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A Review of Physico-Chemical Study

Mayank[1]*, Dr. Sarita Tiwari[2]

[1] Research Scholar, Singhania University

[2] Associate Professor Dept. of Chemistry, Singhania University

Abstract - The word surfactant is a blend of surface active agents. The surfactants are typically organic compounds that are amphiphilic. Surfactant & amphiphile are two terms that are occasionally used interchangeably. The phrase refers to the fact that all surfactant molecules have at least two components, tthat is soluble in a certain fluid (the lyophilic part) and the other of which is insoluble in that fluid (the insoluble part) (the lyophobic part). When the fluid is water, the hydrophilic and hydrophobic parts are frequently discussed. The interfacial adsorption & micellization of SDS in aqueous liquid-vapor PEG of various chain lengths were investigated using surface tension, conductance, & spectrophotometric methods.

Keywords - physico-chemical, chemical, surfactants, micelles

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1. INTRODUCTION

A surfactant is an atom that is made up of two parts: one that dissolves in water (hydrophilic or polar) & that dissolves in oil (hydrophobic or non-polar). The hydrophilic portion is referred to as the headgroup, while the hydrophobic portion is referred to as the tailgroup. Surfactants are referred to as detergents and soaps, depending on the starting point.

Soaps: Soaps are contains natural chemicals that dissolve in water and are usually sodium or potassium salts of unsaturated lipids. Cleansers are made by synthetically treating fats & oils, or their unsaturated fats, with a solid alkali. In hard water, they are less solvent. Sodium palmitate, sodium oleate, sodium cholate, and other salts are examples.[1]

Surfactants are also classified according on their headgroup. Anionic and cationic surfactants contain oppositely charged headgroups, whereas zwitterionic surfactants have both emphatically and contrarily charged headgroups (normally reliant on pH). The headgroups of nonionic surfactants have no charge. The surfactant surface is dynamic because It adsorbs, or accumulates, at polar-non-polar interfaces, with the headgroup solvated in the polar medium & tailgroup solvated in the non-polar medium. Interactions between water and air, as well as water and oil, are examples of such interfaces. The interface between hydrophobic & hydrophilic media is always problematic, framework is continuously trying to limit the interfacial territory, thus limiting the framework's vitality. This 1s why oil beads in water or water drops in the air, for example. take on circular shapes (dismissing gravitational impacts). When a surfactant adsorbs to an interface. the contact's free liveliness diminishes (causing adsorption), allowing for bigger interfacial zones in the system. The framed oil beads in the water will be considerable if oil is blended in water under mixing conditions, for example. Because the oil is thinner, the beads will gradually mix into larger beads, reducing interfacial vitality, and finally ascend to the surface. Surfactant, on the other hand, will adsorb to the water-oil interface, lowering the surface liveliness and leading in smaller oil particles and the creation of an emulsion. The emulsion can separate into a thermodynamically temperamental macroemulsion or a thermodynamically stable microemulsion after a specific length of time. Surfactants' capacity to lower interfacial energy is crucial in the development of froths & scatterings.[2]

Because of its wide range of applications, polymer-surfactant communication is an exciting & promising subject of study. Such frameworks have pulled in extreme consideration inferable from its characteristic logical intrigue, its potential for abuses in modern procedures, for example, upgraded oil recuperation process arrangement of pharmaceutical items, sustenance stuffs, beauty care products, paints, and so on. Likewise it is parallel with natural organized themes. Polymer-surfactant totals are utilized to control rheological properties, stage practices, interfacial properties, and so on.

