CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Characteristic feature of detergent

2.1.1 General structure features

Surface – active agents have a characteristic molecular structure consisting of a structural group that have very little attraction for the solvent, known as a lyophobic group. Together with a group that has strong attraction for the solvent, it is called the lyophilic group. This is known as an amphipathic structure when a surface–active agent is dissolved in a solvent, the presence of the lyophobic group in the interior of the solvent may cause distortion of the solvent liquid structure, increasing the free energy of the system. In an aqueous solution of a surfactant this distortion of the water by the lyophobic group of the surfactant. The resulting increase in the free energy of the system when it is dissolved means that less work is needed to bring a surfactant molecule than a water molecule to the surface. The surfactant therefore concentrates at the surface. Since less work is now needed to bring molecules to the surface, the presence of the surfactant decreases the work needed to create a unit area of surface (the surface tension). On the other hand, the presence of the lyophilic group prevents the surfactant from being expelled completely from the solvent as a separate phase, since that would require dehydration of the hydrophilic group. The amphipathic structure of the surfactant therefore causes not only concentration of the surfactant at the surface and reduction of the surface tension of the water, but also orientation aqueous phase and

its hydrophobic group is oriented away from it. So a surfactant is a substance which in solution is particularly an aqueous solution; it tends to congregate at the bonding surface, i.e. the air – solution interface, the walls of the containing vessel and liquid – liquid interface if a second liquid phase is present. As a result, the various interfacial tensions are reduced [9].

2.1.2 Classification of surfactants

Surfactants are classified according to the nature of their hydrophilic parts.

1.<u>Anionic surfactant</u>

: A surfactant in the hydrophilic part carries a negative charge.

Examples: soaps, $RCOO^-$; alkyl sulphates, $ROSO_3^-$.

2.<u>Nonionic surfactant</u>

: A surfactant in which the hydrophilic part is uncharged.

Examples: acyl diethanolamides, $RCON(C_2H_4OH)_2$; ethoxylated

fatty alcohol, $R(OC_2H_4)_nOH$.

3.<u>Cationic surfactant</u>

: A surfactant in which the hydrophilic part carries a positive charge.

Examples: alkyltrimethylammonium salts, $RN^+(CH_3)_3$;

alkyldimethylbenzylammonium salts, $RN^+(CH_3)_2CH_2C_6H_5$.

4.<u>Amphoteric surfactant</u>

: A surfactant in which the hydrophilic part contains both positive and negative charges. Examples: alkylaminopropionates, RNH_2^+ $(CH_2)_2COO^-$; alkylbetaines, $RN^+(CH_3)_2CH_2COO^-$. It is possible for amphoteric surfantants to have more than one charge of either sign, or to lose one charge by addition or removal of a proton.

2.2 General effects of the nature of the hydrophobic group to the physical properties of detergent [10]

2.2.1 Length of the hydrophobic group

Increase in the length of the hydrophobic group

(1) Decreases the solubility or the surfactant in water and increases its solubility in organic solvents.

(2) Causes closer packing of the surfactant molecules at the interface.

(3) Increases the tendency of the surfactant to adsorb at an interface or to form micelles

(4) Increases the melting point of the surfactant and of the adsorbed film.

(5) Increases the sensitivity of the surfactant, if it is ionic, to precipitation from water by counterions.

2.2.2 Branch, unsaturation

The introduction of branching or unsaturation into the hydrophobic group

(1) Increases the solubility of the surfactant in water or in organic solvents.

(2) Decreases the melting point of the surfactant and of adsorbed film.

(3) Causes looser packing of the surfactant molecules at the interface and inhibits liquid-cystal formation in solution.

(4) May cause oxidation and color formation in unsaturated compounds.

(5) May decrease biodegradability in branched-chain compounds.

2.2.3 Aromatic nucleus

The presence of an aromatic nucleus in the hydrophobic group may

(1) Increase the adsorption of the surfactant onto polar surfaces.

(2) Decrease its biodegradability.

(3) Cause looser packing of the surfactant molecules at the interface.

2.2.4 Polyoxypropylene chain

The presence of this in the hydrophobic group

(1) Increase adsorption of the surfactant onto polar surfaces via the hydrophobic group.

(2) Increase the solubility of the surfactant in organic solvents.

