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A Review: Surfactant Properties and Micellar Structure

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Abstract- Surfactants, an essential class of compounds, exhibit distinctive properties owing to their amphiphilic nature, possessing both hydrophobic and hydrophilic characteristics. Understanding surfactant properties is crucial in elucidating their behavior at interfaces and in solution. These properties include their ability to reduce surface tension, form micelles, and solubilize hydrophobic substances. These properties are paramount in various applications, including drug delivery, enhanced oil recovery, and the formulation of consumer products. an understanding of surfactant properties and micellar structures is pivotal in a wide array of scientific and industrial applications.

KeywordS- Micellisation, CMC, Kraft point, Cloud point, and HLB.

I.INTRODUCTION

Surfactants are amphiphilic molecules. They have two specifically different characteristics in different parts of the same molecule, known as polar and nonpolar. Therefore, a surfactant molecule has hydrophilic (water-loving) and hydrophobic (water-hating) characteristics. A surfactant molecule can be represented as having a polar head and a nonpolar "tail". The hydrophilic portion of a surfactant may carry a negative or positive charge, both positive and negative charges or no charge at all.

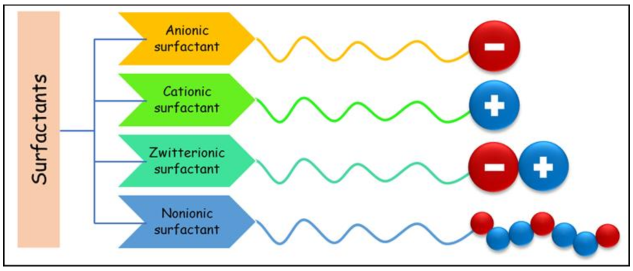


Figure 1: Schematic Representation of Different types of Surfactant molecules

Surfactants are usually classified according to the nature of head group. [1] The hydrophobic part of a surfactant may consist of one or several hydrocarbon chains containing from 8 to 20 carbon atoms; the chain may be saturated or unsaturated, linear or branched and may have hetero (oxygen) atoms, aromatic rings, amides, esters or other functional groups. Based on the charge on the polar head group and its molecular structure, they have been classified as anionic, cationic, amphoteric (or zwitterionic) or nonionic surfactant. The science of surfactants is rapidly growing with its wide applications in different industries, medical sciences, life sciences, chemistry, physics, engineering pollution control, etc.

II.PROPERTIES OF SURFACTANTS

Micellisation

Depending on the molecular structure and characteristics of surfactants, some properties like critical micelle concentration (CMC), cloud point (CP), Krafft point (KP), hydrophilic-lipophilic balance (HLB), etc, are significant. In both cases, KP and CP are dependent on temperature due to the solubility of the surfactant is very interesting. The solubility of surfactant is dependent on temperature. There are some exciting properties described below.

McBain and later G.S Hartley were the first to discover the presence of micelle. When surfactant molecules dissolve in water, they form a variety of aggregate formations known as micelles. [2,3] A surfactant self-assembles into micelles, tiny spheres with hydrophilic heads pointing out and hydrophobic tails pointing in when added to water. Figure 2 depicts a schematic representation of micelle.

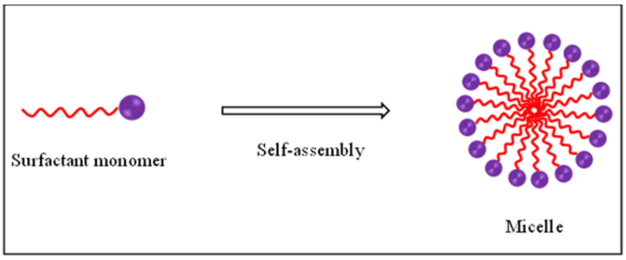


Figure 2: Schematic representation of micelle

The first appearance of micelle formation at a particular concentration is called critical micelle concentration (CMC). Various methods can be used to find CMC, including specific conductivity, surface tension, turbidity, solubilisation, magnetic resonance, etc. A graph of different physicochemical properties versus concentration is plotted in Figure 3, where the dotted line shows CMC at a particular concentration.

