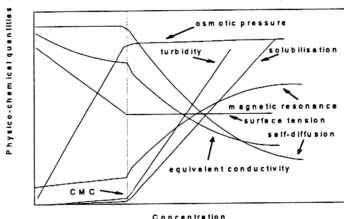


Figure 1-01 : Changes in concentration dependence of a wide range of physico-chemical quantities around the critical micelle concentration .

Micelles are not static species but are in dynamic equilibrium with coexisting monomers . (Micelles are not frozen assemblies , they constantly exchange amphiphiles with the bulk (intermicellar) phase .) A number of independent measurements indicate that the rate constants for dissociation of individual surfactant molecules from the micelle are large and may be in the 10^3 sec^{-1} range .

The core or the micelle is composed of the hydrophobic chains of the surfactant molecules . Surrounding the core is the Stern layer , which is occupied by the regularly spaced charged head groups of the ionic micelle together with a certain number of counterions . The exterior boundary of the Stern layer corresponds closely with the micellar shear surface . Hence the counterions within the Stern layer , which are sufficient to neutralize 50-70 percent of the surface charges , are tightly bound and form part of the kinetic micelle . The remainder of the counterions are less tightly

associated with the micelle and form a Gouy-Chapman layer several hundred angstroms in thickness (Figure 1-02) .

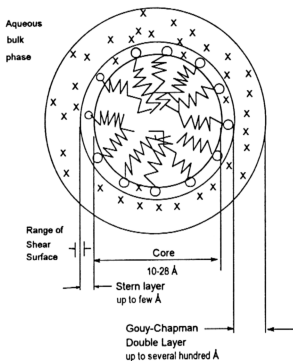


Figure 1-02 : A two-dimensional schematic representation of the regions of a spherical ionic micelle . The counterions (X) , the head groups (O) , and the hydrocarbon chains (WW) are schematically indicated to denote their relative locations but not their number , distribution , or configuration .

There are three potentials of note in micelles . The phase boundary potential is the total difference , which may be several hundred millivolts , between the micellar core and the solution . The Gouy-Chapman and zeta potentials are , respectively , those between the exterior surface of the Stern layer and between the shear surface and the bulk solution ; these are usually not very different . The potential drop across the

micellar surface may be several ten thousand volts per centimeter because the interface extends over only a short distance .

The shape of the micelles depends strongly upon the actual packing parameters in micellar assembly . At low concentration , the aggregates are generally spherical , globular micelles . However , in some cases it is possible to obtain other (higher order) aggregates such as cylindrical micelles , multilayer vesicles ,etc. The existence of such complex structures depends mainly on the surfactant structure and concentration , ionic strength of the solution , and the temperature . In some cationic surfactant systems as well as some nonionic and anionic surfactant systems , long threadlike or wormlike micelles form at higher concentration and/or upon addition of salt or acid . The counterion binding suppresses the micellar charge and decreases the surface area per surfactant molecule by reducing the electrostatic repulsion between the head groups , thus promoting the spherical-to-wormlike micelle transition .

(II) Functionalized surfactants and metallomicelles

Functionalized surfactants are simply defined as compounds containing reactive functions covalently bound to the molecular structure . The functions most frequently used are those present in the active sites of hydrolytic enzymes : hydroxyl, amino (imidazole, in particular) or sulfhydryl groups . In the kinetic studies , functionalized surfactants provide the hydrophobic environment for binding the substrate and the function that may perform the catalytic process [2(a)] . Metallosurfactants must contain a chelating head group for metal-ion fixation . In the metallosurfactant, lipophilic ligands are used to form metal ion complexes and the metal ion sites in the complexes are presumed to act as the polar head groups of surfactants [3(a)] . Metallomicelles made up of functionalized surfactants capable of effective chelation of metal ions appear as an obvious step toward more versatile systems which may mimic hydrolytic metalloenzymes [2(b)]. A lot of metal chelating surfactants have been synthesized . As can be seen from Figure 1-03 , metallosurfactants that consist of different ligands had been reported , such as imidazole (structure a and b [3(b),3(c)]) ; pyridine (structures c , d and e [2(c)-2(g)]) ; benzimidazole (structures f and g [4]) ; phenanthroline (structure h [5(a),5(b)]) ; triethylenetetramine (structure i [6]) ; ethylenediamine (structures j [7] and k [8]) , sarcophagines (cage type) (structure l [9]) and also tetraaza macrocyclic ligand (structure m [10]) . The use of cosurfactant (such as CTAB) may be necessary because of the insolubility of the ligands in water .

Lim et. al. had studied micellar and kinetic properties of several surface active copper(II) amine and mixed chelate complexes (using ligand *j*) by varying the chain length and counterion [11(a)-11(d)] .

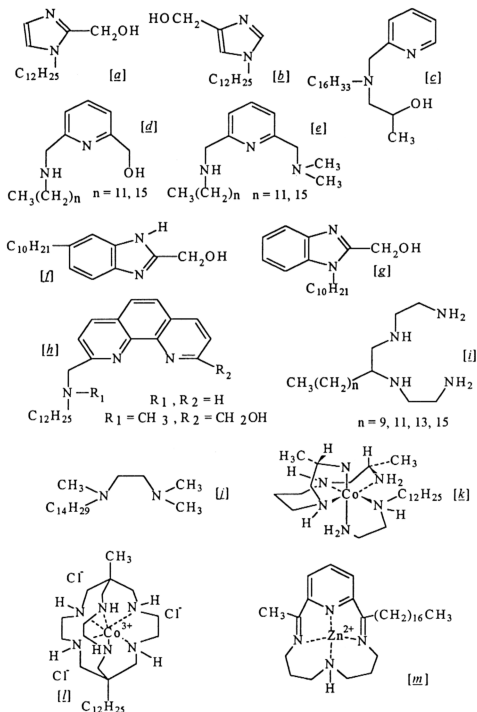


Figure 1-03 : Metallosurfactants with various types of ligands reported in the literature .

(III) Mixed Micelles ^[12]

A mixed micelle is a micelle composed of different surfactants capable themselves of forming micelles . Micelles are not a separate phase but a chemical species , and mixed micelles also should be treated as a chemical species [1(b)].

In solutions containing mixtures of surfactants , the tendency to form aggregated structures (mixed micelles) can be substantially different from the solutions containing only the constituent single surfactants . Specific interactions , (synergistic or antagonistic) between surfactants result in solutions of surfactant mixtures having micellar and phase behavior properties significantly different from those of the constituent single surfactants .

In order to tailor surfactant mixtures to a particular application , the surfactant technologist has to be able to predict and manipulate [13]

- (I) the tendency of surfactant mixtures to form monolayers , micelles , and other self-assembling aggregates in solution .
- (II) the properties of the aggregates such as their shape and size
- (III) the distribution of the various surfactant species between monomers and aggregates
- (IV) the phase behavior and phase equilibria of solutions containing surfactant mixtures .

One of the objectives of this project is to investigate the formation of binary mixed micelles from copper (II) surfactant , $\text{Cu}(\text{C}_{12}\text{med})(\text{acac})\text{Cl}$ and three common

surfactants (sodium dodecyl sulfate (SDS) ; cetyltrimethylammonium bromide (CTAB) and octaethylene glycol monododecyl ether ($C_{12}E_8$)) . The surface tension data are used to fit the various theoretical equations and to obtain the interaction parameter as well as the micellar and monolayer mole fractions . These equations are based on various models developed by using Regular Solution theory and Gibbs-Duhem approach .

[B] Modeling of Mixed Micelles

- an Overview

(I) Pseudophase Separation Models :

Mixed micelle models were originally developed in the 1950s for ideal mixing in binary surfactant systems by Lange [14] and Shinoda [15] . Since then , ideal models have been extended to include explicit treatment of different counterions such as Na^+ , K^+ , Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} [16] , monomer concentrations and micellar compositions [17] , two phase systems [18] , and multiple surfactants components [18,19] .

An important development has been the nonideal mixing treatment of micelles via the regular solution approximation . This was first applied by Rubingh [21] to a wide range of binary surfactant mixtures with success . The primary advantage of this approach is the use of a single adjustable parameter (β) to describe mixing in binary systems , thus providing a tractable means of treating nonideality in the mixed pseudo-phase .