2.2.5 Perfluoroalkyl or polysilioxane group

The presence of either of these groups as the hydrophobic group in the surfactant permits reduction of the surface tension of water to lower values, those attainable with a hydrocarbon-based hydrophobic group.

2.3 Properties of detergent

2.3.1 Surface tension

The tension acting in the surface of a phase directed towards the interior of the phase is caused by intermolecular attractions between the molecules at the surface and those located the surface. But the interfacial tension is the tension at the interface between two phases.

Reduction of surface or interfacial tension is one of the most commonly measured properties of surfactants in solution. Since it depends directly on the replacement of molecules of solvent at the interface by molecules of surfactant, and therefore on the surface (or interfacial) excess concentration of the surfactant (Figure 2.1).

The molecules at the surface of a liquid have potential energies greater than similar molecules in the interior of the liquid. This is because attractive interactions of molecules at the surface with those in the interior of the liquid are greater than the widely separated molecules in the gas phase. Because the potential energies of molecules at the surface are greater in the interior of the phase, an amount of work equal to this difference in the potential energy must be expended to bring a molecule from the interior to the surface. The surface free energy per unit area, or surface tension, is a measure of this work; it is the minimum amount of work required to bring sufficient molecules to the surface from the interior to expand it by unit area.

At the interface between two condensed phases, the dissimilar molecules in the adjacent layers facing each other across the interface also have potential

energies different from those in their respective phases. If we now add to a system of two immiscible phases (e.g., heptane and water), a surface-active agent is adsorbed at the interface between them, it will orient itself there, mainly with the hydrophilic group toward the water and the hydrophobic group toward the heptane. When the surfactant molecules replace water and heptane molecules, the interaction across the interface is now between the hydrophilic group of the surfactant and water molecules on one side of the interface and between the hydrophobic group of the surfactant and heptane on the other side of the interface. Since these interactions are now much stronger than the original interaction between the highly dissimilar heptane and water molecules, the tension across the interface is significantly reduced by the presence they're of the surfactant. Since air consists of molecules that are mainly nonpolar, surface tension reduction by surfactants at the air-aqueous solution interface is similar in many respects to interfacial tension reduction at the heptane-aqueous solution interface.

Measurement of the surface or interfacial tension of liquid systems is accomplished readily by methods, which were the most useful and precise for solutions of surfactants are probably the drop-weight and Wilhelmy plate method. An excellent discussion of the various methods for determining surface and interfacial tension is included in the monograph on emulsions.

2.3.2 Micelle formation by surfactants

Now turn the attention to a property of surfactants that may be as fundamental, and certainly is as important, as their property of being adsorbed at interfaces. This property of micelle formation, or micellization, is an important phenomenon not only because of a number of important interfacial phenomena, such as detergency and solubilization.

2.3.2.1 The critical micelle concentration (C.M.C.)

When the equivalent conductivity of an anionic surfactant of type Na^+R^- in water is plotted against the square root of the solution, the curve obtained, instead of being the smoothly decreasing curve characteristic of ionic electrolytes of this type, has a sharp break in it, at low concentrations.

The concentration at which this phenomenon occurs is called the critical micelle concentration (C.M.C.). Similar breaks in almost every measurable physical property that depends on the size or number of particles in solution are shown by all types of surfactants-nonionic, anionic, cationic, and zwitterionic in aqueous media. The determination of the value of the C.M.C. can be made by the use of any of these physical properties, but most commonly the breaks in the electrical conductivity. Surface tension, light scattering, or refractive index concentration curves have been used for this purpose. Critical micelle concentrations have also very frequently been determined from the change in the spectral characteristics of some dyestuff added to the surfactant solution when the C.M.C. of the latter is reached. However, this method is opened to the serious

objection that the presence of the dyestuff may affect the value of the C.M.C.

2.3.2.2 Micellar structure and shape

The shape of the micelle produced in the aqueous media is of importance in determining various properties of the surfactant solution, such as its viscosity, its capacity to solubilize water-insoluble material, and cloud point. At the present time, the major types of micelles appear to be (Figure 2.2.):

(1) Relatively small, spherical structures.

(2) Elongated cylindrical, rodlike micelles with hemispherical ends.

(3) Large, flat lamellar micelles.

(4) Vesicles, more or less spherical structures consisting of lamella micelles arranged in one or more concentric spheres.