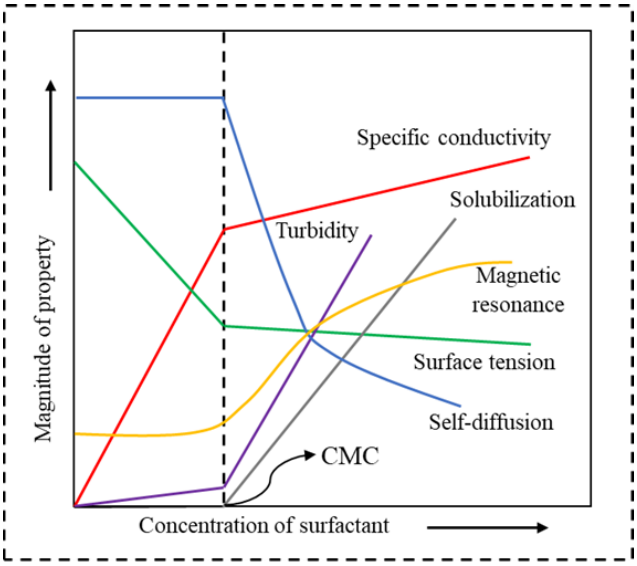


Figure 3: Schematic representation of the determination of CMC using different methods

The molecules swim freely below the CMC, looking for places to connect and producing mono-molecular layers to absorb. Surfactant molecules arrange themselves at the air/water interface, thereby lessening surface tension before reaching the CMC. The added surfactant exhibits self-assembly behaviour above the CMC, generating a micelle. The surface tension in the surfactant solution remains constant after that point. Surface tension decreases dramatically as surfactant concentration increases to a point, then stabilises. The CMC is the moment at which the plot breaks or inflexion occurs. A schematic representation of micelles before and after CMC is shown in Figure 4.

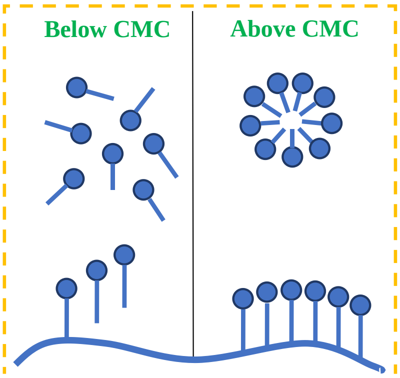


Figure 4: Schematic representation of micelles before and after CMC

Micelles are labile, non-covalently bonded aggregates of surfactant monomers. They can attain the shape of a sphere, cylinder or disc. The size and morphology of the micelles are determined by the existence of surfactant and the conditions of solutions such as temperature, pH, concentration of surfactant, ionic strength, etc. [4,5]

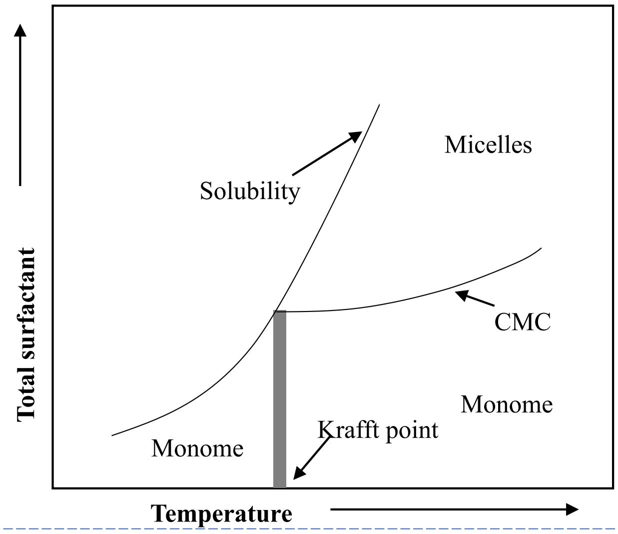


Figure 5: Temperature and total relationship with surfactant

A comparison of total surfactant concentration and temperature and its total relationship with surfactant states are depicted in Figure 5.

Krafft point

The Krafft point (KP) is a property that varies with temperature. The KP of a surfactant is the temperature at which the solubility of the surfactant equals its CMC. In other terms, micelles can only form above a specific temperature, known as the Krafft temperature (Tk). [6] The temperature at which a surfactant's solubility equals its CMC is known as the KP of an ionic surfactant [Figure 6]. The presence of additions impacts the KP of the specific surfactant. Electrolytes are added, and thus raise the KP at its CMC. Branching alkyl chains or two alkyl chains have lower KP than ionic head groups or polar head groups. Since micelles can only form at temperatures higher than the KP, it is frequently necessary for a surfactant to have a KP value lower than the temperature at which it is used.

A surfactant's KP is influenced by several factors, including its size and the characteristics of the nonpolar tail, polar head groups, and counter ions that make up its constituent elements. Some critical variations of KP in alkyl chains are shown below. Surfactants having linear hydrophobic chains containing surfactants have higher KP than their branched isomers. A longer hydrophobic chain increases the KP. The presence of nitrogen (N) and oxygen (O) containing polar atoms or double bond present in the hydrophobic chain decreases the KP. The addition of salts frequently leads to increases in KP.

