

Thermodynamic Evaluation of the Critical Micelle Concentration of 1-Hexadecanol

¹Obi, C., Nwabueze, ¹C.C, ¹Uzoma, J.E. and ^{1,2*}Ibezim-Ezeani M.U

¹Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Rivers State, Nigeria

^{2*}Niger Delta Aqua Research Group, Department of Biochemistry and Chemistry Technology, School of Science Laboratory Technology, University of Port Harcourt, Port Harcourt, P. M. B. 5323, Choba, Rivers State, Nigeria

*Corresponding author: E-mail: millicent.ibezi-ezeani@uniport.edu.ng

Abstract

The critical micelle concentration of 1-hexadecanol surfactant was determined by means of viscosity, conductivity and absorbance measurements. The viscosity was evaluated using the Ostwald viscometer while conductivity and absorbance was evaluated using conductivity meter and Ultraviolet Visible (UV) Spectrophotometer. The solubility of 1-hexadecanol was also evaluated at various temperatures. The result revealed that above critical micelle concentration value according to viscosity measurements (0.08 M); there was a sharp increase in the viscosity values that might be due to micelle formation in the solution. It was also observed that as temperature increased, viscosity reduced accordingly. The critical micelle concentration using the absorbance and conductivity measurements were found to be 0.14 M and this showed a precise value for the critical micelle concentration of non-ionic surfactant. The van't Hoff's equation and Eyring formula of thermodynamics were employed to evaluate the enthalpy of micellization (ΔH°_{CMC}). The enthalpy of micellization was found to be exothermic (- 2.31kJ/mol) while the Gibbs free energy change of micellization (ΔG°_{CMC}) ranging from (- 6.68 to -7.52 J/K/mol) was found to decrease as temperature increases. The entropy change of micellization (ΔS°_{CMC}), showed positive values (+ 22.98 to + 30.22 J/K) throughout the temperatures tested. The Krafft temperature was found to be 50 °C. The study reveals that viscosity, conductivity and absorbance evaluations are important physical parameters in the determination of the critical micelle concentration of environmentally benign non-ionic surfactants.

Keywords: 1-hexadecanol, critical micelle concentration, solubility, Krafft temperature, thermodynamics

Introduction

The study of surfactants has become a global issue due to the important role they play in many technological applications such as dispersion stabilization, drug formulation, enhanced oil recovery, and lubrication (Ottaviani *et al.*, 2015; Sonalika and Ashok, 2019).

Surfactants or surface active agents are a special class of versatile amphiphilic compounds that possess spatially distinct polar (hydrophilic head) and non-polar (hydrophobic tail) groups (Rosen, 2004). The polar portion exhibits a strong affinity for polar solvents, especially water, and it is often called hydrophilic part or hydrophile while the apolar part is called hydrophobe or lipophile. Due to its dual affinity, amphiphilic molecules are not always stable when found in polar or non-polar solvent environment. This is why amphiphilic molecules exhibit a very strong tendency to migrate to interfaces or surfaces and to orientate so that the polar group lies in water and the apolar group is placed out of it, and eventually in oil or grease as the case may be (David and Maria, 2007; Gregory *et al.*, 2013).

Surfactants display interesting phenomena in solution by modifying the interfacial and bulk-solvent properties (Moroi, 1992). In view of its amphiphilic nature and distinctive capability of lowering the interfacial tension, surfactants find applications in almost every aspect of our daily activities (Schramm, 2000; Hakiki *et al.*, 2016).

However, surfactants are basically classified according to polar head group. The one with no charge at the head is referred to as non-ionic surfactant while the one with charge at the head is referred to as ionic surfactant. The ionic surfactant could be anionic (having negative charge at the head) or cationic (having positive charge at the head). On the other hand, if the surfactant contains a head with two oppositely charged groups, it is called zwitterionic.

An important property of non-ionic surfactant is the possession of covalently bonded oxygen-containing hydrophilic groups, which are bonded to hydrophobic parent structures (Percival *et al.*, 2017). This property enhances the decrease in the solubility of non-ionic surfactant with increase in temperature. Another striking factor about non-ionic surfactant is that they are less sensitive to electrolytes found in both saline and hard water systems.

An extensive use of surfactant is found in detergents. Detergents refer to a combination of synthetic surfactants with other substances (organic or inorganic); that is formulated to enhance functional performance especially as cleaning agents (Holmberg *et al.*, 2002).