In the aqueous media, the surfactant molecules are oriented, in all these structures with their polar heads toward the aqueous phase and their hydrophobic groups away from it. In vesicle, there will also be an aqueous phase in the interior of the structure. In ionic micelles, the aqueous solution-micelle interfacial region contains the ionic head groups. The interior region of the micelle, containing the hydrophobic groups, is of radius approximately equal to the length of the fully extended hydrophobic chain. The aqueous phase is believed to penetrate into the

micelle beyond the hydrophobic head groups, and the first few methylene groups of the hydrophobic chain adjacent to the hydrophobic head are often considered in the hydration sphere.

In a nonpolar media, the structure of the micelle is similar, but reversed with the hydrophilic heads comprising the interior region surrounded by an outer region containing the hydrophobic groups and nonpolar solvent. Dipole-dipole interactions hold the hydrophilic heads together in the core. Changing in temperature,
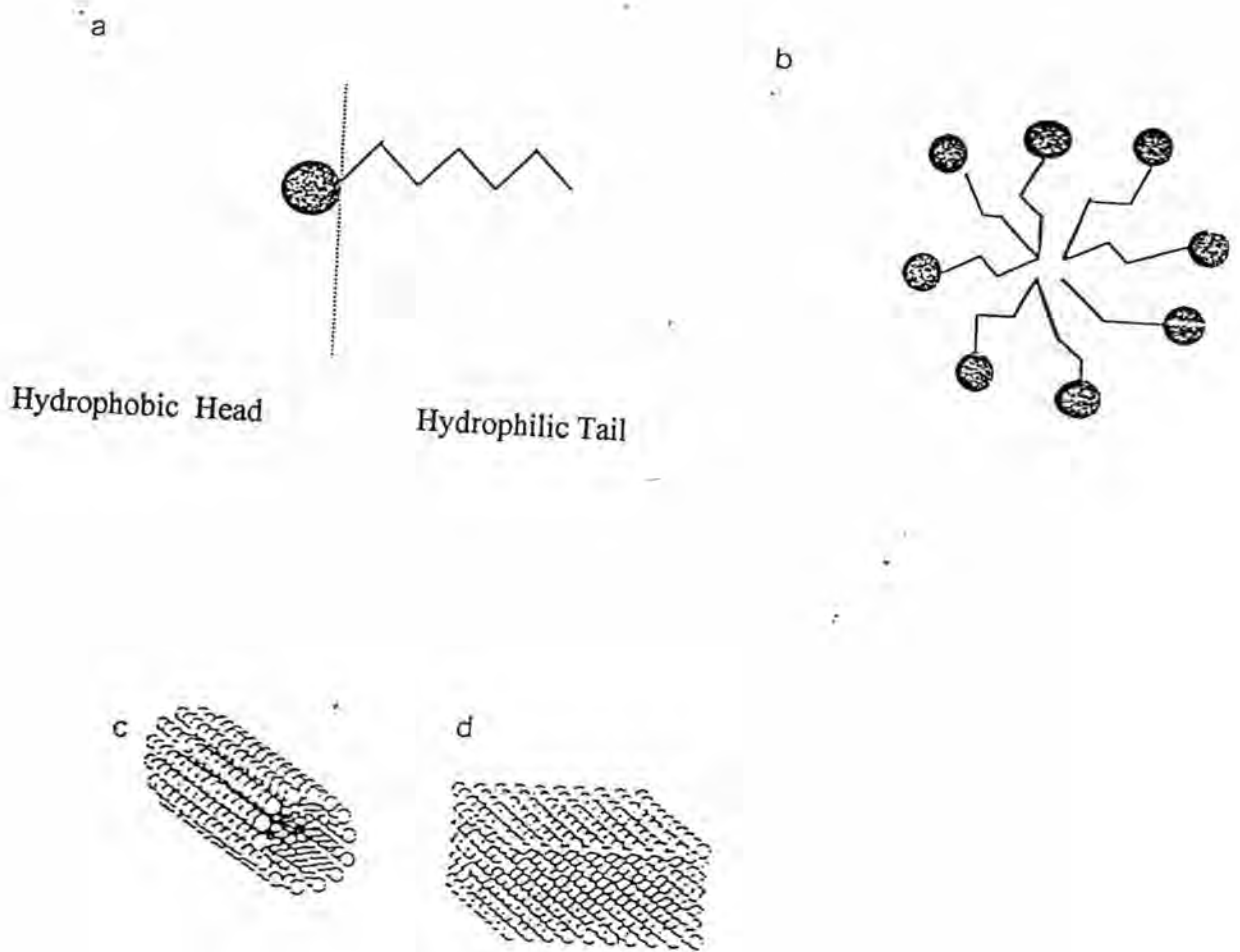
a