Relationship of polyions with oppositely charged surfactants (unadulterated and in addition in mix with nonionic surfactants) has been examined widely by various agents. The examinations include the cooperation of surfactants with manufactured polyanion or polycation and in addition characteristic polymers (both of plant and creature birthplace). Such investigations have been performed utilizing various procedures, viz. color testing, surface pressure, thickness, turbidity, fluorimetry, static and dynamic light dispersing,conductance and e.m.f. estimations, and so forth. [3]

2. SURFACTANTS AND MICELLES

The self-association process of surfactant molecules into micelles. vesicles or membranes plays an important role in many fields ranging from biological systems to technical applications. This aggregation. as well as protein and nucleic acid folding and their association, is governed by the intricate balance between hydrophobioc interactions and other types of noncovalent solute- solute and solute-solvent interactions (Schramm 2000). This interest continues to grow because of the flexibility of the properties of these surfactants. A surfactant is a chemical that has the ability to adsorb at interfaces (a shortening of the word "surface active agent"). Surfactants adsorb on surfaces (interfaces) that are made up of 2 immiscible liquids, a liquid-gas (air) surface, or a solid & liquid. Amphiphiles, surface-active agents, and "soft-matter" are all terms used to describe surfactants. There are two sections to surfactant molecules: a hydrophilic (polar) part that likes water and a hydrophobic (nonpolar) part that doesn't. When surfactants are dissolved in aqueous or non-aqueous solutions, their amphiphilic nature causes a variety of interesting events. The lyophobic (hydrophobic) group of a surfactant dissolved in aqueous medium changes the structure of the water by breaking hydrogen bonds between water molecules & results an orientation of the water in the vicinity of the hydrophobic group. As a result of this distortion some of the surfactant molecules are expelled to the interfaces of the system with their hydrophobic groups oriented so as to minimize contact with the water molecules. The concentration above which aggregate (known as micelle) formation becomes appreciable is termed CMC.[4]

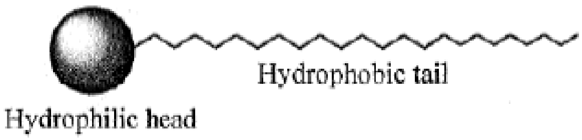


Figure 1: Schematic representation of a surfactant molecule

The hydrophobic part of a surfactant is usually a long-chain hydrocarbon residue, and less often halogenated or oxygenated hydrocarbon or siloxane chain. The hydrophilic group on the other hand is an ionic or highly polar group. Depending on the nature of the hydrophilic groups, surfactants are classified as:[5]

1. Anionic. The surface-active portion of the molecule bears a negative charge, e.g. RCOO-Nat (soap). RC6tLS03-Na+ (alkyl benzene sulfate).

2. Cationic. The surface-active portion of the molecule bears a positive charge, e.g. RNH3+ (salt of long chain amine), RN(CH3)3+Br- (quaternary ammonium bromide).

3. Zwitterion. Both positive and negative charges may be present in the surface-active portion, e.g. RN+(CH3)2CH2CH2803- (sulfobetaine), RN+H2CH2COO- (long-chairl amino acid).

4. Nonionic. The surface active portion bears no apparent iomic charge, e.g. RCOOCH2CHOHCH20H (monoglyceride or long chain fatty acid). RC6H4 (0C2H4) xOH (polyoxyethylenated alkylphenol).

Surfactants, despite being present in very minute amounts in solution, have a significant impact on the overall parameters of the system, like as surface tension, osmotic pressure, solubility, etcetera, due to their propensity to adsorb at surfaces & form micelles. In fact, a large number of experimental observations can be summed up and almost all physicho-chemical properties versus r" lots for a given surfactant-solvent system will show an abrupt change in slope in a narrow concentration range (the erne value), that can be illustrated by a classic graph, shown in Figure 2. The features of surfactants have piqued the scientific community's interest. De Gennes' Nobel Lecture in 1991, for example, was on "Soft Matter," which included polymers, surfactants, & liquid crystals. A colloidal entity in dynamic equilibrium with the monomer from which it is generated is referred to as a "micelle." When the surfactant concentration climbs above the erne, fresh monomer is added, resulting in the creation of new micelles, keeping the monomer concentration virtually constant & near to the likewise known. . Due to three- dimensional hydrogen bonding, water has an open structure that allows for the formation of clusters of water molecules with voids of specified sizes that can admit nonpolar chains.[6]