The oldest surfactant is soap which dates back well over 2000 years although the modern surfactant industry has developed essentially since the Second World War, utilizing the expansion of the petrochemical industry as one of its main sources of raw materials (Richard, 2006).

The critical micelle concentration (CMC) is the concentration above which micelles are observed (Andrew and Athanassios, 2016) and it is a remarkable concentration when dealing with surfactants in aqueous and non-aqueous solutions. The effect of temperature on the CMC has been reported in several works as being complex (Carolina and Barney, 2003). It was reported by Rosen (2004) that CMC-temperature dependence was found to be approximately 25 °C for ionic surfactant (alkylbenzenesulfonate) and around 50°C for non-ionic surfactant (polyoxyethylenated alcohol). Studies have shown that micellization is affected by temperature, as the tail and head groups interaction change with temperature variations (Al-Soufi *et al.*, 2012; Hakiki *et al.*, 2016). In this study, 1-hexadecanol was used to evaluate its thermodynamics of micellization, solubility and critical micelle concentration. 1-hexadecanol is white, waxy solid organic molecule having a molecular weight of 242.44 g/mol and a chemical formula of $\text{CH}_3(\text{CH}_2)_{15}\text{OH}$. The melting point of 1-hexadecanol is between 45°C and 49°C, and its boiling point is 334°C. 1-hexadecanol is a vital

component in many preparations, such as cosmetic creams or lotions, pharmaceutical hydrophilic ointments, shampoos and hair conditioners, emulsifier, thickeners, etc. 1-hexadecanol is generally believed to be cetyl alcohol, but commercial grades often contain measurable amounts of stearyl alcohol and other long-chain aliphatic alcohols. It is a vegetable-derived fatty alcohol typically used as a stabilizer and skin lubricant (Saliva and Morsy, 2014; Milica *et al.*, 2016) and also used as an emollient to prevent drying and chapping of the skin because of its water-binding property (Helena *et al.*, 2004). 1-hexadecanol is a non-ionic surfactant and is referred to as a non-toxic amphiphilic substance that enhances desorption and bioavailability by increasing solubility and dispersion of poorly soluble hydrocarbons and oils (Gregory *et al.*, 2013). Due to their properties, economy, formulation, effectiveness and ease of handling, they are widely used for emulsion polymerization and polymer stabilization in plastics and elastomers (Sonalika and Ashok, 2019).

Sequel to the limitations of previous investigations (Jones *et al.*, 2001; Mohajeri and Noudeh, 2012; Mahmood and Al-Koofe, 2013) and due to the versatility of the surfactant in its applications, there is need to study the formation of these micelles under a wide range of temperatures considering their solubility properties and other physical parameters like viscosity, absorbance and conductivity.

In this study, 1-hexadecanol, a non-toxic surfactant was evaluated to ascertain the temperature contribution on the CMC ranging from 25°C to 75°C with respect to its solubility and equally determine the CMC using viscosity, conductivity and absorbance measurements.

Materials and Methods

Analytical grade 1-hexadecanol and distilled water were purchased from Joechem Ventures Co., Port Harcourt. Ostwald viscometer, conductivity meter, UV-Visible Spectrophotometer, electronic weighing balance (JJ500), heating mantle (ZDHW-1000 USA), thermometer and some latent apparatus were used in the analysis

Viscosity Measurement

Aqueous stock solutions of 0.2 M 1-hexadecanol were prepared by dissolving 4.84 g in distilled water up to 100 ml mark of volumetric flask. The mixture of 0.2 M 1-hexadecanol and distilled water were placed in 9 different test tubes. A mixture of 2 ml of 0.2 M 1-hexadecanol and 18 ml of distilled water was prepared first, followed by 4ml in 16ml and continued in that order until 18 ml of 1-hexadecanol and 2 ml of distilled water was prepared. The various sets of the mixture were placed into the Ostwald viscometer where the time taken for the solution to completely go down to the next compartment of the viscometer was measured. This step was repeated for all the remaining sets of 1-hexadecanol in distilled water. After the time has been determined, a viscosity formula is used to determine the kinematic viscosity of each solution.

