INTELLECTUAL INCEPTION: A Multidisciplinary Research Journal of Bhojpur Campus
(Peer Reviewed)
ISSN: 2990-7934, Volume 2, Issue 1, June 2024, pp 100-111
Published by Research Management Cell (RMC), Bhojpur Multiple Campus, Bhojpur E-mail: rmcbhojpur@gmail.com

Determination of Critical Micelle Concentration (CMC) of Sodium Stearate and FESEM Study

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Article History: Submitted 15 April 2024; Reviewed 17 May 2024; Revised 11 June 2024
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Abstract:

Surfactant is an organic compound with polar and nonpolar parts. The 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. The conductivity of the surfactant increases with an increase in temperature and concentration of solution. The critical micelle concentration (CMC) of sodium stearate determined at temperature 298.15 K is 0.00095 M using the easy plot software. FESEM image shows the morphological structure of the sodium stearate surfactant.

Keywords: Surfactant, specific conductivity, polar, FESEM, EDX

Introduction

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 (Yadav et al., 2024). These surfactants contain hydrophobic tails made up of non-polar hydrocarbon chains and hydrophilic heads 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. The 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 and amphoteric or zwitterionic surfactants have both positive and negative heads.

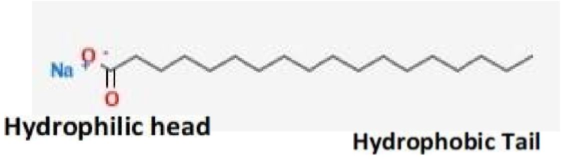

Figure1. General representation of Surfactant molecule with hydrophobic tail and hydrophilic head

The surfactants are categorized into four 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 (Bhattarai et al., 2017). 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+, etc. Cationic surfactant: Cationic surfactants contain a positively charged group or cation at their head, like ammonium as a surface active group. It is used as a corrosion inhibitor, anti-microbial, anti-fungal, mineral floatation, sterilization, etc. Examples of cationic surfactants are benzalkonium chloride (BZlC), cetylpyridinium chloride (CPC), benzethonium chloride (BZT), etc. ii)Non-ionic surfactants: Surfactants having no charge at their head and are not ionized into ions in aqueous solution are called non-ionic surfactants. They have been widely applied in the production of medicines, dyes, pesticides, food, textiles, etc. Examples of non-ionic surfactants are polyoxyethylene alcohol, alkylphenol ethoxylate, etc. 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 and cause mild effects on the skin so they are used in different personal care products and cosmetics as well as softeners in different industries (Rafati et al., 2008). Several of these surfactants include Lauramidopropyl betaine, Cocamidopropyl betaine, etc. iv) Speciality surfactants: They are a special class of surfactants having the 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 specialty surfactants. However, they are limited to commercial applications due to their expensive nature. Silicone surfactants: Silicone surfactants are based on silicones and are often used in cosmetics and personal care products. Example: Dimethicone copolyol.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.

The critical micelle concentration (CMC) is the low concentration of surfactants (free or unassociated surfactant molecules) that 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).

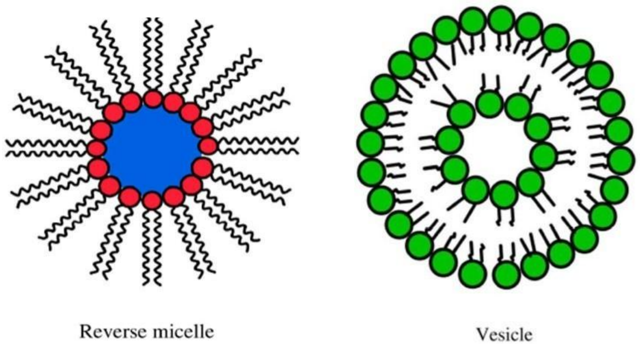

Figure 2. Schematic representation of aggregation of surfactant depending on the concentration (Ali et al., 2014)

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 as 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 concentrations of salt) when the packing parameter approaches unity. Several factors affect the value of CMC. It includes the molecular structure of surfactants, temperature, and additives, etc.

From the data of values of CMC of different surfactants, several general observations on the variation of the CMC with surfactant molecular structure can be made as illustrated. The CMC decreases dramatically as the length of the alkyl chain increases It is because of an increase in hydrophobicity with an increase in chain length (Yadav & Bhattarai, 2014). 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 (Naik et al., 2024). 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 is indeed affected the 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 (Shah et al., 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).

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 (Bhattarai, 2020). 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 (Sachin et al., 2018).

This study aims to determine the conductance of sodium stearate at 298.15, 308.15, and 318.15 K, calculate its CMC at 298.15 K from conductivity methods, and analyze its FESEM.

