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Determination of Critical Micelle Concentration (CMC) of Sodium Stearate Solution in Distilled Water

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Abstract:

Surfactant is an organic compound having polar and nonpolar parts. The specific conductivity of sodium stearate surfactant in double distilled water has been studied by conductometric method at three temperatures (298.15, 308.15, and 318.15) K. conductivity of the surfactant increases with increase in temperature and concentration of solution. Critical Micelle Concentration (CMC) of sodium stearate was determined attemperature 298.15 K is 0.00095Mol/lit using the easy plot software. FESEM image shows themorphological structure of the sodium stearate surfactant.

Keynote: Surfactant, specific conductivity, polar, FESEM, EDX**.**

Introduction

Surfactants: Surface active substances known as surfactants have incredible interfacial activity. Amphiphilic chemicals with both lipophilic and hydrophilic tendencies on the same molecules make up all known surfactants(Bhattarai & Das, 2008). These surfactants contain hydrophobic tail made up of non-polar hydrocarbon chain andhydrophilic head made from polar groups as well as ions various electronegative atoms as shown in (Fig. 1). In water, these molecules create a network of hydrogen bonds. Therefore, the hydrophilic group composition is a determining factor in the classification of surfactants into these groups. Based on the characteristics of their hydrophilic head groups, surfactants are categorized into four categories i.e. cationic, anionic, amphoteric or zwitterionic and non-ionic surfactants(Prasad Tajpuriya et al., 2021). Aside from that, surfactants are categorized based on their applications; as they are such versatile substances, many surfactants have several uses. Molecular formula of sodium stearate is $C_{18}H_{35}NaO_2$.Nonionic surfactants do not have any charge in their heads, cationic surfactants have positive heads, amphoteric or zwitterionic surfactants have both positive and negative heads.

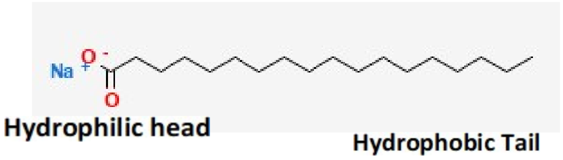


Figure1.General representation of Surfactant molecule with hydrophobic tail and hydrophilic head

Classification of Surfactants

The surfactants are categorized into the following groups according to their polarity and composition:

i) **Ionic surfactants:**

Ionic Surfactants are the surfactants that have charge on their head groups. They can be positively or negatively charged. They are further categorized into anionic or cationic surfactants depending on the functional group(s) that carry the positive and negative charges(Ghosh et al., 2009).

Anionic surfactants:

Anionic surfactants contain negatively charged groups (anions) at their head, such as sulfonate, phosphate, sulfate, and carboxylates). They are widely used as foaming agents, detergents, emulsifiers and stabilizers. Some anionic surfactants are Sodium Stearate $CH_3(CH_2)_{16}COO^-$ Na^+, Sodium Dodecyl Sulphate $CH_3(CH_2)_{11}SO_4^{-}$-Na^+, Sodium dodecyl Benzene Sulphonate $CH_3(CH_2)_{11}C_6H_4SO_3^-$ -Na^+

Cationic Surfactant:

Cationic surfactants contain positively charged group or cation at their head, like ammonium as surface active group. It is used as corrosion inhibitors, anti-microbial, anti-fungal, mineral floatation, sterilization, etc. Examples of cationic surfactants are Benzalkonium chloride (BZlC), Cetylpyridinium chloride (CPC), Benzethonium chloride (BZT)

ii) **Non-ionic Surfactants:**

Surfactants having no charge at their head and arenot ionized into ions in aqueous solution are called non-ionic surfactants. The have widely applied in the production of medicines, dyes, pesticides, food, textiles etc. Examples of non-ionic surfactants are Polyoxyehylene alcohol $C_nH_{2n+1}(OCH_2CH_2)_mOH$, AlkylphenolEthoxylate C_9H_{19}–C_6H_4–$(OCH_2CH_2)_nOH$, Cocamidopropyl betaine $C_{19}H_{38}N_2O_3$.(Bhattarai & Das, 2008)

iii) **Amphoteric or zwitterionic surfactants:**

Amphoteric or zwitterionic surfactants are those that include both cationic and anionic functional groups in a single surfactant molecule. The same molecule is connected to cationic and anionic centers. They are highly biodegradable in nature and cause mild effect to skin so they are used in different personal care products and cosmetics as well as softener in different industries(Rafati et al., 2008).