In the past 15 years or so , the nonideal mixed micelle model has been successfully applied to a wide variety of different mixed micellar system [20-26] . Subsequent developments include extension to multicomponent surfactant systems [20(a)] , explicit treatment of counterion effects for the binary ionic-nonionic systems [27(a),27(b)] .

Although the regular solution approximation has been criticized on fundamental grounds such as the non-zero entropy of mixing [28] , nevertheless its approach has proved to be able to provide an easy means of describing the properties of the mixed-micellar system .

Alternatives to the regular solution approach have also been developed . For example , Scamehorn et. al. [29(a)] and Motomura et. al. [30] have separately applied Gibbs-Duhem equation to calculate the properties of the system based on the experimental CMC data . Models which account for the excess entropy of mixing [28] and counterion binding [27(a),27(b),31,32] have been developed . An interesting pseudophase model developed by Rathman et. al. [33] is based on electrostatic interaction only and is applied to ionic-nonionic mixed micelle systems .

Beginning from page 13, a more detailed discussion of the treatment of this model by various workers will be given .

(II) Mass Action Models :

Compared to pseudophase separation approach mentioned in the earlier paragraphs , mass action model has been applied to model only a few systems because of the number of parameters required and the complexity of the models . In the mass action model , the chemical potential depends on the aggregation numbers of the micelle and micellization is described in term of equilibrium among micelles of different sizes [27(c),34] . Because with the mass action approach a finite number of micelles are formally present at all concentrations , it becomes necessary to define the CMC as a surfactant concentration at which only some (small) specified fraction of the total surfactant exist as micelles in the system . The model can be simplified by assuming the micelles to be monodisperse . In the limit of large aggregate size , when the micelle

aggregate number is greater than 50 [27(c)] , the mass action model becomes equivalent to the pseudophase separation approach .

(III) Molecular Models :

Molecular models are theories using molecular thermodynamic expressions for the free energy of micelle formation with contributions from different molecular interactions and properties . The theories can relate the molecular geometry , size , chemical nature of surfactant hydrophilic / hydrophobic groups to both the macroscopic properties of the mixed system and the size of the micellar aggregate .

Approaches based on a variation principle and statistical thermodynamics have been explored [35,36] . The first molecular approach for nonideal mixed micelles was developed by Nagarajan [37(a)] in 1985 . The theory predicted CMC , the size and the composition distributions of spherical , globular and rodlike mixed micelles . Central to the model are the expressions for various contributions to the free energy of formation of mixed micelles . The contribution including transfer free energy of the surfactant tails , deformation free energy of the surfactant tails , aggregate core-water interfacial free energy , head group steric interactions , head group dipole interactions , head group ionic interactions and free energy of mixing of surfactant tails . Negative and positive deviations from ideal behavior are observed for the surfactant systems considered . Improvements to the theory were made recently [37(b)] .

The molecular-thermodynamic theory of Puvvada and Blankschtein [13,38] describes and predicts micellization , phase behavior and phase separation of mixed

micellar solutions . In the formulation of the theory , the thermodynamic theory of mixed micellar solutions is blended with a molecular model of mixed micellization . The predicted properties include a wide spectrum of properties , such as CMCs , size and composition distributions , micellar shape , phase transitions including the coexistence curve between micellar-rich and micellar-poor phases in surfactant systems . These can be evaluated from knowledge of two molecular contributions : the free energy of mixed micellization g_{mic} (reflecting intramicellar interactions) , and a mean-field intermicellar interaction parameter , C_{eff} . It is of interest to note that their approach also allows calculation of regular solution interaction parameters .

(IV) Group Contribution Method :

The theory can predict the properties of surfactants solutions , e.g. the mixed CMC , the mutual solubilities of two kinds of mixed micelles , the adsorption on air-water interface , the alkyl chain length dependence of immiscibility [39] . The information required include CMC , K_g (the micelle counterion binding parameter) , molecular structure data of pure components and the group interaction parameters . The activity coefficient was divided into combinatorial and residual component . A combinatorial part is essentially based on differences in size and shape of the constituent functional groups of a surfactant . A residual part essentially is based on energy interactions . The concentration and composition of each surfactant are given on the basis of Shinoda's equation .

(V) Various treatments based on Pseudophase

Separation Model

(a) Development of ideal mixing models

The following workers have been responsible for the development of ideal model for mixed micelles system :

Von Hermann Lange , Kozo Shinoda, John H. Clint

Hermann Lange et. al.

By ignoring ionic effects and assuming ideal mixing , Lange and Beck [14] derived equation for the CMC of the mixture , C_{12}^M , as a function of the mixing ratio , α in the mixed surfactant solution . The CMC of the mixture is given by :

$$C_{12}^M = \frac{1}{\frac{\alpha}{C_1^M} + \frac{(1-\alpha)}{C_2^M}} \quad (1-01)$$

where

C_1^M, C_2^M, C_{12}^M = CMC of the pure surfactants 1 , 2 and the mixture

α = mole fraction of surfactant 1 in the mixture

John H. Clint

Clint [17] further developed Lange and Beck's model and calculated the concentrations of monomer for each component as a function of total concentration , C .

Below the CMC of the mixture ($C < C_{12}^M$) , the concentrations of monomers are

$$C_{1m} = \alpha C \quad (1-02)$$

$$C_{2m} = (1 - \alpha)C \quad (1-03)$$

where

C_{1m} , C_{2m} = concentration of unassociated monomeric surfactants 1 and 2

For concentrations above the CMC , equation (1-04) is used (taking only the positive root) to calculate C_{1m} and then equation (1-06) to calculate C_{2m} .

$$C_{1m} = \frac{-(C - \Delta) \pm \left[(C - \Delta)^2 + 4\alpha C \Delta \right]^{\frac{1}{2}}}{2 \left(\frac{C_2^M}{C_1^M} - 1 \right)} \quad (1-04)$$

where

$$\Delta = C_2^M - C_1^M \quad (1-05)$$

$$C_{2m} = \left[1 - \left(\frac{C_{1m}}{C_1^M} \right) \right] C_2^M \quad (1-06)$$

Kozo Shinoda

Shinoda [15(b)] determined the mixed CMC's for the binary mixtures of potassium soaps, then derived equation for the CMC of the mixtures by assuming that the surfactants mixed ideally in the micelles.

The CMC of the mixture was given by :

$$(C_1^M)^{1+K_g} \alpha + (C_2^M)^{1+K_g} (1 - \alpha) = (C_{12}^M)^{1+K_g} \quad (1-07)$$

where

C_1^M, C_2^M, C_{12}^M = CMC of pure surfactants 1, 2 and the mixtures

$\alpha, (1 - \alpha)$ = mole fractions of the surfactants 1 and 2

K_g = experimental constant for the particular surface active agent.

(b) Development of nonideal mixing models

The following workers :

Donn N. Rubingh , Milton J. Rosen & coworkers , Paul M. Holland , Kinsi Motomura, John F. Scamehorn et. al. , Zhi-Jian Yu et. al. , Robert F. Kamrath et. al. , H. Hoffmann et. al . have in one way or another , contributed to the development of the nonideal model of mixing .

(i) Regular Solution approach

Donn N. Rubingh

Rubingh [21] applied regular solution approach to treat the mixed micelle system by assuming that the excess entropy is zero for the mixed micelle system . The treatment differs from the ideal solutions , where the interaction between surfactant molecules within the micelle was included and therefore provide a better physical description for a wider range of different surfactant combinations . Nonideality due to interactions between different surfactant components in the mixed micelle is characterized by the interaction parameter β^M . β^M was related to molecular interactions in the mixed micelle :

$$\beta^M = \frac{N(W_{11} + W_{22} - 2W_{12})}{RT} \quad (1-08)$$

where

W_{11}, W_{22}, W_{12} = energies of interaction between molecules in the pure micelle 1, 2
and in the mixed micelle .

N = Avogadro's number .

β^M was introduced into the activity coefficient terms :

$$f_1^M = \exp \beta^M (1 - x^M)^2 \quad (1-09)$$

$$f_2^M = \exp \beta^M (x^M)^2 \quad (1-10)$$

where

f_1^M, f_2^M = activity coefficients of surfactants 1 and 2 in the mixed micelle .

x^M = mole fraction of surfactant 1 in the mixed micelle .