Materials and Methods Materials

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

Methods

For the preparation of sodium stearate (SS) solution, 0.364 gm of SS was weighed and dissolved with double distilled water in 100 ml volumetric flask to make 0.01M concentration. Conductance measurement was carried out using conductivity meter having the frequency 2000 Hz using the dip type of cell with a 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 the method given by Lind and co-workers (Lind Jr.et al., 1959). 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 the works to the reproducibility of the result.

The correction of specific conductance was made by subtracting the specific conductance of relative solvent to specific conductance of soultion having a known concentration reference was made with measured the conductivity using internal dilution method. The conductance of SS in double distilled water was measured at the temperature 298. 15 K which is shown in Fig. 3. The effect of concentration onconductance of surfactant in double distilled was studied.

Results and Discussion

Effect of concentration on the conductance of surfactant

The easy plot of the graph shows conductivity increases with an increase in concentration. The specific conductivity of SS in double distilled water at 298.15 K is shown in Fig. 3.

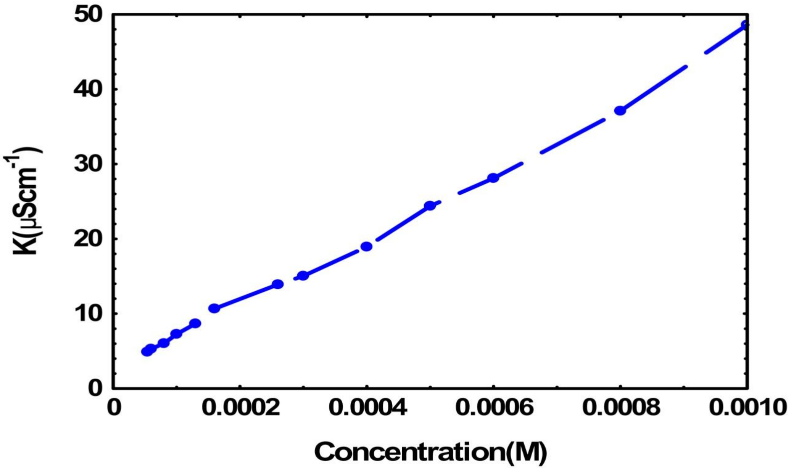

Figure 3. Plot of specific conductance of SS surfactant versus concentration.

Effect of temperature on the conductance of surfactant

The variation of specific conductivities of sodium stearate in double distilled at 298.15, 308.15, and 318.15 K is shown in Fig. 4.

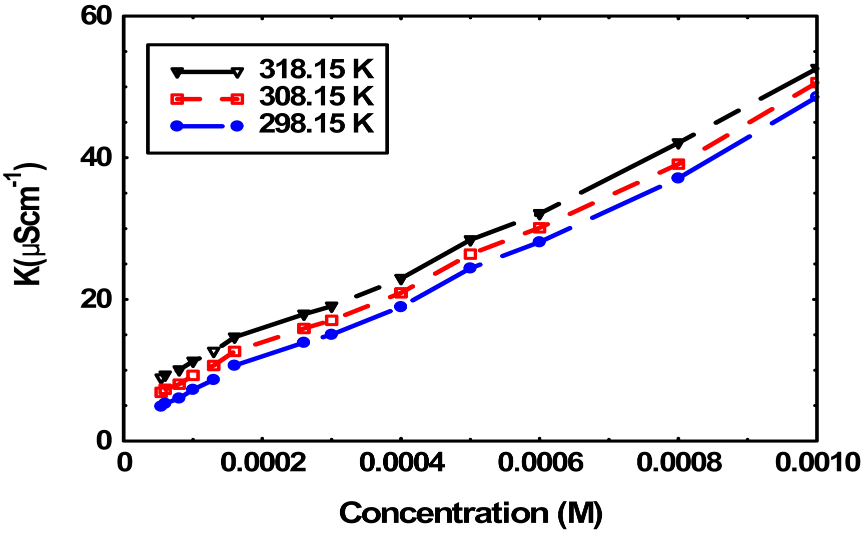

Figure 4. Plot of Specific conductance at SS surfactants at (298.15, 308.15, 318.15) K.

Because of the increased ion mobility in the solution, specific conductivity rises as temperature rises. The decrease in solution viscosity is another component that accounts for the increase in conductivity with temperature. The temperature increases cause an increase in the interionic force of attraction between ions, which causes the ions to move more quickly (Yadav & Bhattarai, 2014). Ionization increases with temperature, which increases the amount of ions in the solution and, therefore, 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. 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.