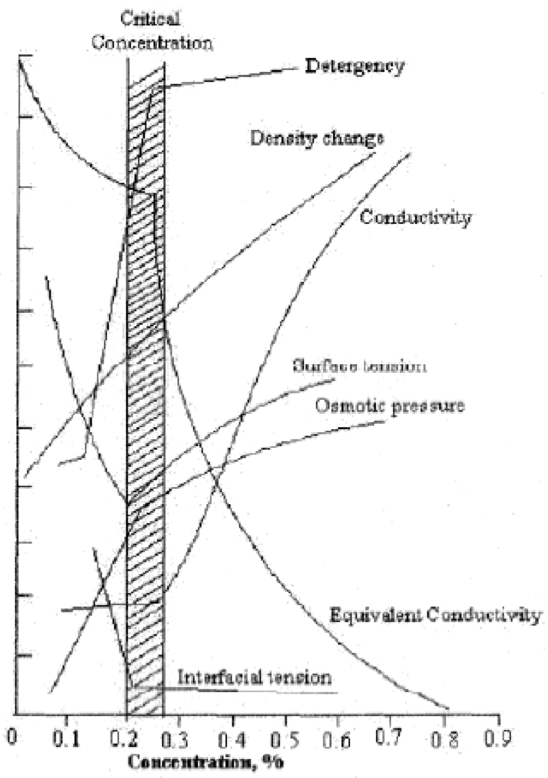


Figure 2: Schematic representation of the concentration dependency of some physical properties for solutions of a micelle forming surfactant.

Creation of the cavity restricts the motions of solvent molecules in the hydration shell of a nonpolar solute. This restriction leads to loss of entropy, which 1s exceptionally large in aqueous solution due to the small size of water molecules. At a given temperature, only a certain amount of monomer could be accommodated in the cavities for a given surfactant, and any extra surfactant would result in the formation of micelles. In other terms, the presence of surfactant acts as a driving force. preventing the monomer hydrocarbon chains from contacting water. According to Langmuir's concept of differential solubility, the hydrocarbon chains cluster to form a core (micellar core), while the polar groups interact with the water.[7]

The size and shape of a micelle are influenced by the number of monomer molecules in each micelle (aggregation number, n). Although the actual size and shape of micelles are unclear, an ionic micelle in dilute aqueous solution is thought to be spherical, though micellar shape changes in the presence of different hydrotops have been seen). Charged (or polar) hydrophilic groups are guided towards the aqueous phase (stern layer), while hydrocarbon chains are directed away from the water (forming the hydrophobic central core). The hydrophobic interior is separated from the majority aqueous phase by the Gouy Chapman double layer. which is near to the stern layer and has a high density of polar head counter-ions. Although it's often assumed that there are well-defined water layers around the micellar surface. there's no agreement on the composition of the micellar core. or whether it's made up of pure hydrocarbon or hydrocarbon mixed with water. Water penetration in the micellar core, on either hand. Continues to be a source of debate.[8]

Low angle neutron scattering tests are the main source of the contentious "water xposure of micelles" concept. The key properties of molecular conformation in micelles are discussed in expressions of predictions from the "phase separation" or "mass action" model. The phase separation model's predictions are congruent with experimental data and, in particular, with some essential elements of micellar structure.

1. As per Langmuir's basic idea of differential solubility, the micellar core is nearly empty of water.

2. Micellar chains are arbitrarily dispersed & ultimate structure is determined by steric forces.

3. Water comes into touch with the hydrophobic sections of the micelle due to a disordered structure in which the terminal groups or chain ends are near to the micellar surface & therefore accessible to bulk water.

Despite the fact that the "water penetration" notion for micelle hydrophobic divisions is now less adequate than the "water exposure" conception, this contentious problem is still being debated.[9]

However the phase separation model along' with the related thermodynamics of micelle formation is discussed in previous research . Another important characteristic of surfactants is there ability to form microemulsion. Microemulsions are compartmentalized liquids having huge application in several physico-chemical and technological processes. They are optically isotropic, transparent, normally low viscous and thermodynamically stable solutions (dispersions) having a prolonged life-span and can be prepared by mixing appropriate proportion of oil, water and surfactant. In many cases the presence of co-surfactants (polar compounds of intermediate chain length, e.g. medium chain alkanols) may stabilize microemulsions by providing the proper balance between hydrophilic properties for the required oil and water phases under the conditions of use. But cosurfactant free microemulsions are also known.