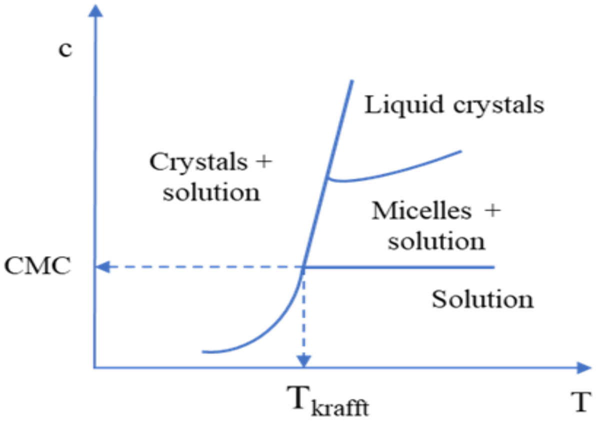


Figure 6: Schematic illustration of Krafft point

Cloud point (CP)

CP is one of the essential characteristics of nonionic surfactants. When a nonionic aqueous solution is heated, it separates into two phases and turns cloudy; this temperature is known as the cloud point (CP). At this point, the solution mixture becomes cloudy. The solubility of the polyethylene oxide (PEO) entity is due to hydrogen bonding in nonionic surfactants because of higher CP. The CP increases as the ethylene oxide (EO) level increases in a nonionic solution. For laundry and cleaning applications, ideal cleaning generally occurs at a temperature above CP. [7,8] The schematic illustration of the Krafft and Cloud points is shown in Figure 7.

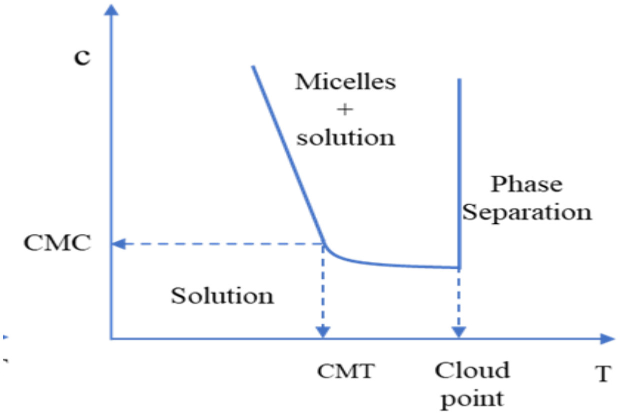


Figure 7: Schematic illustration of cloud point

The CP decreases with an increase in the nonpolar hydrocarbon tail and an increase in the polar PEO hydrophilic group. The CP of surfactants with long polyoxyethylene chains may surpass 100°C. Such surfactants are often determined in electrolyte arrangements since most salts bring down the CP. 'Salting in' and 'Salting out' effects are frequently used to describe how different salts affect nonionic surfactants in terms of increasing or lowering CP. Salting in or salting out electrolytes can exist. 'Salting in' electrolytes aids in the solubilisation of organic compounds in water that are insufficiently solvent, and the effect can be significant. Named after a well-known paper from the late 1800s is the Hofmeister series, in which ions were ranked by their power to salt out proteins, which shows how salts fall on this scale. [9]

The Hofmeister series for anion is:

$SO_4^{2-} > HPO_4^{2-} > CH_3COO^- > Cl^- > NO_3^- > Br^- > ClO_3^- > I^- > ClO_4^- > SCN^-$

For cation, it is:

$NH_4^+ > K^+ > Na^+ > Li^+ > Mg^{2+} > Ca^{2+} >$ guanidinium

Hydrophilic-lipophilic balance (HLB)

The hydrophilic-lipophilic balance, abbreviated as HLB value, which denotes a proportional ratio of polar and nonpolar groups in the surfactant, is used to classify surfactants. [10] According to the strength and size of the hydrophilic and lipophilic parts of the surfactant molecule, Griffin has endeavoured to group as per the hydrophilic and lipophilic (hydrophobic) bits of their atom. The 'hydrophilic-lipophilic balance' (abbreviated as the HLB value) describes the equilibrium of these two limiting groups. A surfactant who's lipophilic (hydrophobic) character is prominent has a low HLB value (9), a surfactant with a predominant hydrophilic character has a high HLB value (> 11), and a surfactant with a moderate hydrophilic and moderate lipophilic nature has an HLB value in the range of 9-11.

The hydrophilic-lipophilic (hydrophobic) balance describes surfactants: an overall proportion of polar and nonpolar gatherings in the surfactant. HLB value: relative ratio of polar and nonpolar groups in surfactant shown in Table 1.

Table 1: HLB value: relative ratio of polar and nonpolar groups in surfactant.