Several of these surfactants include

Lauramidopropyl Betain $C_{11}H_{23}CONH\ (CH_2)\ 3N^+(CH_3)\ 2CH_2COOC$,

Dodecyl Betain $C_{12}H_{25}N^+\ (CH_3)_2CH_2COO^-$

iv) **Speciality Surfactants:** They are special class of surfactant having capacity to reduce surface tension than conventional surfactants. They also named as are superwetters having high wetting and spreading capacity. Fluorocarbon and Silicone Surfactants are two sub classes of speciality surfactants. But, they are limited commercial application due to their expensive nature.

Silicone Surfactants:

Silicone surfactants are based on silicones and are often used in cosmetics and personal care products. Example: Dimethiconecopolyol

Fluorinated Surfactants:

Fluorinated surfactants contain fluorine atoms in their hydrophobic tails and are used for applications where high water repellency is required.

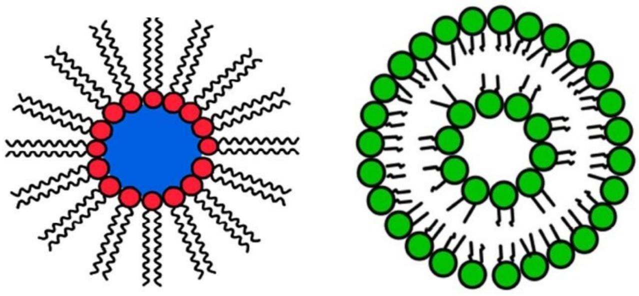
Example: Perfluorooctanoic acid (PFOA): $C_8HF_{15}O_2$

Critical Micelle Concentration (CMC):

Low concentrations of surfactants (free or unassociated surfactant molecules) exist in aqueous solution as monomers. At the contact, these monomers pack together to produce a monolayer that reduces interfacial strain and surface tension. The strong interactions between molecules at the interface and their nearby neighbors allow for the measurement of the rheological properties of the monolayer, even though this event is very dynamic because surfactant molecules enter and exit the contact on a very short time scale. The properties of surfactants at low concentrations in water are similar to those of simple electrolytes, with the notable exception that surface tension drops significantly with concentration (Shahi et al., 2021).

When micelles form in an aqueous medium, the critical micelle concentration (CMC) is the critical aggregation concentration (CAC). Surfactant monomers assemble to form a closed aggregate (micelle) at a certain concentration, with the hydrophilic heads facing water and the hydrophobic tails shielded from it.

When monolayer adsorption is complete and the surface-active properties are at their best, the surfactant property known as the CMC reflects this. Above the CMC, monomer concentrations are almost constant. Because the monomers are the cause of the surface activity, the surfactant characteristics of the solution remain unchanged. Because they lack surface activity, micelles' structure is impacted by increases in surfactant concentration rather than the quantity of monomers in the solution(Rafati et al., 2008).



Reverse micelle

Vesicle

Figure 2. Schematic representation of aggregation of surfactant depending on the concentration (Ali et al., 2014)

A hypothesis concerning aggregate structure was created based on the region that the hydrophilic and hydrophobic groups of surfactants occupied. The surface of a surfactant aggregate must have hydrophilic heads, while the interior of the aggregate must have the hydrophobic portion of the surfactant molecule for the aggregate structure to be stable in an aqueous medium (Fig. 2) (Ali et al., 2014). The same charge repulsion will cause the polar head groups in water to repel one another if they are ionic. Stronger repulsion and a lower likelihood of collective formation are associated with larger charges(Sachin et al., 2019).