b

Hydrophobic Head   Hydrophilic Tail

c   d

Figure 2.2 Structure of micelles
   a) molecule of surfactant
   b) circular micelle
   c) rod shaped micelle
   d) vesicle representation

concentration of surfactant, additives in the liquid phase, and structural groups in the surfactant may all cause change in the size, shape, and aggregation number of the micelle, with the structure varying from spherical through rod- or dislike to lamellar in shape.

In aqueous media, surfactants with bulky or loosely packed hydrophilic groups and long, thin hydrophobic groups tend to form spherical micelles, while those with short, bulky hydrophobic groups and small, close-packed hydrophilic groups tend to form lamellar or cylindrical micelles. Surfactants having two long alkyl chains may, upon signification in aqueous media, form vesicles. Whether vesicle form depends upon the length of the alkyl chain and the nature of the hydrophilic group, increase in the length of the alkyl chain and weak electrostatic repulsion between the hydrophilic groups promotes vesicle formation.

2.3.3 Detergency

The term detergency, as used to describe a property of surface-active agents, has a special meaning. As a general term, it means cleaning power, but no surfactant by itself can clean a surface. The term detergency, when applied to a surface-active agent, means the special property it has of enhancing the cleaning power of a liquid. This is accomplishing by a combination of effects involving adsorption at interface alteration of interfacial tensions, solubilization, emulsification, and the formation and dissipation of surface charges.

Mechanisms of the cleaning process

Three elements are present in every cleaning process:

(1) the substrate (the surface that is to be cleaned)

(2) the soil (material that is to be removed from the substrate in cleaning

process)

(3) the cleaning solution or "bath" (the liquid that is applied to the

substrate to remove the soil)

The difficulty in developing a unified mechanism for the cleaning process lies in the almost infinite variety of the first two elements, the substrate and the soil. The substrate may vary form an impervious, smooth, hard surface like that of a glass plate to a soft, porous, complex surface like that of a piece of cotton or wool yarn. The soil may be liquid or solid, ionic or nonpolar, finely or coarsely ground, inert or reactive toward the cleaning bath. As a result of this great variability of substrate and soils, there is no one single mechanism of detergency, but a number of different mechanisms, depending on the nature of substrate and soil. The bath is generally a solution of various materials, collectively called the detergent, in the cleaning liquid. Except in the bath is water.

In general, cleaning consists essentially of two processes:

(1) Removal of the soil from the substrate.

(2) Suspension of the soil in the bath and prevention of its redeposition.

This second process is equally as important as the first, since it prevents redeposition of the soil onto another part of the substrate.

2.3.4 Solubilization

One of the important properties of surfactants that are directly related to micelle formation is solubilization. Solubilization may be defined as the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. Although both solvent-soluble and solvent-insoluble materials may be dissolved by the solubilization mechanism, the importance of the phenomenon from the practical point of view is that and it makes possible the dissolving of substances in solvents in which they are normally insoluble. For example, although ethylbenzene is normally insoluble in water, almost 5 g of it may be dissolved in 100 ml of a 0.3M aqueous solution of potassium hexadecanoate to yield a clear solution.
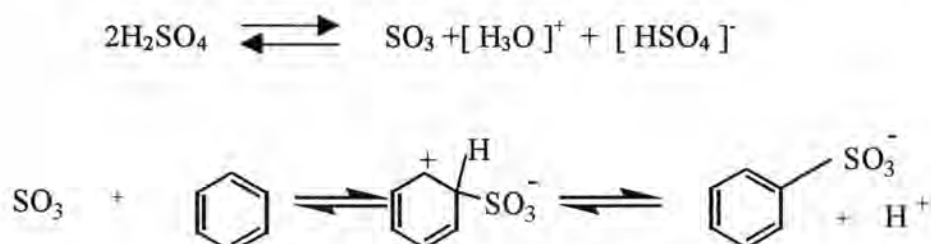
2.4 Sulfonation of aromatic compounds

Sulfonation is a typical example of electrophilic aromatic substitution. Sulfonation of benzene and a less reactive aromatic compound (C_6H_5Br, $C_6H_5NO_2$) is usually effected by means of fuming sulfuric acid, H_2SO_4 + dissolved SO_3, sometimes called oleum. For more active compounds, such as toluene, xylenes, and phenols, concentrated sulfuric acid suffices. When a sulfonyl chloride is desired, this can be obtained directly by chlorosulfonation with chlorosulfonic acid, $ClSO_3H$, an excellent sulfonating agent.