Microemulsions are of two types, based on the nature of the dispersed phase: oil-in water (0/W) and water-in-oil (W /0) having average particle size within the range of 5-100 nm. Pictorial representations of reverse micelles and microemulsions are shown in Figure 1.3. They are polydispersed in nature and the polydispersity decreases with decreasing particle size. In the formation of microemulsions. one of the two immiscible liquids (viz. oil or water) breaks up into particles that are dispersed in the second liquid. They can be formed with expenditure of a very little energy (can be supplemented by the thermal energy of the system) and are thus thermodynamically stable. A mixture of the right proportion of water, amphiphile and oil may spontaneously homogenize itself forming a micro emulsion. In case of W /0 micro emulsion each water droplet is covered be an oriented monolayer of surfactant molecules.

In recent years microemulsion have been extensively applied to many fields, such as chemical reactions nanometerials preparation and drug delivery systems. Reactions performed therein may significantly deviate from the normal courses and are often catalyzed in compartmentalized environments. Recently, attempts have also been made to prepare and study nonaqueous microemulsions for ionic liquids. These microemulsions have attracted much interest from both theoretical (thermodynamics, particle interactions, etc.) and practical (potential use as a novel reaction media) view point.[10]

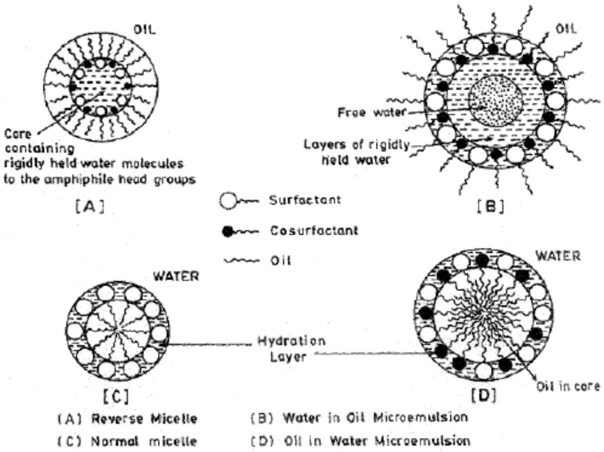


Figure 3: Schematic representations of reverse micelles and microemulsions.

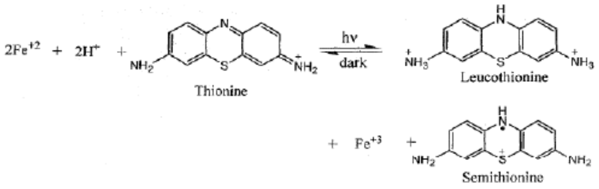
3. DYE- SURFACTANT INTERACTIONS

Although colour changes in ionic dyes in the influence of opposite charges ionic surfactants in aqueous solution have led numerous researchers to hypothesise dimer & multimer formation of dye molecules in the surfactant micelle since the beginning. this area are still important and interesting for the theoretical, ecological and technological point of view. The enhanced energy transfer between dyes in dye-surfactant systems made them good model membrane systems of chloroplast. The peculiar behaviour in both absorption and fluorescence spectra of dyes in the presence of surfactants of opposite charge were attributed to the formation of a continuum of dye-surfactant aggregates or mixed micelles depending on the surfactant: dye ratio (S/D). Among other things, the investigations into the behaviour of different dyes in surfactant aqueous solutions, give information about the mechanisms according to which surfactants operate as leveling agents and provide information on the influence of dye-surfactant interactions on the thermodynamics and kinetics of dyeing process. This may directly affect the quality of dyeing, which is one of the goals of textile finishing. Surfactants are also used as solubilizers for water insoluble dyes, to break down dye aggregates in order to accelerate adsorption process on fiber, as auxiliaries for improving dye adsorption and as leveling or dispersing agents. Surfactants employed as levelling agents work in different ways depending on the structures of the dye & substrate. As a result, a lot of work has been done on dyesurfactant interactions in binary mixtures, such as interactions between ionic dyes & ionic surfactants of opposite and same charges, ionic dyes & nonionic surfactants, and nonionic dyes & ionic or nonionic surfactants in the submicellar & micellar concentration ranges of surfactants.Hydrophobic interactions are likely to occur once electrostatic forces have brought electrostatic force molecules together, substantially altering the environment perceived by the chromophore. Studying the chemical equilibria, mechanism, & kinetics of surfactant sensitive colour processes will benefit greatly from knowledge of dye surfactant interaction.