1. Single chain surfactants with large head group areas, such anionic surfactants, exhibit a surfactant packing parameter of less than one-third, which leads to the formation of spherical micelles. The greatest length of the surfactant molecule when stretched out is almost equal to the radius of the spherical aggregates.
2. Cylindrical micelles form when the surfactant packing parameter falls between 1/3 and 1/2 (Single Chain Surfactants with Small Head Group Areas: non-ionic surfactants, ionic surfactants in high concentration of salt). The aggregate will become more cylindrical in size and form if there is a shift in the characteristics of the fluid that decreases the hydrophilic head groups' effective size.

The lamella flattens and becomes planar (double chain anionic surfactants in high concentration of salt) when the packing parameter approaches unity.

Factors affecting to the formation of CMC of the surfactant

Several factors affect the value of CMC. It includes the molecular structure of surfactants (including hydrophobictail, head, and counterions) temperature and additives etc.

Molecular structure of surfactants

From the data of values of CMC of different surfactants, several general observationson the variation of the CMC with surfactant molecular structure can be made asillustrated. The CMC decreases dramatically as the length of the alkyl chainincreases It is because of an increase in hydrophobicity with an increase inchain length(Yadav & Bhattarai,n.d.). A fixed number of carbons in the alkyl chain is best for comparing different classes of surfactants. Non-ionic CMCs are significantly lower than ionic CMCs (Bhattarai et al., 2012). The length of the alkyl chain influences the relationship. Aside from the significant difference between ionics and non-ionics, the effect of the head group is mild. Cationics usually have a higher CMC than anionics.

Temperature

The abbreviation "CMC" typically stands for "Critical Micelle Concentration." It is the concentration at which surfactant molecules in a solution aggregate to form micelles, which are structures that can solubilize non-polar substances in polar solvents like water.

Temperature is indeed affected the Critical Micelle Concentration (CMC) in different ways:

Thermodynamic Effect: Generally, increasing temperature tends to decrease the CMC. This is because at higher temperatures, the thermal energy disrupts the cohesive forces between surfactant molecules, making it easier for them to form micelles. So, higher temperatures favor micelle formation and lower the CMC(Bhattarai & Das, 2009).

Entropy Effect: At higher temperatures, there's typically an increase in entropy (disorder) in the system. Micelle formation often involves an increase in entropy since it allows the water molecules to have more freedom of movement around the hydrophobic tails of the surfactant molecules. This increased entropy at higher temperatures facilitates micelle formation and thus lowers the CMC.

Effect on Solubility: Temperature can also affect the solubility of surfactants. Some surfactants may become less soluble at higher temperatures, which could affect their ability to form micelles. However, this effect might vary depending on the specific surfactant and the system in question.

Effect on Molecular Kinetics: Temperature can also affect the kinetics of micelle formation. Higher temperatures generally increase the rate of molecular motion and collisions, promoting micelle formation and thus lowering the CMC(Shahi et al., 2023).

Additives

Surfactant molecules' micellar characteristics can be changed by exogenous additions on their surface, which can change thermodynamic parameters like the enthalpy and entropy of micellization as well as Gibbs' free energy of micellization. In a similar vein, the CMC of ionic surfactant compounds in mixed alcohol solutions is altered by the addition of alcohol molecules, which solvate the hydrophobic component of the surfactant tail. The surface and viscosity properties of external additives, such as electrolytes, diluted alcohol in water, azo dyes, polyelectrolytes, etc., have a substantial impact on the micellar activities of surfactants creation of a complex.

Because surfactants can alter wetting qualities, stabilize emulsions, and reduce surface tension, they are used in a wide range of industries. Several typical uses for surfactants include (Sachin et al., 2018):

Literature review

Materials and Methods

Materials

Sodium Stearate Surfactant (SS), Digital weight balance, distilled water (DW), volumetric flask (Borosilicate glass), Conductivity meter (306 Milwaukee MW301 PRO Conductivity Meter), Water bath, Electrode, Contact thermometer, Pipette.

