

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 General structural features

A surfactant (a contraction of the term *surface-active agent*) is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). The term *interface* indicates a boundary between any two immiscible phases; the term *surface* denotes an interface where one phase is a gas, usually air.

Surface-active agents have a characteristic molecule structure consisting of a structural group that has very little attraction for the solvent, known as a *lyophobic group*, together with a group that has strong attraction for the solvent, 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 (hydrophobic) group of the surfactant, and 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 decrease the work needed to create unit area of surface (the surface free energy per unit area, or surface tension). On the other hand, the presence of the lyophilic (hydrophilic) 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 of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it [5].

2.2 Type of surfactants

The chemical structures of groupings suitable as the lyophobic and lyophilic portions of the surfactant molecule vary with the nature of the solvent and the conditions of use. In a highly polar solvent such as water, the lyophobic group may be a hydrocarbon or fluorocarbon or siloxane chain of proper length, whereas in a less polar solvent only some of these may be suitable. In a polar solvent such as water, ionic or highly polar groups may act as lyophilic groups, whereas in a nonpolar solvent such as heptane they may act as lyophobic groups. As the temperature and use conditions (e.g., presence of electrolyte or organic additives) vary, modifications in the structure of the lyophobic and lyophilic groups may become necessary to maintain surface activity at suitable level. Thus, for surface activity in a particular system the surfactant molecule must have a chemical structure that is amphipathic *in that solvent under the conditions of use*.

The hydrophobic group is usually a long-chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane; the hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified as :

1. *Anionic*. The surface-active portion of the molecule bears a negative charge, for example, RCOO^-Na^+ (soap), $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$ (alkylbenzene sulfonate).
2. *Cationic*. The surface-active portion bears a positive charge, for example, $\text{RNH}_3^+\text{Cl}^-$ (salt of a long-chain amine), $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$ (quaternary ammonium chloride).
3. *Zwitterionic*. Both positive and negative charges may be present in the surface-active portion, for example, $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$ (long-chain amino acid), $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ (sulfobetaine).

4. *Nonionic*. The surface-active portion bears no apparent ionic charge, for example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid), $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alkylphenol).

2.3 Properties of surfactant

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.

The molecule at the surface of a liquid have potential energies greater than those of 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 those with the widely separated molecules in the gas phase. Because the potential energies of molecules at the surface are greater than those in the interior of the phase, an amount of work equal to this difference in 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. Although more correctly thought of as a surface free energy per unit area, surface tension is often conceptualized as a force per unit length *at a right angle to the force* required to pull apart the surface molecules in order to permit expansion of the surface by movement into it of molecules from the phase underneath it.

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. Each molecule at the interface has a potential energy greater than that of a similar molecule in the interior of its bulk phase by an amount equal to its interaction energy with the molecules in the interior of its bulk phase minus its interaction energy with the molecules in the bulk phase across the interface.

If we now add to a system of two immiscible phases (e.g., heptane and water), a surface-active agent that 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/or heptane molecules of the original interface, 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 there 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 system is accomplished readily by a number of methods of which the most useful and precise for solutions of surfactants are probably the drop-weight and Wilhelmy plate methods. An excellent discussion of the various methods for determining surface and interfacial tension is included in the monograph on emulsions[5, 6].

2.3.2 Critical micelle concentration (C.M.C.)

A property of surfactants that may be as fundamental, and certainly is as important, as their property of being adsorbed at interfaces. This property is micelle formation - the property that surface-active solutes have of forming colloidal-sized clusters in solution. Micelle formation, or micellization, is an important phenomenon not only because a number of important interfacial phenomena, such as detergency and solubilization, depend on the existence of micelles in solution, but because it affects other interfacial phenomena, such as surface or interfacial tension reduction, that do not directly involve micelles.

Almost from the very beginning of the study of the properties of surfactant solutions (actually, soap solutions), it was recognized that their bulk properties were unusual and indicated the presence of colloidal particles in the solution.

When the equivalent conductivity (specific conductance per gram-equivalent of solute) of an anionic surfactant of the type Na^+R^- in water is plotted against the square root of the normality 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 (Figure 2.1). This break in the curve, with its sharp reduction in the conductivity of the solution, indicating a sharp increase in the mass per unit charge of the material in solution, is interpreted as evidence of the formation at that point of micelles from the unassociated molecules of surfactant with part of the charge of the micelle neutralized by associated counterions.