The use of regular solution approach results in a set of relations between mixed micelle CMC (C_{12}^M), micelle composition (x^M), monomer concentration (C_{1m}, C_{2m}) and the interaction parameter (β^M) .

At the mixed CMC ,

$$\alpha C_{12}^M = x^M f_1^M C_1^M \quad (1-11)$$

$$(1 - \alpha) C_{12}^M = (1 - x^M) f_2^M C_2^M \quad (1-12)$$

where

C_1^M, C_2^M, C_{12}^M = CMC of pure surfactants 1, 2 and the mixed system

α = mole fraction of surfactant 1 in total mixed solute

From equations (1-09) and (1-11) ,

$$\beta^M = \frac{\ln\left(\frac{\alpha C_{12}^M}{x^M C_1^M}\right)}{(1-x^M)^2} \quad (1-13)$$

From equations (1-10) and (1-12) ,

$$\beta^M = \frac{\ln\left[\frac{(1-\alpha)C_{12}^M}{(1-x^M)C_2^M}\right]}{(x^M)^2} \quad (1-14)$$

From equations (1-13) and (1-14) ,

$$\frac{(x^M)^2 \ln\left[\frac{\alpha C_{12}^M}{x^M C_1^M}\right]}{(1-x^M)^2 \ln\left[\frac{(1-\alpha)C_{12}^M}{(1-x^M)C_2^M}\right]} = 1 \quad (1-15)$$

Equation (1-15) can be solved iteratively for x^M and then substitute x^M into equation (1-13) to get β^M at each experimental mole fraction . A near constant value of β^M is usually obtained for mixed surfactants at varying composition .

As x^M varies with total surfactants concentration , C , the value of x^M for any C can be obtained from the following equation once β^M is known .

$$x^M = \frac{-(C-\Delta) \pm \sqrt{(C-\Delta)^2 + 4\alpha C\Delta}}{2\Delta} \quad (1-16)$$

where

$$\Delta = f_2^M C_2^M - f_1^M C_1^M \quad (1-17)$$

The concentrations of monomeric surfactants 1 or 2 are given by

$$C_{1m} = x^M f_1^M C_1^M \quad (1-18)$$

$$C_{2m} = (1 - x^M) f_2^M C_2^M \quad (1-19)$$

The monomer concentrations of the two surfactants in the system can also be obtained from the following two equations :

$$C_{1m} = \frac{-(C - \Delta) \pm \sqrt{(C - \Delta)^2 + 4\alpha C \Delta}}{2 \left(\frac{f_2^M C_2^M}{f_1^M C_1^M} - 1 \right)} \quad (1-20)$$

$$C_{2m} = \left(1 - \frac{C_{1m}}{f_1^M C_1^M} \right) f_2^M C_2^M \quad (1-21)$$

Since regular solution is defined as one in which the excess entropy of mixing vanishes , and the origin of the nonideality is the enthalpic effect , correlations based on regular solution theory may be simply a curve fitting procedure rather than representative of a fundamental process [28] .

Significance of β^M value

The sign of β^M value corresponds to positive or negative deviation from ideality ; it is also an index of interaction between the surfactants . If β^M is zero then the mixtures behave ideally and there is no additional interaction of the two surfactants . If β^M is negative , there is attractive interaction occurring ; the CMC of the mixtures will be lower than for an ideal system . If β^M is positive then the CMC will be higher than for an ideal system . In practice β^M value is generally negative for many mixed surfactant systems that have been reported in literature . Typical values of β^M are shown in Table 1-01 .

	Anionic	Nonionic
Anionic	0 to -1	-
Nonionic	-1 to -5	< -1
Amphoteric	-5 to -15	< -1
Cationic	-15 to -25	-1 to -5

Table 1-01 : Typical values of β^M for various type of mixed surfactant solutions

In the case of cationic-anionic surfactant mixtures , large negative β^M value is obtained , indicating strong attractive interaction between the surfactants .

Milton J. Rosen and coworkers

Rosen et. al. [22(f)] have extended the Regular Solution model to the mixed monolayer formation . By equating chemical potential of surfactant 1 in the monolayer at the interface to that in the bulk solution phase , they derived the following equations :

$$\frac{(x^\sigma)^2 \ln \left[\frac{\alpha C_{12}}{x^\sigma C_1^0} \right] - \frac{\gamma}{RT} (A_1^0 - A_1)}{(1-x^\sigma)^2 \ln \left[\frac{(1-\alpha) C_{12}}{(1-x^\sigma) C_2^0} \right] - \frac{\gamma}{RT} (A_1^0 - A_2)} = 1 \quad (1-22)$$

$$\beta^\sigma = \frac{\ln \left[\frac{\alpha C_{12}}{x^\sigma C_1^0} \right] - \frac{\gamma (A_1^0 - A_1)}{RT}}{(1-x^\sigma)^2} \quad (1-23)$$

where

γ = surface tension value

α = mole fraction of surfactant 1 in total solute

C_1^0, C_2^0, C_{12} = molar concentrations of individual surfactants 1 and 2 and their mixture at a given value of α , respectively , required to yield a surface tension at certain γ value .

x^σ = monolayer mole fraction of surfactant 1 in the mixture

β^σ = monolayer interaction parameter

A_1, A_2 = the partial molar interface areas occupied by surfactants 1 and 2 , respectively , at the mixed surfactant interface .

A_1^0, A_2^0 = the molar interface areas occupied by surfactants 1 and 2 , respectively , at the pure surfactant interface .

Based on the 2-dimensional gas approach [22(f)] , 2 treatments (treatment 'R' and 'E') to calculate the mole fraction of mixed monolayer at the solution-air interface were introduced .

In treatment "R" , it is assumed that

$$\frac{A_1}{A_2} = \frac{A_1^0}{A_2^0} \quad (1-24)$$

and

$$A_{av} = x^\sigma A_1 + (1 - x^\sigma) A_2 \quad (1-25)$$

$$A_1 = \frac{A_1^0 A_{av}}{x^\sigma A_1^0 + (1 - x^\sigma) A_2^0} \quad (1-26)$$

$$A_2 = \frac{A_2^0 A_{av}}{x^\sigma A_1^0 + (1 - x^\sigma) A_2^0} \quad (1-27)$$

where

A_{av} = the average area per surfactant molecule in the mixed monolayer
at the interface

$$\frac{(x^{\sigma R})^2 \ln \left[\frac{\alpha C_{12}}{x^{\sigma R} C_1^0} \right] - \frac{\gamma A_1^0}{RT} \left[1 - \frac{A_{av}}{x^{\sigma R} A_1^0 + (1 - x^{\sigma R}) A_2^0} \right]}{(1 - x^{\sigma R})^2 \ln \left[\frac{(1 - \alpha) C_{12}}{(1 - x^{\sigma R}) C_2^0} \right] - \frac{\gamma A_2^0}{RT} \left[1 - \frac{A_{av}}{x^{\sigma R} A_1^0 + (1 - x^{\sigma R}) A_2^0} \right]} = 1 \quad (1-28)$$

$$\beta^{\sigma R} = \frac{\ln \left[\frac{C_1}{x^{\sigma R} C_1^0} \right] - \frac{\gamma A_1^0}{RT} \left[1 - \frac{A_{av}}{x^{\sigma R} A_2^0 + (1 - x^{\sigma R}) A_2^0} \right]}{(1 - x^{\sigma R})^2} \quad (1-29)$$

In treatment "E" , it is assumed that $A_1 \approx A_1^0$ and $A_2 \approx A_2^0$

$$\frac{(x^{\sigma E})^2 \ln \left[\frac{\alpha C_{12}}{x^{\sigma E} C_1^0} \right]}{(1-x^{\sigma E})^2 \ln \left[\frac{(1-\alpha)C_{12}}{(1-x^{\sigma E})C_2^0} \right]} = 1 \quad (1-30)$$

$$\beta^{\sigma E} = \frac{\ln \left[\frac{\alpha C_{12}}{x^{\sigma E} C_1^0} \right]}{(1-x^{\sigma E})^2} \quad (1-31)$$

When the "packing deviation factor" $1 - \frac{A_{av}}{[xA_1^0 + (1-x)A_2^0]}$ decreases , the two sets of equations become more and more similar and that when the quantity equals zero , the two sets of equations are the same . When the "packing deviation factor" is positive , then $\beta^{\sigma R}$ will be more negative than $\beta^{\sigma E}$; when it is negative , then $\beta^{\sigma R}$ will be more positive than $\beta^{\sigma E}$. The difference between $\beta^{\sigma E}$ and $\beta^{\sigma R}$ also decreases with decrease in the value of γ

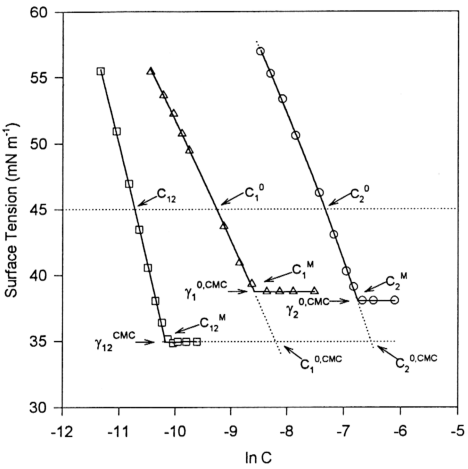


Figure 1-04 : Synergism in surface tension reduction efficiency , in mixed micelle formation and in surface tension reduction effectiveness .