Preparation of SS solution For the preparation of SS solution 0.364 gm of SS was weighted and dissolved with double distilled water in 100ml volumetric flask. The concentration of the solution was 0.01M which was used as the stock solution. Conductance measurement was carried out using conductivity meter (306) having the frequency 2000 Hz using the dip type of cell with cell constant 1.15 per cm and having an uncertainty of 0.01%. The cell was calibrated by using the KCl solution that is with method given by Lind and co-worker. The measurements were carried out in the water bath. Temperature was kept constant (required temperature ± 0.005 K) using the temperature increase or decrease switch. Many solutions were prepared and run the works to reproducibility of the result. Correction of specific conductance was made by subtracting the specific conductance of relative solvent to specific conductance of electrolytic solution. Surfactants solution having known concentration was made with reference solution then measured the conductivity using internal dilution method. The conductance of **SS** in double distilled water was measured at the temperatures **298.15 K.** which is indicated in **figure 3.**The effect of concentration on conductance of surfactant in double distilled was studied.

Results and Discussion

Effect of concentration on conductance of surfactant

Easy plot of graph shows conductivity increases with increase in concentration. Specific Conductivities of SS in double distilled water at 298.15 Kis shown in figure 3.

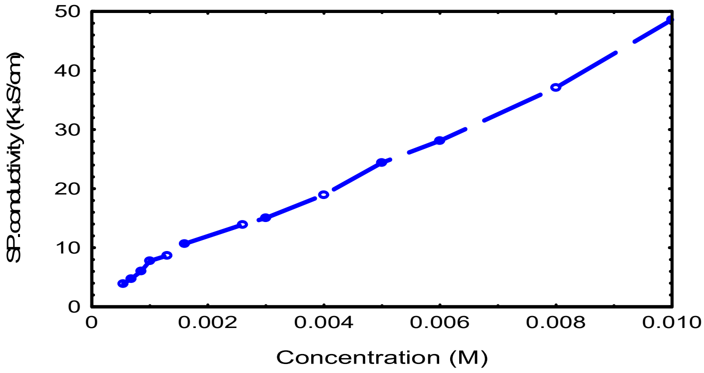


Figure 3. Plot of Specific conductance of SS surfactants verses concentrations.

Effect of temperature on conductance of surfactant

Verification of Specific Conductivities of Sodium Stearate in double distilled at 298.15, 308.15, and 318.15 K.