The detailed mechanism of sulfonation is not as well established as that of other electrophilic aromatic substitution reactions. The attacking electrophilic species appear to be sulfur trioxide, an electrically neutral but electron-deficient molecule.

Sulfur trioxide is present in the fuming sulfuric acid commonly used for sulfonation; in concentrated sulfuric acid it may be formed by interaction of two molecules of the acid. Attack of the aromatic system, though a series of reversible reaction, leads to the

$$2H_2SO_4 \rightleftharpoons SO_3 + [H_3O]^+ + [HSO_4]^-$$

dissociated arylsulfonic acid. Evidence from studies with deuterated compounds discloses a pronounced isotope effect, indicating that the rate-determining step is the breaking of a C-H bond of the aromatic ring. Sulfonation, like Friedel-Crafts alkylations, is a reversible process and the distribution of isomeric substitution products varies widely with the experimental condition [11].

The sulfonation can be carried out as a batch or a continuous process. The main variables, which are likely to have a significant effect on the quality of the product, are:

1. The ratio of sulfonating agent and alkylate

2. Sulfonation temperature

3. Reaction time (a combination of addition time and digestion time for batch process)

Table 2.1 Suggested sulfonation conditions for linear alkylbenzene

Sulfonating Reagent	Quantity of Reagent Required Molar Ratio	Addition Temp °C	Digestion Temp °C	Digestion Time mins.
Gaseous SO₃	1.02/1	50-55	55	5-20
22.5%oleum	2.90/1	50-60	40	90
98% H₂SO₄	4/1	45-55	55	180-210

2.5 Literature Reviews

Chakradhar D. et al. [12] invented the new ether type condensation reaction products prepared from phenol having unsaturated and/or saturated hydrocarbon substituents on the nucleus, such as those present in the cashew nut shell liquid group. According to the present invention, non-ionic surface active agents are produced by incorporating an alkylene oxide for example ethylene oxide, propylene oxide or the like in the hydrophobic long chain phenols which was obtained by the distillation of cashew nut shell liquid, Bhilawan Shell liquid and/or urushiol. The desired amount of alkylene oxide may be added in gaseous or liquid-state to the aforesaid phenols at a temperature lying generally between 80 and 200 °C in a closed vessel and preferably in an inert

atmosphere of nitrogen. The catalysts for the reaction could be caustic alkalies, alkali alkoxides, tertiary organic bases and the like.

Henkel et al. [13] discovered a process that used sulfur trioxide attached to saturated fatty acid to produce fatty acid ester, which contain fatty acids with 8 to 18 carbon atoms in the molecule, by the sulfonation. Preferably the fatty acids, which are obtained from natural fats of plants and marine animals, but may also be of synthetic origin are used.

Naae et al. [14] found a method of producing surfactants from lignin. This was carried out by reducing lignin in the presence of a carbon monoxide or hydrogen at high temperature and pressure to produce low molecular weight lignin phenols and subjecting the lignin phenols to one or a combination of several reactions such as alkoxylation, alkylation, sulfonation, sulfation, alkoxysulfation and sulfomethylation. The lignin surfactants so produced can be employed in a surfactant system to recover oil from underground formation.

Lew and Straus [15] synthesized a low viscosity aqueous alkyl toluene or xylene sulfonate, which was suitable for use as a surfactant in enhanced oil recovery. It was prepared by neutralizing the alkyl toluene or xylene sulfonic acid obtained by the sulfurtrioxide sulfonation of alkyl toluene or alkyl xylene. It had an average molecular weight of 300 to 365. The alkyl side chain on the toluene or xylene may be straight, i.e. linear or branched chain in structure and will contain from 12 to 24 carbon atoms.