The findings of spectrum experiments on phenosafranin, a cationic phenaz:ine dye, in aqueous solutions containing three different types of surfactants, including CTAB, sodium lauryl sulphate (SLS), & Triton X 100, were published. Triton X- 100 and SLS create 1:1 molecular compounds with the dye, however phenosafranin has no interaction with CTAB. According to the thermodynamic & spectrophotometric features of these complexes, phenosafranin forms a strong charge-transfer (CT) or electrondonor-acceptor (EDA) complex with Triton X-100, while the interaction with SLS is coulombic. Photovoltage & photoconductivity measurements of phenosafranin in these surfactants support this result. The CT interaction of Triton X-100 with other cationic dyes such as crystal violet, fuchsin, & rhodamin B has been confirmed in the same investigations. Thiazine dyes are structurally comparable to phenosafranin, thus we've picked thionine, methylene blue, azure A, azure B, & azure C to study.

4. ELECTROCHEMICAL BEHAVIOUR OF DYES

The search for renewable sources of energy has led to an increasing interest in photochemical cells because of their possible role as transducers of solar to electrical energy. It has been observed that photo effects in electrochemical systems are enhanced if the electrodes are coated with dye stuft wherein their redox chemistry plays a vital role. Dyes as sensitizers in photo-electrochemical devices for solar energy conversion have been reported to have very low energy conversion efficiency in the past. The delayed discharge of photo-produced intermediate dye radicals (i.e., semi-reduced 'leuco' dyes) at the cell electrode, as opposed to the radical-radical recombination reaction in the bulk of the solution, has been variously attributed to this issue. The reaction with thionine can be stated as follows:



To enable the discharge process more favourable, the recombination reaction must be stopped in the bulk homogenous phase. Initiatives to slow down bulk reactions in a suitable micellar media have been made in the past. In this connection some oxazine dyes have been considered sensitizers in photogalvanic devices in the past. The dye surfactant interactions have piqued researchers' interest because they resemble many biological processes that occur between big organic molecules & biomembranes, and they can serve as a model redox system.

Furthermore, interactions between ionic dyes & charged surfaces are of relevance in a variety of applications, spanning from electronic device prototype to drug delivery system evaluation. It has been reported that pure metal electrodes becomes sensitive to light when coated with a dye or immersed in a dye solution. Phenothiazine and substituted-phenothiazine dyes are thought to be important in the direct conversion of solar energy to electricity.

For example, the photochemical redox reaction between thionine and Fe2+ has been used advantageously to devise and understand the mechanism of the photogalvanic cell. Early workers have extensively examined the photogalvanic activity of various dyes with reversible and irreversible reducing agents. In order to understand the mechanism of photogalvanic action it is essential to investigate the electrochemical behaviour of these dyes.

5. CONCLUSION

Surfactant refers to a mixture of surface active chemicals. The surfactants are usually amphiphilic organic molecules. Surfactant & amphiphile are two terms that are occasionally utilized interchangeably. The phrase refers to the fact that all surfactant molecules have at least two components, one of which is soluble in a certain fluid (the lyophilic part) & other of which is insoluble in that fluid (the insoluble part) (the lyophobic part). When the fluid is water, the hydrophilic & hydrophobic parts are frequently discussed. The hydrophilic portion is known as the polar head group, while the hydrophobic portion is known as the tail. Surface active molecules align themselves at the two-phase contact. Surface active agents lower the surface tension between two phases, have a tendency to stick together near the interface, and act as an excellent mediator when two phases disagree.

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Corresponding Author

Mayank*

Research Scholar, Singhania University