Rosen et. al. [22(b)] have been developing theory of synergism of binary mixtures of surfactants since 1980's . There are 3 types of synergism for binary mixtures of surfactants :

- (1). *Synergism in surface tension reduction efficiency* , when a given surface tension (reduction) is attained at a total mixed surfactant concentration lower than that required for either component of the mixture by itself ;
- (2). *Synergism in the mixed micelle formation* , when the CMC of the mixture is less than the CMC of either component by itself ;
- (3). *Synergism in surface tension reduction effectiveness* , when the surface tension of the mixture at its CMC is less than that attained with either component by itself .

The conditions for the existence of synergism for these 3 phenomena are :

- 1) surface tension reduction efficiency :

$$\beta^{\sigma} < 0 \quad (1-32)$$

$$|\beta^{\sigma}| > \left| \ln \left(\frac{C_1^0}{C_2^0} \right) \right| \quad (1-33)$$

- 2) mixed micelle formation :

$$\beta^M < 0 \quad (1-34)$$

$$|\beta^M| > \left| \ln \left(\frac{C_1^M}{C_2^M} \right) \right| \quad (1-35)$$

- 3) surface tension reduction effectiveness :

$$\beta^{\sigma} < 0 \quad (1-36)$$

$$(\beta^s - \beta^M) < 0 \quad (1-37)$$

$$|\beta^\sigma - \beta^M| = \left| \ln \left(\frac{C_1^0}{C_2^0} \frac{C_2^M}{C_1^M} \right) \right| \quad (1-38)$$

where

C_1^0, C_2^0, C_{12} = molar concentrations of individual surfactants 1 and 2 and their mixture at a given value of α , respectively, required to yield a surface tension at certain γ value.

$C_1^{0,CMC}, C_2^{0,CMC}$ = molar concentrations of individual surfactants 1 and 2, respectively, required to yield a surface tension equal to γ_{12}^{CMC} of any mixture

C_1^M, C_2^M, C_{12}^M = CMC's of individual surfactants 1,2 and mixture

β^M is obtained from the Rubingh Equation.

At the point of maximum synergism for mixed monolayer and mixed micelle, the composition of the mixed interfacial layer (α^*) equals to the composition of the mixed micelle (x^σ):

$$x^\sigma = \alpha^* = \frac{\ln \left(\frac{C_1^0}{C_2^0} \right) + \beta^\sigma}{2\beta^\sigma} \quad (1-39)$$

The minimum or maximum CMC of the mixture is given by

$$C_{12,\min} = C_1^0 \exp \left[\frac{\left(\beta^\sigma - \ln \left(\frac{C_1^0}{C_2^0} \right) \right)^2}{4\beta^\sigma} \right] \quad (1-40)$$

(a). The more negative the value of β^σ or β^M and

(b). The smaller the absolute value of $\ln\left(\frac{C_1^M}{C_2^M}\right)$ or $\ln\left(\frac{C_1^0}{C_2^0}\right)$, the greater will be the extent of synergism .

For a given value of β^σ or β^M , maximum synergism will occur when $\ln\left(\frac{C_1^M}{C_2^M}\right)$ or

$\ln\left(\frac{C_1^0}{C_2^0}\right) = 0$, that is, when both surfactants have the same CMC or surface reducing efficiency .

The degree of synergism in surface tension reduction efficiency in a mixture is measured by the maximum decrease in the molar concentration of (mixed) surfactant needed to produce a given surface tension value relative to that required of the more efficient of the two individual surfactants by itself : i.e. $\frac{(C_1^0 - C_{12,\min})}{C_1^0}$ or $1 - \frac{C_{12,\min}}{C_1^0}$, where $C_{12,\min}$ is the minimum concentration of mixed surfactant that can produce this surface tension and C_1^0 is the concentration required of the more efficient surfactant .

The ratio, $\frac{C_{12,\min}}{C_1^0}$ is given by the relationship

$$\frac{C_{12,\min}}{C_1^0} = \exp \left[\frac{\left(\beta^\sigma - \ln\left(\frac{C_1^0}{C_2^0}\right) \right)^2}{4\beta^\sigma} \right] \quad (1-41)$$

The greater the value of $1 - \frac{C_{12,\min}}{C_1^0}$, the greater the degree of synergism .

At the CMC, the activity of each surfactant in the mixed monolayer at the aqueous solution / air interface is lower than its activity in the mixed micelle .

$$f_1^\sigma x^\sigma < f_1^M x^M \quad (1-42)$$

The experimental data needed to determine whether a binary surfactant system is capable of synergism are as below :

- (a). The surface tension / log concentration curves of the individual surfactants in the vicinity of their critical micelle concentrations (CMC) , including the portion of each for some distance below the CMC .
- (b). The CMC of at least one mixture of the two surfactants .
- (c). The solution phase concentration of at least one mixture of the two surfactants needed to produce a surface tension attainable by both individual surfactants .

Paul M. Holland

Holland and Rubingh [20(a)] had developed a generalized multicomponent nonideal mixed micelle model based on the pseudophase separation approach . Nonideality due to interactions between different surfactant components in the mixed micelle is treated via a regular solution approximation .

Activity coefficients in multicomponent cases are given by :

$$\ln f_i^M = \sum_{\substack{j=1 \\ (j \neq i)}}^n \beta_{ij}^M (x_j^M)^2 + \sum_{\substack{j=1 \\ (j \neq i \neq k)}}^{j-1} \sum_{k=1}^{j-1} (\beta_{ij}^M + \beta_{ik}^M - \beta_{jk}^M) x_j^M x_k^M \quad (1-43)$$

where

β_{ij}^M = net (pairwise) interaction between components i and j .

f_i^M = activity coefficient of surfactant i in mixed micelles

x_j^M = mole fraction of j th component in the mixed micelles

For n components , there will be a total of

$$C_2^n = \frac{n!}{(n-2)! 2!} \quad (1-44)$$

different (pairwise) parameters (β_{ij}^M).

With β^M parameters determined independently from binary mixtures , x_i^M can be solved to obtain activity coefficients .

A generalized pseudophase separation model for the treatment of nonideality at interfaces in mixed micellar solutions had also been developed by Holland [20(c),20(d)]. Surface pressures and areas per mole are explicitly taken into account by developing a nonideal analog of Butler's equation [40] which is

$$\pi A_1 = RT \ln \left(\frac{f_i^M x_i^M}{f_i^S x_i^S} \right) + \pi_i^{\max} A_i^o \quad (1-45)$$

If assume $A_i^o = A_i$

$$\pi = \frac{RT}{A_i^o} \ln \left(\frac{f_i^M x_i^M}{f_i^S x_i^S} \right) + \pi_i^{\max} \quad (1-46)$$

The activity coefficients of the components at the interface are given by

$$f_1^S = \exp \beta^S (1 - x_1^S)^2 \quad (1-47)$$

$$f_2^S = \exp \beta^S (x_1^S)^2 \quad (1-48)$$

where

π = surface pressure in mixed system

π_i^{\max} = surface pressure of surfactant component i at or above CMC in pure system

A_i^o = area per mole of surfactant i in pure system

A_i = area per mole of surfactant i in mixed system

f_i^M = activity coefficient of surfactant i in mixed micelles

f_i^S = activity coefficient of surfactant i in mixed surface pseudo-phase

From Gibbs equation , the areas per mole (A) are obtained from the slopes of the surface tension versus log concentration plots below the CMC , and surface pressures (π) come from surface tension results . It is always necessary first to calculate the micellar mole fractions (x^M) and activities (f_i^M) from the underlying mixed micelle model developed by Rubingh [21] .