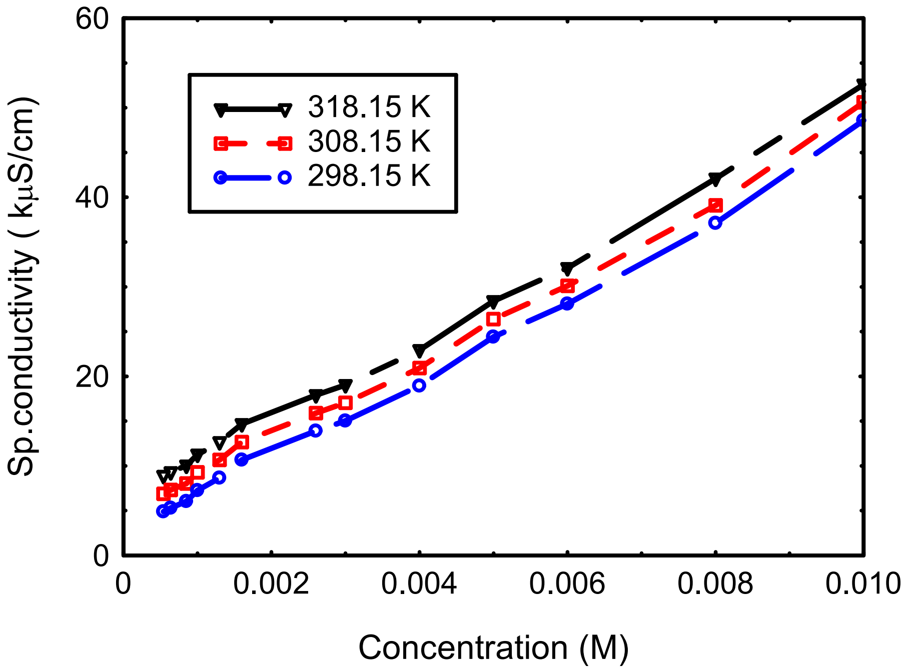


Figure 4. Plot of Specific conductance at SS surfactants at (298.15, 308.15, 318.15) K.

Because of the increased ion mobility in the solution, specific conductivity rises as temperature rises. The decrease in solution viscosity is another element that accounts for the increase in conductivity with temperature. The temperature increases cause an increase in the inter-ionic force of attraction between ions, which causes the ions to move more quickly (Yadav & Bhattarai, n.d.). The degree of ionization increases with increasing solution temperature, which increases the amount of ions in the solution and, consequently, conductance.

Calculation of CMC of surfactant

CMC is the concentration at which micelles, or aggregates form. Beyond and after this point, several physiochemical properties (conductivity, surface tension, viscosity, density, etc.) of surfactant solutions are changed. A physico chemical property of interest is often plotted against the concentration of the surfactant, and the break in the plot is used to determine the CMC value of a surfactant micelle.Table 1 lists the techniques used to determine CMC most frequently. It should be noted that various experimental methods could result in somewhat values for a surfactant's CMC.

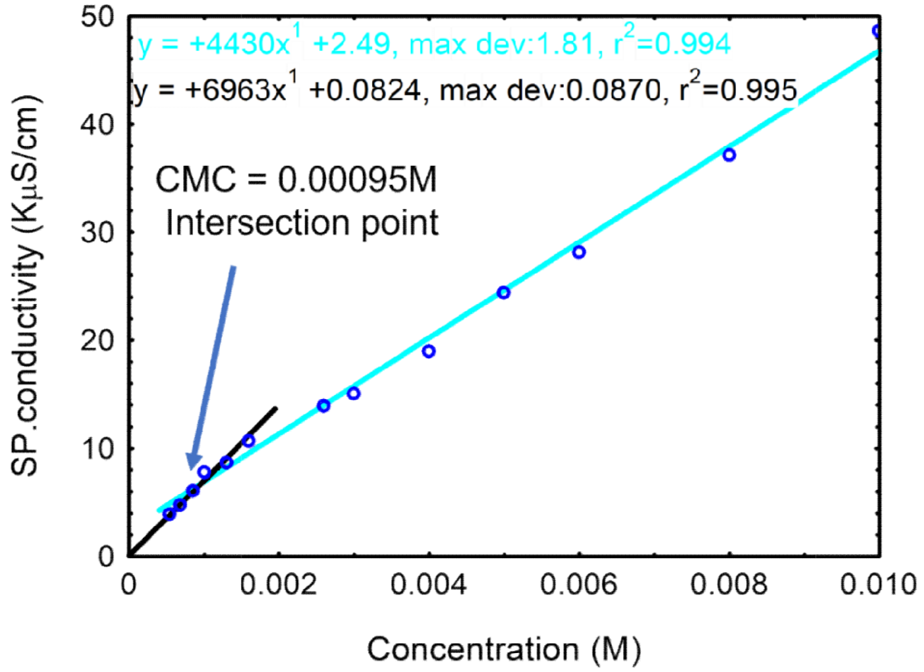


Figure 5.Conductivity of double distilled solution with the presence of SSatvarious concentrations.