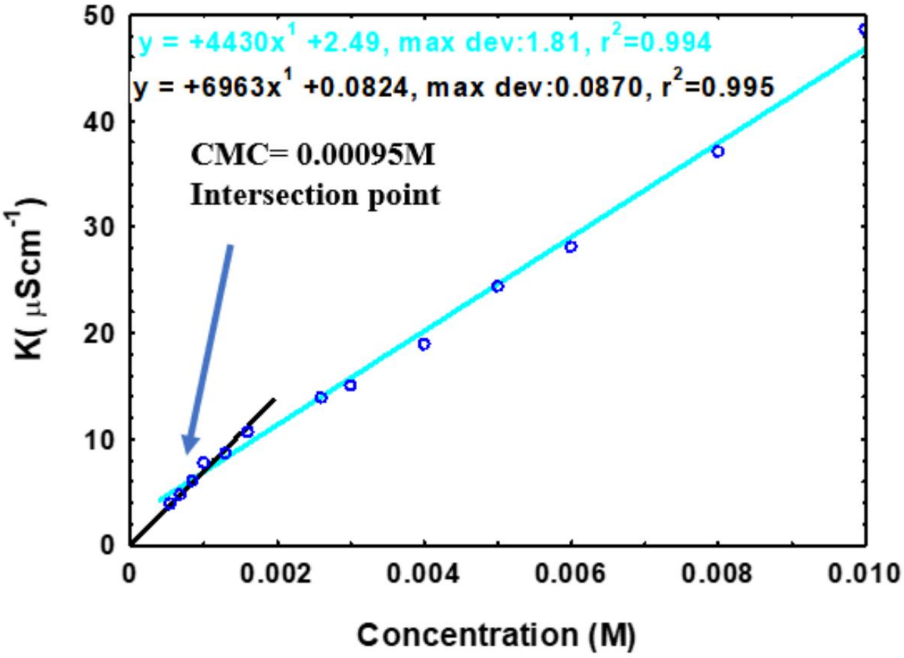

Figure 5. The plot of conductivity versus the various concentrations of SS at 298.15 K

Straight line, $y = +4430x^1+2.49$
Straight line, $y = +6963x^1+0.0824$

Fig. 5 shows how the conductivity of the solution rises with the addition of sodium stearate. 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 Wu et al. (2020), the critical micelle concentration of SS in double-distilled water is 0.00098M. The critical micelle concentration (CMC) of the SS in distilled water is found to be 0.00095M. 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 Shah et al.(2016), 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	Conductivity	0.00095M

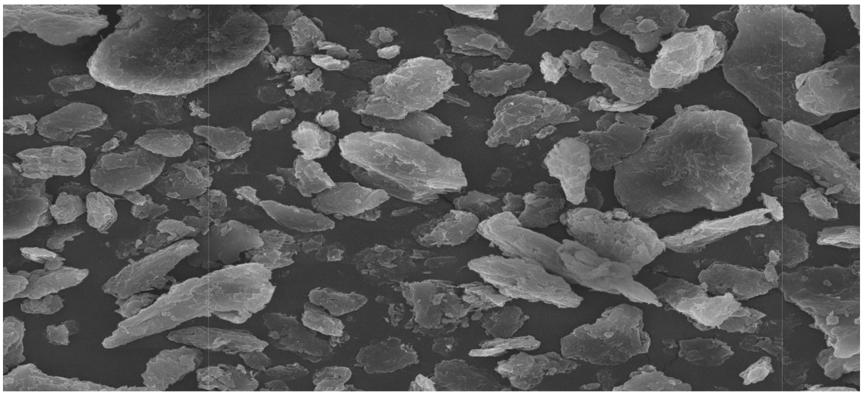

Figure 6. FESEM image of Sodium Stearate (Source: CSIR IMMT Research Lab, Bhubaneswar, Odisha, India).

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. Sodium stearate is a common fatty acid salt found in a variety of household and commercial products, such as soap, shampoo, and cosmetics (Schmitt, 2001).

In an FESEM image (Fig.6) of sodium stearate, we 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 behavior 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

By measuring the specific conductivity by conductometry, the effects of different temperatures have been examined in sodium stearate surfactant in double distilled water at 298.15, 308.15, and 318.15 K. Based on the above results and discussion, it is concluded that specific conductance increases as temperature and concentration rise. The CMC of sodium stearate is calculated using the easy plot method and obtained as 0.00095 M at 298.15 K. FESEM image indicates the surface morphology of sodium stearate surfactant.

Acknowledgments

One of the authors Brahamdeo Yadav would like to thanks Dean office, Insitute of Science and Technology, Tribhuvan University for providing Mini research grant for this work. Thank also goes to Prof. Dr. Amar Prasad Yadav for giving the working facility in the research lab and Chandradip Kumar Yadav would like to thank Yogesh Chaudhary, and Salila Kumar Shethi for FESEM image from CSIR IMMT research lab, Bhubhaneswar, Odisha, India.

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