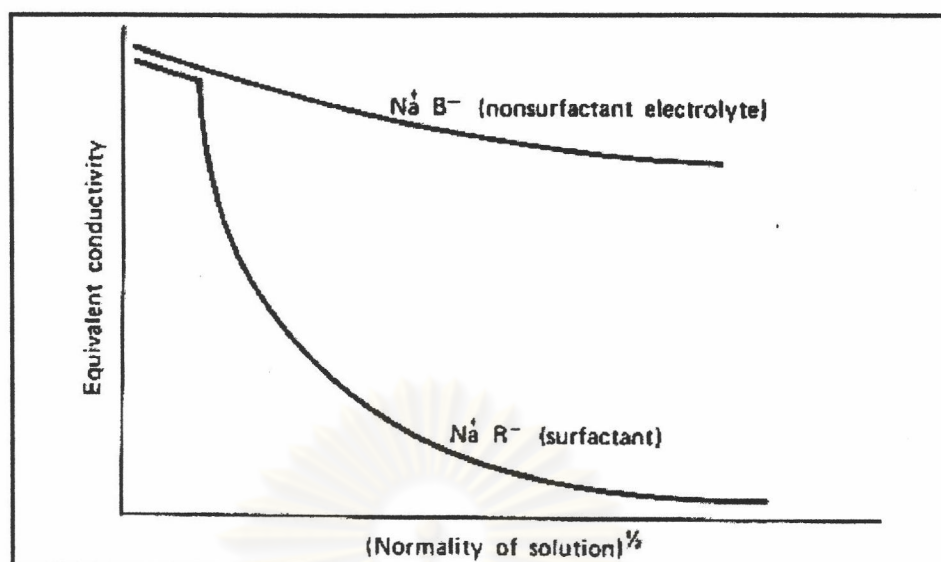


Figure 2.1 Plot of equivalent conductivity versus (normality of solution)^{1/2} for an aqueous solution of surfactant of type Na⁺ R⁻.

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 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 use of any of these 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 open to the serious objection that the presence of the dyestuff may affect the value of the C.M.C.

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 it accomplishes by a combination of effects involving adsorption at interfaces, 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 (the material that is to be removed from the substrate in the cleaning process), and (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 from 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 on 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.

Solubilization into aqueous media is of major practical importance in such areas as the formulation of products containing water-insoluble ingredients, where it can replace the use of organic solvents or cosolvents; in detergency, where solubilization is believed to be one of the major mechanisms involved in the removal of oily soil; in micellar catalysis of organic reactions; in emulsion polymerization, where it appears to be an important factor in the initiation step; in the separation of materials for manufacturing or analytical purposes; and in enhanced oil recovery, where solubilization produces the ultralow interfacial tension required for mobilization of the oil.

2.4 Sulfonation of aromatic compounds

The sulfonation of aromatic compounds can be handled with oleum, sulfuric acid or gaseous sulfur trioxide. The sulfonate group is introduced into the benzene ring primarily in the *p*-position. The process may be operated either as a batch or continuous process.

The detail mechanism of sulfonation is a type of electrophilic aromatic substitution. Aromatic sulfonation places a sulfonyl group ($-\text{SO}_3\text{H}$) onto the benzene ring. It accomplishes this by the use of sulfur trioxide in the presence of sulfuric acid (Figure 2.2-a) [7].