Straight line, $y = +4430x^1 +2.49$

Straight line, $y = +6963x^1 +0.0824$

In order for the CMC value of SS to exert such a significant influence, two factors must be considered. The figure shows how the conductivity of the solution rises with the addition of sodium stearate surfactant. This surge is due to a higher concentration of sodium stearate ions. When the concentration of micelles hits a certain threshold, micelles form. Individual surfactant molecules are substantially smaller than the aggregated micelle (Shahi et al., 2023).

The bigger micelle's mobility is less than that of a single SS surfactant molecule, though, and this causes the conductivity to rise more slowly. The concentration and conductivity plots' changing slopes clearly show this shift in velocity. According to Rafati et al. (2008), the critical micelle concentration of SS in double-distilled water is 0.00095Mol/lit.The critical micelle concentration (CMC) of the surfactant in distilled water is usually 8.3 m M. The observed dip in the CMC of sodium stearate surfactant in a double distilled water solution is mostly due to a decrease in electrostatic repulsion between the anionic hydrophilic head group. According to Bhattarai et al. (2011), repulsion to micellization contributes less as a result of this reduction.

Table 1. *Represents the CMC of sodium stearate (SS)*

Chemical	Method	CMC
Sodium Stearate (SS)	Conductivity Methods	0.00095Mol/lit

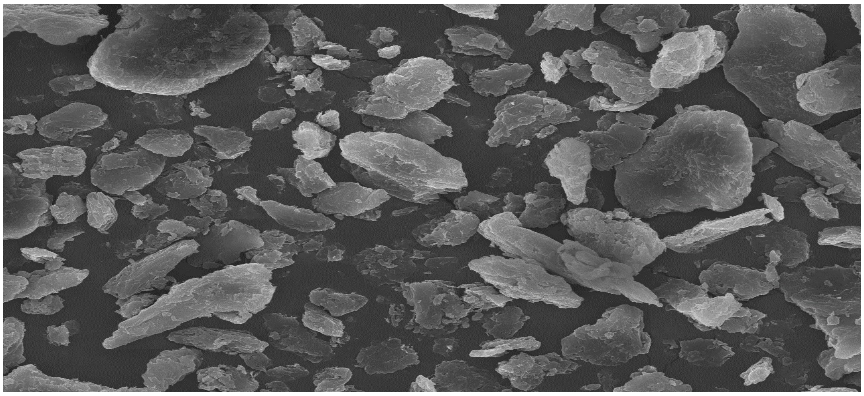


Figure 6. FESEM image of Sodium Stearate (Source: CSIR IMMT Research Lab, Bhubanesar, and Odisha).

A comprehensive visual depiction of sodium stearate's surface morphology at the micro- or nanoscale could be obtained using a FESEM (Field Emission Scanning Electron Microscopy) image. A common fatty acid salt used in a variety of commercial and domestic items, including soap, shampoo, and cosmetics, is sodium stearate (Holland &Rubingh, 1993).

In an FESEM image of sodium stearate, you would typically see the surface of the compound magnified to a high degree, allowing for the observation of its structural features, such as the arrangement of molecules, crystalline structures, and any surface irregularities or textures. The image would be generated by scanning the surface of the sample with a focused beam of electrons, and detecting the signals emitted by interactions between the electrons and the atoms in the sample.

FESEM images can reveal important information about the morphology and structure of materials, which is valuable for various fields of study, including materials science, chemistry, and nanotechnology. In the case of sodium stearate, such images could help researchers understand its physical properties, its behaviour in different environments, and its interactions with other substances. This information can be crucial for optimizing the formulation and performance of products that contain sodium stearate, as well as for fundamental research into the properties of this compound(Jia et al., 2019).

Conclusion

Effect of different three temperatures, 298.15K, 308.15K, and 318.15K in sodium stearate surfactant in double distilled water have been studied by measuring the specific conductivity by conductometric method. From above result and discussion, it is concluded that the specific conductance increases with rise in temperature and with increase in concentration. Similarly, CMC of sodium stearate is calculated using the easy plot method and was obtained as 0.00095 M at 298.15 K. FESEM imageindicate the surface morphology of sodium stearate surfactant.

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