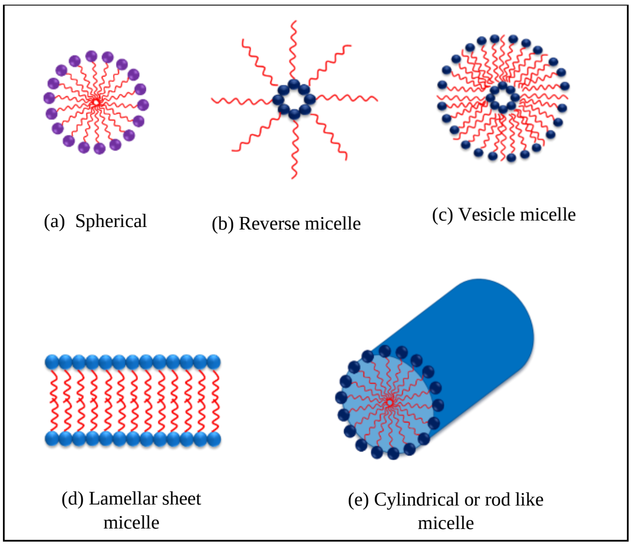
HLB value	Applications
1-3.5	Antifoaming agents
3.5-8	Water-in-Oil Emulsions
7-9	Wetting and spreading agents
8-16	Oil-in-Water Emulsifiers
13-16	Detergents
16-40	Solubilising agents

The CMC decreases as the number of carbon atoms in the hydrophobic tail approaches 16 in an aqueous medium. The CMC is typically calculated by dividing the number of carbon atoms in the ionic surfactant by the number of methylene ($-CH_2$) groups it contains. However, the CMC decrease is significantly more significant for nonionic and zwitterionic (amphoteric) surfactants. Chain branching and hydrophobic chain unsaturation also influence CMC. [11,12]

Micellar structure

Surfactants spontaneously self-assemble into a range of micelle-like microstructures in an aqueous solution. They are made up of a hydrophobic chain core that is protected from water by hydrophilic head groups. Surfactant hydrophilic units combine to create a micellar corona. The surfactant's chemical composition affects CMC. Micelles have different types and shapes, such as spherical micelle, reverse micelle, vesical micelle, lamellar sheet micelle, cylindrical or rod-like micelle, etc., shown in the figure below.

Spherical micelle shown in Figure 8, molecules arrange themselves into tiny clusters called spherical micelles.



(a) Spherical (b) Reverse micelle (c) Vesicle micelle

(d) Lamellar sheet micelle (e) Cylindrical or rod like micelle

Figure 8: Different types of Micelles

Reverse micelle, shown in Figure 8, is formed in a nonpolar medium. In the case of the reverse micelle, the orientations of the surfactants are opposite to the micelles formed in polar solvents. The head groups are oriented inward, with the hydrocarbon moieties remaining solubilised in the nonpolar solvent. Thus, a nonpolar solvent can be dispersed in a polar solvent and vice versa with the help of surfactants.

Vesical micelle The aggregation is called vesical when a micelle of disc shape expands with curvature and becomes spherical with the solvent inside. The water content decreased by spherical < cylindrical or rod-like < lamellar sheet micelle < reverse micelle, etc.

Aggregation number (Nagg)

"Aggregation number" (Nagg) is the number of surfactant monomers (unimers) in a micelle. They are groups of 50 to 200 surfactant molecules that have their own shape and size. Their size and shape are determined by the amount of energy they have. We can figure out the aggregation number using scattering techniques like dynamic light scattering (DLS), small angle neutron scattering (SANS), small angle X-ray scattering (SAXS), and other methods like fluorescence and osmometry.

When the CMC goes up, the Nagg goes down. CMC and Nagg are affected by a number of factors, such as the type of the hydrophilic and hydrophobic groups, the amount of counterion binding, the presence of additives, and some parameters like temperature, pressure, pH, etc. The nonionic surfactants are temperature dependent, but anionic and cationic surfactants are not; nonionic surfactants have higher Nagg than ionic surfactants (anionic and cationic). Because electrostatic repulsion between ionic head groups is larger than steric repulsion between nonionic head groups, ionic surfactants produce smaller micelles with aggregation numbers ranging from 10 to 70 than nonionic surfactants with aggregation numbers ranging from 100 to 100. This is due to the fact that the electrostatic repulsion between ionic head groups is stronger than the steric repulsion between nonionic head groups. Micelle structures can range from spherical to rod-like in form.

III.CONCLUSIONS

Over the past 30 years, new surfactant molecules have been appearing at a relatively rapid pace. Micellar properties and structures play a very crucial role as the deciding factors for characterization of suitable micellar molecules. Hence, knowledge of various parameters such as CP, KP, HLB values, aggregation numbers are very important so that it can be applicable in various applications, such as pharma, drug, consumer products, etc.

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