The surface interaction parameter β^S is not equivalent to monolayer interaction parameter β^σ used by Rosen and co-workers , as β^S is designed to be suitable for extension to multicomponent mixtures .

(ii) Gibbs-Duhem Approach

Motomura, K. et. al.

Motomura et. al. [30] developed a thermodynamic method to obtain the composition of surfactant in the mixed micelle based on Gibbs-Duhem equation .

For binary mixtures with surfactants 1 and 2 , the former dissociates into $\nu_{1,a}$ - surfactant molecules and $\nu_{1,c}$ -counterions and the latter dissociates into $\nu_{2,b}$ - surfactant molecules and $\nu_{2,d}$ -counterions .

The composition of mixed micelle formed by surfactants 1 and 2 is derived using the relationship

$$\overline{x_2^M} = \overline{\alpha_2} - n \left(\frac{\overline{\alpha_1 \alpha_2}}{\overline{C_{12}^M}} \right) \left(\frac{\partial \overline{C_{12}^M}}{\partial \alpha_2} \right)_{T,P} \quad (1-49)$$

where

$$n = \frac{\nu_{1,c} \overline{\nu_2 \alpha_1} + \nu_{2,d} \overline{\nu_1 \alpha_2}}{\nu_{1,c} \overline{\nu_2 \alpha_1} + \nu_{2,d} \overline{\nu_1 \alpha_2} - \delta_d^c \nu_{1,c} \nu_{2,d}} \quad (1-50)$$

$$\overline{C_{12}^M} = (\nu_1 \alpha_1 + \nu_2 \alpha_2) C_{12}^M \quad (1-51)$$

$$\overline{\alpha_i} = \frac{\nu_i \alpha_i}{\nu_1 \alpha_1 + \nu_2 \alpha_2} \quad (1-52)$$

$$\overline{x_2^M} = \frac{\nu_1 x_1^M}{\nu_1 x_1^M + \nu_2 x_2^M} \quad (1-53)$$

$$\nu_1 = \nu_{1,a} + \nu_{1,c} \quad (1-54)$$

$$\nu_2 = \nu_{2,b} + \nu_{2,d} \quad (1-55)$$

δ_d^c is the Kronecker delta defined by

$$\delta_d^c = 0, d \neq c \text{ (no common ion)} \quad (1-56)$$

$$\delta_d^c = 1, d = c \text{ (with common ion)} \quad (1-57)$$

Scamehorn, J.F. et. al.

By applying Gibbs-Duhem equation and pseudophase model to mixed micelles , a method to determine monomer-micelle equilibrium compositions (analogous to vapor-liquid equilibria) and the resulting activity coefficients (f_i) of surfactant components in mixed micelles had been proposed . The method needs only CMC data as a function of monomer composition (α_i) , but is limited to binary surfactant systems [29(a)].

They derived the following equation

$$\left(\frac{d \ln C_{12}^M}{d\alpha} \right) = \frac{\alpha - x}{\alpha(1 - \alpha)} \quad (1-58)$$

The slope of $\ln (C_{12}^M)$ versus α can be used to calculate the value of x at a given α ; i.e. , the micellar composition (x_i) at the CMC can be found at any monomer composition (α_i) from CMC data alone .

$$x = \alpha \left[1 - (1 - \alpha) \left(\frac{d \ln C_{12}^M}{d\alpha} \right) \right] \quad (1-59)$$

The activity coefficients can be calculated at a given micellar composition by the following formula :

$$f_1 = \frac{\alpha C_{12}^M}{x C_1^M} \quad (1-60)$$

$$f_2 = \frac{(1-\alpha) C_{12}^M}{(1-x) C_2^M} \quad (1-61)$$

For ionic surfactants it is applicable only in the presence of swamping electrolyte . It cannot be effectively applied when the pure-component CMC values of the two surfactants used are highly dissimilar (e.g. : anionic-cationic) ; therefore it is applied to cationic / cationic , cationic / nonionic , and anionic / nonionic surfactant pairs .

The monomer-monolayer equilibrium compositions and monolayer activity coefficients of the mixed systems were obtained by a similar method proposed earlier for the mixed micelle [29(b)] . Comparing with the Gibbs adsorption method , this method requires less data to calculate thermodynamic parameters . In addition , the results are almost identical to the calculated one from the regular solution theory .

Yu, Z.-J. et. al.

The molar ratio of the cationic surfactant to the anionic surfactant in the mixed micelles is deduced by applying the Gibbs-Duhem equation to the measured CMC [41] .

$$\sum_{i=1}^L n_i d \ln a_i = 0 \quad (1-62)$$

Under the conditions of constant ionic strength and dilute solution , $a_i \approx C_i$

where

- L = number of components in the micellar solution
 n_i = molar number of the i th component in the micellar phase
 a_i = activity of the i th species in the solvent phase
 C_i = concentration of surfactant i in the solvent phase

Varying the concentrations of two species of interest , and keeping the concentrations of all the other species constant or much larger than of the two species of interest so that their changes , if any , are negligible ,

$$n_1 d \ln C_1 + n_2 d \ln C_2 = 0 \quad (1-63)$$

or

$$\frac{n_1}{n_2} = - \frac{d \ln C_2}{d \ln C_1} \quad (1-64)$$

One can determine the molar ratio , $\frac{n_1}{n_2}$, of two species in a micellar phase at the CMC

from experimentally available CMC data . Micellar compositions can be deduced by Gibbs-Duhem approach without any CMC information of the pure surfactant systems .

This approach has the advantage that it can be used to evaluate micellar compositions for a mixed micellar system in which the short chain compounds do not form micelles in its pure form .

(iii) Other methods

Kamrath, R.F. and Frances, E.I.

Kamrath and Frances [27(a),27(b)] developed a general pseudophase separation model for micellization of binary nonionic and binary ionic surfactants where the counterion binding parameter K_g was considered .

The CMC of the mixtures (for ionic surfactants in the presence of salt of concentration C_s), $C_{12}^M(C_s)$, is found from

$$\frac{1}{C_{12}^M(C_s)[C_{12}^M(C_s) + C_s]^{K_g}} = \frac{\alpha}{f_1(x)(C_1^M)^{(1+K_g)}} + \frac{(1-\alpha)}{f_2(x)(C_2^M)^{(1+K_g)}} \quad (1-65)$$

$$\alpha C_{12}^M(C_s)[C_{12}^M(C_s) + C_s]^{K_g} = x(C_1^M)^{(1+K_g)} f_1(x) \quad (1-66)$$

where

- x = micellar mole fraction at the CMC
- α = mole fraction of 1 in binary surfactant mixture
- K_g = micelle counterion binding parameter
- C_s = concentration of salt.

$f_1(x), f_2(x)$ = activity coefficients of surfactants 1 and 2

When there is no added salt , $C_s = 0$ and $C_{12}^M(C_s) = C_{12}^M$

Shinoda, K. et. al.

Shinoda et. al. [42] had derived equation for studies of mixtures of fluorocarbon and hydrocarbon surfactant, where counterion binding constants are considered. By assuming $K_{g1} \approx K_{g2} = K_g$, the following equation is obtained.

$$\frac{w_{12}}{kT} = \frac{\ln \left[\frac{\alpha C_{12}^M (C_g)^{K_g}}{x (C_1^M)^{1+K_g}} \right]}{(1-x)^2} = \frac{\ln \left[\frac{(1-\alpha) C_{12}^M (C_g)^{K_g}}{(1-x) (C_2^M)^{1+K_g}} \right]}{x^2} \quad (1-67)$$

where

K_{g1}, K_{g2}, K_g = counterion binding constant for surfactant 1, 2 and mixtures.

w_{12} = interchange energy per molecule

α, x = mole fraction of surfactants 1 in the total mixed solute and in the mixed micelle

C_1^M, C_2^M, C_{12}^M = CMC of pure surfactants 1, 2 and the mixed surfactant

C_g = concentration of counterion

K_g was obtained by plotting the logarithm of the CMC versus the logarithm of the concentration of the counterion C_g .