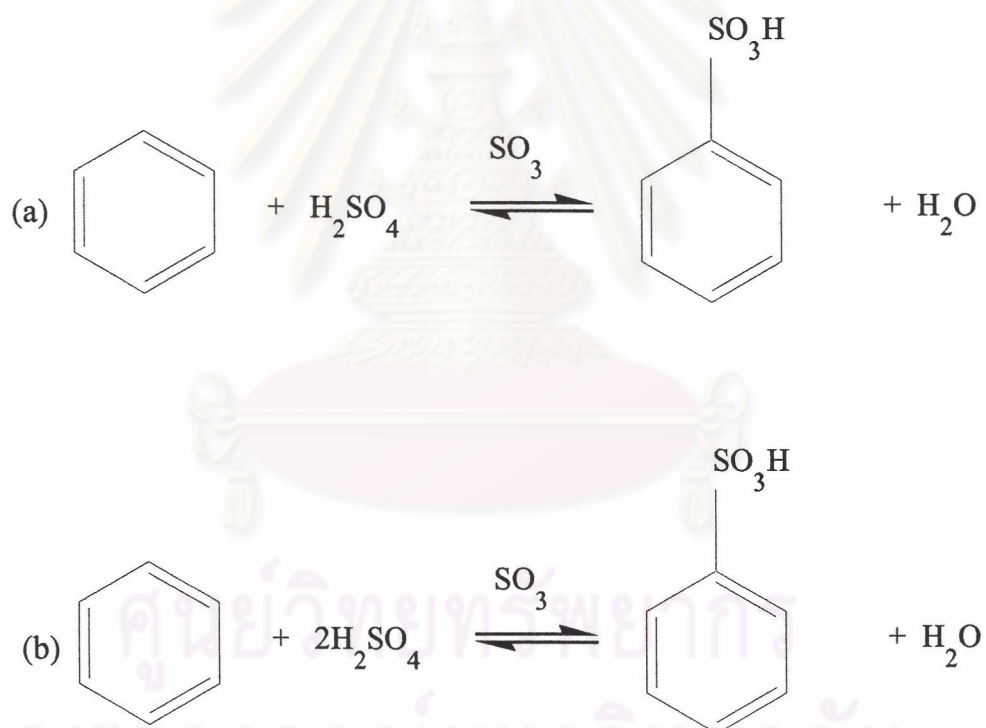


Figure 2.2 Reaction of Aromatic sulfonation of benzene.

Sulfur trioxide gas is dissolved into concentrated sulfuric acid at 20% to give what is called "fuming sulfuric acid" which earns its name by billowing out white plumes of smokey SO_3 fumes when the bottle is opened. The sulfur trioxide (SO_3) serves two purposes. It acts first as the sulfonating agent, and it prevents the unfavorable reversible of this equilibrium by reacting with and effectively removing the water product thus driving this equilibrium to the right.



The sulfonation can be accomplished without the sulfur trioxide by using excess sulfuric acid (Figure 2.2-b) [7]. The extra sulfuric acid will act as a dehydrating agent absorbing the water and preventing the reversal of the equilibrium. This is not as efficient as the sulfur trioxide so the reaction is much slower.

The reaction mechanism in the presence of the sulfur trioxide differs by that of excess concentrated sulfuric acid in that step 1 in the mechanism shown in Figure 2.3 below is not necessary, and the mechanism begins essentially with step 2. In both environment the SO_3 is apparently the sulfonating agent (step 2 in Figure 2.3) [7].

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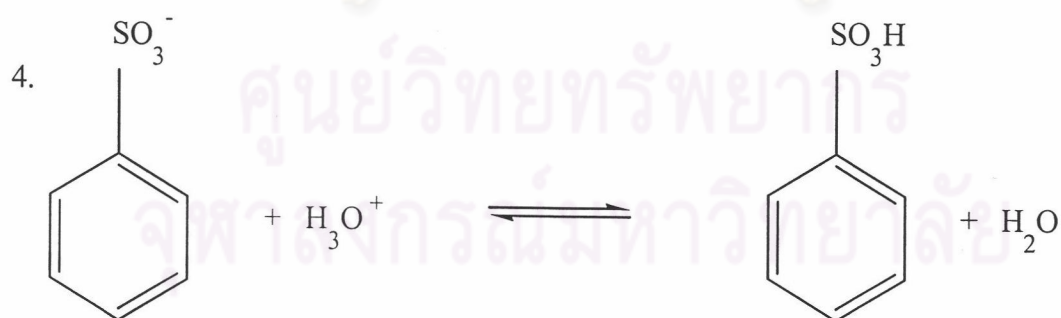


Figure 2.3 The reaction mechanism of aromatic sulfonation

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) [7,8].

Table 2.1 Suggested sulfonation conditions for linear alkylbenzene

Sulfonating Reagent	Quantity of Reagent Required Molar Ratio	Addition Temperature (°C)	Digestion Temperature (°C)	Digestion Time (mins.)
Gaseous SO ₃	1.02/1	50-55	55	5-20
22.5% oleum	2.90/1	50-60	40	90
98%H ₂ SO ₄	4/1	45-55	55	180-210

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2.5 Literature Reviews

Chakradhar D. [9] 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 catalyst for the reaction could be caustic alkalies, alkali alkoxides, tertiary organic bases and the like.

Dohhen K. C. [10] invented the process for preparation of sulfurized calcium phenate detergents from cashew nut shell liquid (CNSL). Distilled or hydrogenated distilled CNSL is reacted with calcium salt and sulphur in the presence of promoters to obtain a reaction mixture. The reaction mixture is subjected to the step of carbonation to obtain basic sulphurized calcium phenate. Such a calcium phenate is added to lubricating oil or grease as an additive.

Pitima S. [11] synthesized the sodium cardanol sulfonate from cashew nut shell liquid by sulfonation using chlorosulfonic acid. Then it was followed by neutralization with sodium bicarbonate to give cardanol sulfonate in 61.34% by mole.