Fung, B.M. et. al.

Fung et. al. [31] found that assumption of equal partial molar volumes of two components in Rubingh equations is not applicable to some mixed hydrocarbon /

fluorocarbon systems . They modified Rubingh's equations by considering an expansion of the Gibbs-Duhem equation to include an additional interaction parameter δ . The terms δ is added to these expressions to account for the inequivalence and mutual phobicity of the two components . By adjustment of the variables β and δ , C_{12}^M can be calculated as a function of α by the use of a nonlinear least-squares fitting program .

$$f_1^M = \exp \left[(1-x)^2 \left(\beta - \frac{\delta}{2} + \delta(1-x) \right) \right] \quad (1-68)$$

$$f_2^M = \exp \left[x^2 (\beta + \delta(1-x)) \right] \quad (1-69)$$

$$\alpha C_{12}^M = x f_1^M C_1^M I_1 \quad (1-70)$$

$$(1-\alpha) C_{12}^M = (1-x) f_2^M C_2^M I_2 \quad (1-71)$$

where

f_1^M, f_2^M = activity coefficients of the surfactant components in the mixed micelle

α, x = mole fraction of surfactant 1 in the bulk solution and in the mixed micelle solution .

β, δ = interaction parameters

C_1^M, C_2^M, C_{12}^M = CMC of pure surfactants 1, 2 and mixed surfactants system .

I_1, I_2 = factors accounting for variations in the ionic strength

K_{g1}, K_{g2} = counterion binding fraction for surfactant 1 and 2

$$I_1 = \left[\frac{C_1^M}{C_{12}^M \alpha} \right]^{K_{g1}} \quad (1-72)$$

$$I_2 = \left[\frac{C_2^M}{C_{12}^M (1-\alpha)} \right]^{K_{g2}} \quad (1-73)$$

Esumi, K. et. al.

Esumi et. al. [32] modified Rubingh equation by considering the counterion effect and an additivity of counterion binding in binary mixtures .

$$\beta = \frac{\ln \left[\frac{\alpha (C_{12}^M)^{1+K_g}}{x (C_1^M)^{1+K_{g1}}} \right]}{(1-x)^2} = \frac{\ln \left[\frac{(1-\alpha) (C_{12}^M)^{1+K_g}}{(1-x) (C_2^M)^{1+K_{g2}}} \right]}{x^2} \quad (1-74)$$

$$K_g = xK_{g1} + (1-x)K_{g2} \quad (1-75)$$

where

K_{g1} , K_{g2} , K_g = counterion binding degrees of surfactants 1 , 2 and the mixtures

Hoffmann, H. et. al.

Hoffmann [43] suggested that system which corresponds to the "regular solution approximation" should be called "symmetrical mixture" , because it is only a special case of Redlich-Kister equation . Redlich and Kister derived molar excess free energy as :

$$\Delta G^E = x_1 (1 - x_1) \sum_{i=1} q_i (2x_1 - 1)^{(i-1)} \quad (1-76)$$

where

q_i = empirical parameters of the Redlich-Kister expansion

x_i = mole fraction of the i th component in the micelle

Relation between excess chemical potential (μ_i^E) with activity coefficient (f_i) and ΔG^E is given by

$$\mu_i^E = RT \ln f_i = \Delta G^E + (1 - x_i) \left(\frac{\partial \Delta G^E}{\partial x_i} \right) \quad (1-77)$$

Expanding equation (1-76) only to the first power, gives :

$$\Delta G^E = x_1(1 - x_1)q_1 \quad (1-78)$$

which was first used by Porter in 1920 [44] and leads to equation (1-79) for the activity coefficients .

$$RT \ln f_i = q_1(1 - x_i)^2 \quad (1-79)$$

From equation (1-09) of Rubingh approach :

$$\ln f_i = \beta(1 - x_i)^2 \quad (1-80)$$

Compare equations (1-79) and (1-80) ,

$$\beta = \frac{q_1}{RT} \quad (1-81)$$

Regular solution theory works only when the system can be described by one parameter β , which means that for every measured C_{12}^M nearly the same value for β is calculated . If this is not the case , the following equation should be used .

$$\ln f_i = \beta(1 - x_i)^2 + x_i(1 - x_i)^2 \left(\frac{\partial \beta}{\partial x_i} \right) \quad (1-82)$$

But the use of equation (1-82) is much more complicated , therefore Hoffmann proposed the following equation to calculate the composition of the micelle :

$$x_1 = \alpha_1 \left[1 - \frac{1 - \alpha_1}{C_{12}^M} \left(\frac{dC_{12}^M}{d\alpha_1} \right) \right] \quad (1-83)$$

This equation is a special case of the Motomura's equation [30].

Hoffmann also calculated error in β by showing that

$$\Delta\beta = \pm \frac{1}{(1-x)x} (\varepsilon_{12} + x\varepsilon_1 + (1-x)\varepsilon_2) \quad (1-84)$$

where

$\Delta\beta$ = error of β

ε_i = relative error of the corresponding CMC values .

For a constant relative error ε , the equation can be simplified to

$$\Delta\beta = \pm \frac{2\varepsilon}{(1-x)x} \quad (1-85)$$

Hoffmann found that even if the CMC's can be determined with an accuracy of $\pm 1\%$, the minimum of $\Delta\beta$ is nearly 0.1 , therefore β can only be reported to the first decimal place .

[C] Kinetic Studies in Micellar and Mixed
Micellar Solutions

(I) Micellar Kinetics - an Overview ^[45]

During the past 40 years, there has been an increasing level of activity in the study of the catalysis of organic reactions by micelles. The subject of micellar catalysis and inhibition of reactions can be divided into the types of reaction occurring, e.g. base-catalyzed and acid-catalyzed hydrolyses, oxidation, etc., or in terms of mechanism, e.g. juxtaposition of reactive groups in micelles, attraction of counterions to an oppositely charged micellar surface, protection by solubilization within nonionic micelles, etc. Micelles not only can alter rate constants of reactions but they can alter the conformation of molecules and thus affect the outcome of a reaction. [46]

Micellar effects upon reaction rates and equilibria have generally been treated in terms of a pseudophase model. In most kinetic treatments, reactivities are considered to be sums of reactions occurring in the bulk aqueous (R_w) and the micellar pseudophases (R_m) [45(b),45(d)] :

$$R_{total} = R_w + R_m \quad (1-86)$$

Rate acceleration or inhibition of organic reactions in micellar solutions arises from different rates of reaction of the substrate in the micellar phase and in the bulk solution and the distribution of the substrate between these two phases. Basically, these rate effects can be attributed to electrostatic and hydrophobic interactions between the substrate and the surfactant aggregate and in some cases to alterations in the structure of the surrounding water [45(c)]. Micelle catalyzed reactions can be treated in a manner analogous to that used for enzymatic catalysis [45(d)].

(II) Metallosurfactants , metallomicelles in kinetic studies ^[47]

Metallomicelles have been developed in order to model the substrate binding properties of enzymes [2(b)] . The adsorption of apolar substrates into or onto these molecular assemblies and their subsequent reaction resemble enzymatic reactions , and large rate accelerations are observed for the hydrolysis of carboxylic , and phosphoric esters in these systems [2(a),48] .

The kinetic studies in surfactants can be grouped into two categories : (i) surfactant micelle acts only as a medium for the reaction . (ii) surfactant participates directly either as a catalyst or as substrate [49] . Most studies of metallomicelles center on the effect of the metal ion . Some possible functions of each species of metallosurfactant that appear in the kinetic studies are listed as below :

- (1) Large rate enhancements due to an increased concentration of the reactants in the micellar pseudophase by hydrophobic binding [45(d)]
- (2) substrate specificity : partition of substrates between the bulk solvent and the micellar pseudophase [5(b)]
- (3) metal ions can lower the pKa of a ligated water molecule (enhanced ionization of water upon coordination to the metal ion) , generating relatively large concentrations of a potent nucleophilic catalyst , the metal-bound hydroxide , near neutral pH .
Therefore metal ions act as a source of hydroxide ions at neutral pH [2(g), 3(b), 3(c), 7] .
- (4) metal ions act as template for coordination and activation of the substrate [5(a), 50].

- (5) formation of ternary complex [2(a),51,52] both productive and nonproductive . The productive one involves ligand , metal ion and substrate . Rate will decrease as the product inhibits reaction by complexing more strongly than the reactant with metal ion .
- (6) the geometry of metal-ion coordination is an important factor in the catalytic activity of metalloenzyme models, and it is likely that ternary complexes of ligand-Zn-substrate adopt a tetrahedral geometry , whereas ligand-Cu-substrate has a planar geometry [5(a),53] .
- (7) metal ions activate electrophiles such as carbonyl , nitrile , and phosphoryl groups (by polarization) toward attack by free hydroxide [5(a),10]
- (8) activation of various leaving groups such as alkoxide ions , hydroxide ions , oxide ions , oximate ions , amide ions , sulfur derivatives and halides
- (9) activation of ambient acids such as water , alcohols , oximes , amines and the C_{α} -H of chelated carbonyl compounds .
- (10) pseudo-intramolecular nucleophilic attack by metal-bound hydroxide ions or ligand hydroxyl at carbonyl, nitrile , phosphoryl, and olefinic groups [10,51]

(III) Kinetic studies in the presence of mixed micellar solutions

One of the earlier works on kinetic studies in the presence of mixed micellar solutions was reported by Gitler et. al. in 1967 [54]. They found that the mixed micelle of N^{α} -myristoyl-L-histidine and CTAB remarkably enhanced the rate of the liberation of *p*-nitrophenol by the hydrolysis of *p*-nitrophenyl acetate (PNPA) .

The catalytic effect of the mixed micelles of lauroylamino acids (LauAm) with SDS , CTAB and $C_{12}E_6$ on the hydrolysis of *p*-nitrophenyl acetate had been studied by Inoue et. al. . Among the detergents used , only CTAB remarkably enhanced the catalytic activity of LauAm [55] .

Oxidation of 3,4-dihydroxy-L-phenylalanine (*L*-DOPA) by optically active *N*-lauroyl *L* or *D*-histidine-Cu(II) complex (*L* or *D*-LauHis-Cu(II)) in CTAB micelles had been studied by Yamada et. al. The reaction showed appreciable enantioselectivity in the presence of the mixed micelles with CTAB [56] .

Effect of mixed micelles of CTAB and Brij 35 on decomposition of 2,4-dinitrochlorobenzene (DNCB) and (*p*-nitrophenyl diphenyl phosphate) PNPDP had been studied by Meyer and Sepulveda . The degree of ionization increased as the nonionic detergent composition of the mixed micelle increased . As the micellar nonionic surfactant content increases , the second rate order constant for both DNCB and PNPDP decrease . The decrease in rate can be attributed to a decrease in the amount of hydroxide ions bound to the micelles [57] .

The studies by Bunton et. al. show that comicelles of dodecyl[2-(hydroximino)-2-phenylethyl]dimethylammonium bromide or N-phenylmyristohydroxamic acid with CTAB are good dephosphorylating agents toward PNPDP at high pH. The major source of the rate enhancements is increased reactant concentration in the micellar pseudophase [58].

The metal ion complexes N-dodecyl-2-hydroxy-methylimidazole- Cu^{2+} and bis(N-octyl-2-imidazolyl) carbinol- Zn^{2+} are remarkably active catalysts in the hydrolysis of *p*-nitrophenyl picolinate (PNPP) when used in the micelles of CTAB. Tagaki et. al. suggest that the site-selective acylation of hydroxyl groups of ligands occurs via the formation of a tetrahedral complex for Zn^{2+} ion and a square planar complex for Cu^{2+} ion [53, 59].

Micelles made up of 2-(hydroxymethyl)-pyridine-functionalized surfactants and Cu^{2+} and Zn^{2+} ions are powerful catalysts for the cleavage of the *p*-nitrophenyl picolinate (PNPP) in the presence of CTAB. Studies from Scrimin and Tonellato et. al. demonstrated that hydroxyl bound to a ligand structure can be activated by transition metal ions and act as effective nucleophile in neutral aqueous media by formation of ternary complex involving ligand, metal ion, and substrate [2(e),60].

Mixed micellar systems made of complex of N-dodecyl-2-aminomethyl-1,10-phenanthroline with Zn^{2+} and Cu^{2+} in the presence of an inert cosurfactant (CTAB or Brij 35) are efficient catalysts in the hydrolysis of *p*-nitrophenyl picolinate (PNPP) and PNPDP. These metallosurfactants operate via a metal-hydroxide-ion catalyzed mechanism and exhibit turn-over behavior while retaining their full catalytic activity [5(a)].

Hydrolysis of *p*-nitrophenyl picolinate in the presence of Zn^{2+} complexes of *n*-alkyl-2-hydroxymethylbenzimidazole with CTAB had been studied by Faivre et. al. The

stoichiometry of the active complexes (1 : 1 or 2 : 1 types) are dependent on the position of alkyl chain on the benzimidazole ring and on the surfactant concentration [4] .

Connolly and Reinsborough had studied complexation of Ni^{2+} with pyridine-2-azo-*p*-dimethylaniline (PADA) in mixed sodium fluorocarbon / hydrocarbon surfactant solutions . They found that mixed micelles can synergically lead to much greater solubilization of substrate as compared to either of the pure surfactants [61] .

When CTAB micelle alone increases the rate of $\text{S}_{\text{N}}2$ reaction of Br^- with methyl naphthalene-2-sulfonate in water , addition of nonionic surfactant (n-decyl methylsulfoxide (C_{10}SO) [62(a)] or C_{10}E_4 [62(b)]) to CTAB inhibits the reaction . Fractional micellar ionization of CTAB is increased by nonionic surfactant , and the loss of Br^- from the micellar surface is the major cause of inhibition .

Hydrolysis of *p*-nitrophenyl diphenyl phosphate in the presence of metallomicelle (structure *j*) had been studied by Menger et. al. [7] , Lim et. al. [11(a),11(b)] and Bunton et. al. [2(g)] . Lim et. al. had also studied the effects of similar copper surfactants on autooxidation of 3,5-di-*tert*-butylcatechol [11(c)] . *However , the effects of co-surfactants have not been reported . Therefore another objective of this project is to investigate the effects of co-surfactants (SDS, CTAB, C_{12}E_8) on the reactivities of PNPDP and 3,5-DTBC .*

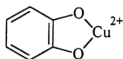
(D) Some Background Information on the
Substrates Used in This Project

Since the metallosurfactant contains copper as the head group and copper is a good oxidizing agent, therefore 3,5-di-*tert*-butylcatechol (3,5-DTBC) is chosen as a substrate in the kinetic studies.

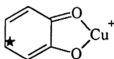
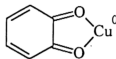
(I) 3,5-di-*tert*-butylcatechol (3,5-DTBC)

Oxidation of catechol catalyzed by transition metal complexes have been widely studied because it is related to biological phenomena which involves enzymes and hemoglobin. Copper proteins such as polyphenol oxidase, tyrosinase catalyze both the ortho hydroxylation of phenols to give catechols (cresolase activity) and oxidation of catechols to quinones (catecholase activity) [63]. Non-heme iron-containing enzymes such as catecholdioxygenase, pyrocatechase and metapyrocatechase catalyze the oxidative cleavage of catecholate derivatives (intradiol or extradiol C-C bond) by molecular oxygen to yield muconic acid, anhydride, pyrone, furone etc. [64]. A number of dinuclear and mononuclear copper(II) complexes have been studied as models for copper oxidases enzymes [65].

Catechol, semiquinone, benzoquinone exhibit two fundamental properties in common with transition metal ions. They show redox behavior at easily accessible (and chemically useful) potentials and they are able to fix substrate molecules by donor-acceptor complexation. The electronic structure of the metal-quinone chelate ring can be viewed in terms of three isoelectronic forms related by the distribution of formal charge over ligand and metal (II) [66].



catecholate (Cat)

*o*-semiquinone (SQ)

benzoquinone (BQ)

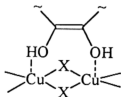
Metal-oxygen bond lengths are often characteristic of a particular oxidation state for metal ; quinone carbon-oxygen lengths are sensitive to the charge of the ligand . Therefore it is possible to classify ligands in most complexes as either catecholate , semiquinone or benzoquinone .

A series of Cu(II)-(3,5-di-*tert*-butyl-*o*-semiquinone) copper(II) complexes had been synthesized and characterized by Thompson and Calabrese [67]. It was concluded that the single-step two-electron oxidation of catechol by Cu(II) complexes is not observed and *o*-benzoquinone was obtained only after exposure of the Cu(II)-*o*-semiquinone to dioxygen or by the addition of small molecules such as pyridine . Their study indicates that the formation of mononuclear Cu(II)-*o*-semiquinone complexes as an intermediate should be considered in the catecholase-mimetic activity of Cu(II) complexes .

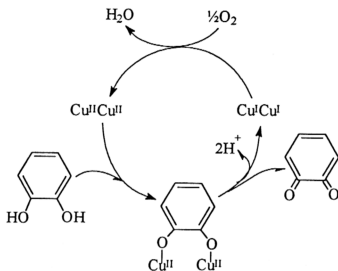
Martell et. al. [68] worked on oxidation of catechols by dinuclear Cu(I) dioxygen complex and a dinuclear Cu(II) complex . In the absence of base (triethylamine) and oxygen , catechols were not converted to their oxidation products . Cu(II) oxidation is an important part of the cycle for the catalytic oxidation beginning with Cu(I) . The Cu(I) produced from the Cu(II) oxidation of substrates is capable of forming the dioxygen complex in the presence of oxygen , consequently , the cycle is perpetuated . Tsuruya and Lintvedt [69] found that the oxidation of 3,5-di-*t*-butylcatechol (3,5-DTBC) by *bis*(1,3,5-triketonato)dicopper(II) complexes , with the

stoichiometry of catechol : $O_2 = 2 : 1$, the observed kinetics were first order in substrate and in dicopper(II) complex concentration , but zero order in O_2 concentration . Their result shows that the rate determining step is the Cu_2^{II} – catecholate complex formation and subsequent electron transfer from substrate to dicopper(II) center to produce a dicopper(I) complex intermediate .

Kida and co-workers [70] have examined a large number of dinuclear and mononuclear Cu(II) complexes with varying coordination geometry and Cu(II)/Cu(I) redox potentials and compared their catalytic activities in the oxidation of 3,5-DTBC or ascorbic acid . The geometry around the copper ions is the most dominant property in determining the catalytic activity of the complexes . The dinuclear complexes show catalytic activity while mononuclear complexes having essentially the same reduction potential are either poor catalysts or are inactive . In non-planar mononuclear copper(II) models , it has been proposed that the two copper(II) atoms must be located at a distance of less than 5 Å for bonding to the hydroxyl groups of the catechols , a mode which should facilitate electron transfer to dioxygen . “Steric match” between the substrate and dicopper(II) center seems to be a required condition



Rogic et. al. [71] have summarized the mechanism proposed for the O_2 oxidation of catechols catalyzed by the copper(I) chloride / pyridine systems .



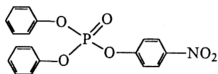
The main features are the formation of the dicopper(II)-catecholate intermediate, electron transfer from the aromatic ring to Cu(II) to give the benzoquinone product plus dicopper(I) compound, and the oxidation of dicopper(I) to generate a copper(II)-oxygen "reagent". This reagent could be a μ -oxo-Cu(II) complex or other species, but it is capable of reacting with catechols to produce dicopper(II)-catecholate complex intermediate. Note that O_2 functions only as an oxidant to convert Cu(I) to Cu(II) and is itself reduced to H_2O . Dioxygen seems to serve to regenerate the Cu(II) catalyst by oxidation of a Cu(I) product.

Effect of SDS and CTAB micelles on the rate and mechanism of oxidation of quinols and catechols to the corresponding quinones by transition metal complexes (hexachloroiridate (IV) and octacyanomolybdate (V)) had been studied by Pelizzetti and Pramaura [72]. The presence of the micelles has a strong influence on the equilibrium of the redox system and kinetics of electron-transfer reactions.

(II) *p*-nitrophenyl diphenyl phosphate (PNPDPP) [73]

The organophosphates are compounds widely used as insecticides and chemical warfare agents, where the typical organophosphates and related compounds are: Paraoxon, Parathion, Diazinon, Diisopropylfluorophosphate, Sarin, Soman, Tabun and VX. The extreme toxicity of these compounds is due to their ability to bind to the amino acid serine and nervous system enzyme acetylcholinesterase, rendering it incapable of participating in a catalytic reaction within an enzyme and the further blocking of the active site by the organophosphate residue [74].

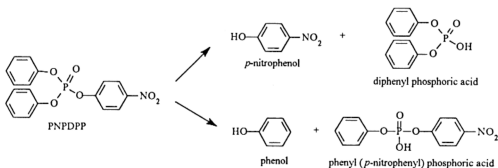
The chemical warfare agents have surface tensions much lower than water -- Soman (24 mN m^{-1}), VX (32 mN m^{-1}) as compared with water (72 mN m^{-1}) [75], which means that not only do these chemicals penetrate readily into cracks and crevices but water based decontaminants cannot enter such locations as readily. Therefore surfactants as additives to water based decontaminants are able to help to dissolve the chemicals in cracks and crevices. Although many chemical reactions, such as base catalyzed hydrolysis or oxidation, can be exploited the reagents used are usually too aggressive towards materials such as paints and plastics to permit their use under field conditions. Therefore attention is being given to the use of metal ion ligand complexes (e.g. copper and zinc) as catalysts for the destruction of chemical agents and some of their simulants in aqueous solution, such as:



p-nitrophenyl diphenyl phosphate

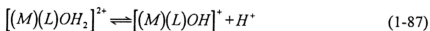
Bunton and co-workers found that micellar cetyltrimethylammonium bromide (CTAB) enhances the reaction of hydroxide and fluoride anions with PNPDP, while anionic micellar sodium dodecyl sulfate (SDS) and nonionic micellar Igepal strongly inhibit the reaction [76(a)]. Subsequent reports from that laboratory showed that greater enhancements resulted from placing a hydroxyl group on the cationic surfactant (CTAOH), near the quaternary center [76(b)]. Moss and co-workers found that PNPDP hydrolysis in aqueous micellar CTACl was catalyzed by iodoso- and iodoxybenzene derivatives with ortho-carboxylate groups [77]. Menger and Whitesell observed a similar catalysis effected by a tetraalkylammonium surfactant containing an aldehyde group at the polar end [78]. Menger et. al. found that $\text{Cu}(\text{C}_{14}\text{tmed})\text{Cl}_2$ possess remarkable catalytic activity toward phosphate triesters, diesters and other phosphorus (V) compounds [7]. Lim et. al. reported that $\text{Cu}(\text{R-tmed})\text{X}_2$ and $\text{Cu}(\text{R-tmed})(\text{acac})\text{X}$ exhibit good catalytic activities toward the hydrolysis PNPDP [11(a),11(b)].

PNPDPP would be hydrolyzed in two ways :



Loss of better leaving group (*p*-nitrophenol) is more preferred in the hydrolysis [10] .

Metal ions can lower the pK_a of a ligated water molecule , generating relatively large concentrations of a potent nucleophilic catalyst , the metal-bound hydroxide , near neutral pH [10] . The active catalytic species has a metal-bound hydroxide formed by dissociation of a proton on a water molecule ligated to the metal center of metal complex .



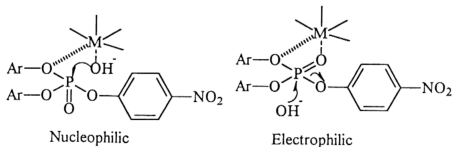
The bound hydroxide acts as a nucleophile , while metal acts as an electrophilic catalyst .

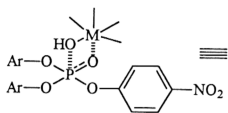
There are two limiting mechanistic possibilities for a catalytic species involving metal complexes and hydroxide :

- (I) a nucleophilic process involving attack on the phosphorus atom by metal-bound hydroxide
- (II) an electrophilic activation of the phosphoryl P-O bond , by coordination to the metal center , toward attack by free hydroxide .

A "hybrid" mechanism is also possible : the metal center delivers a coordinated hydroxide nucleophilically to a PNPDPP molecule , while simultaneously drawing electron density away from the phosphorus atom by interacting with the phosphoryl oxygen .

Lewis acid facilitation of nucleophilic reactions at phosphorus (V) centers has been observed .





Polarize P=O bond