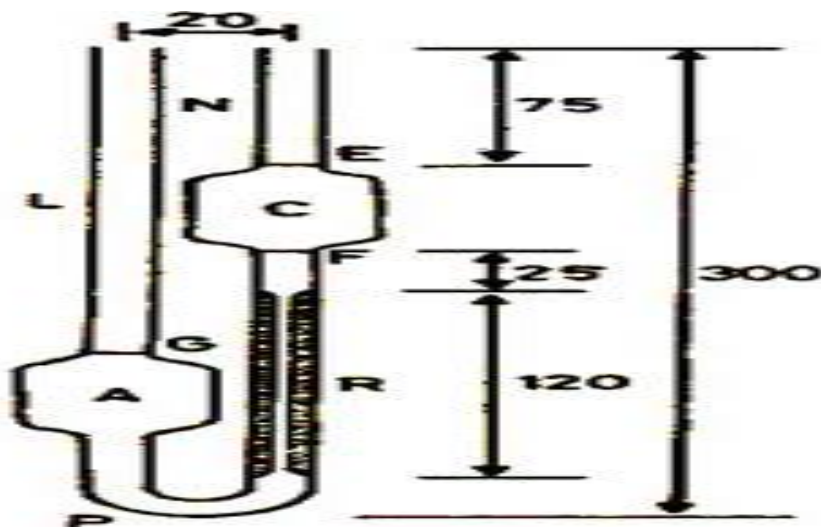


Fig. 1: A typical diagram of the Ostwald Viscometer (Ankur, 2008)

Solubility Measurement

Distilled water (10 ml) was put in nine different test tubes. In the first test tube, 9.58 g of 1-hexadecanol was weighed out and recorded. The first test tube was heated up to 45°C after which a scoop of the weighed 1-hexadecanol was put into the 10 ml of distilled water and was agitated 40 times with a stopper on the test tube. More grams of 1-hexadecanol were added, 1 g at a time until no more 1-hexadecanol dissolved, and the solution became saturated. Finally, the mass of 1-hexadecanol remaining was weighed and subtracted from the original mass to determine the amount of 1-hexadecanol that was dissolved in 10 ml of distilled water that formed the saturated solution. This procedure was repeated for the remaining 8 test tubes at different temperatures to determine the solubility.

Effect of Temperature on the CMC of 1-Hexadecanol

The solution of 0.2 M 1-hexadecanol was placed on a heating mantle and there was increase in the temperature of the surfactant. 1-hexadecanol was insoluble with water at room temperature, but dissolved as the temperature increased. This was repeated for all surfactant solution at various temperatures. The CMC was determined and a plot of critical micelle concentration of the surfactant versus temperature was carefully examined and studied in order to understand and evaluate the thermodynamic properties of micellization.

Conductivity Measurement

The prepared 0.2 M 1-hexadecanol was heated to dissolve completely at a temperature of 69°C and allowed to cool to room temperature. 1-hexadecanol stock solution (2 ml) was first pipetted into water (18 ml) and stirred thoroughly; the conductivity of the solution was recorded at time (min) intervals with the aid of a conductivity meter. This step was repeated until all the 1-hexadecanol stock solutions have been added to the water.

Absorbance Measurement

The absorbance of the solution was measured using the UV-Visible spectrophotometer over a wavelength range of 400 – 600 nm and baseline correction was made using de-ionized water. Methyl orange dye was prepared by dissolving 1.0 g of solute in 30 ml of 99.7 % ethanol, and diluted with 70 ml distilled water. 1-hexadecanol stock solution (2 ml) was pipetted firstly into 18 ml de-ionized water. Methyl orange dye was added (2-3 drops) and the solution was stirred thoroughly and placed in the UV-visible spectrophotometer and absorbance was recorded. This step was repeated until all the 1-hexadecanol solutions have been added to the water at time (min) intervals.

RESULTS AND DISCUSSION

CMC of 1-Hexadecanol with respect to Viscosity, Solubility and Temperature

The viscosity was evaluated using equation 1 and the plot of surfactant's viscosity as a function of concentration is shown in Figure 2.

$$\text{Viscosity } (\eta) = k\rho t \quad (1)$$

Where k is the viscometer constant, ρ is the density, and t is the time of flow.

The surfactant's solubility was evaluated using equation 2 and the plot of solubility as a function of temperature is presented in Figure 2.

$$\text{Solubility} = \frac{\text{Initial mass} - \text{Final mass}}{\text{Volume}} \quad (2)$$

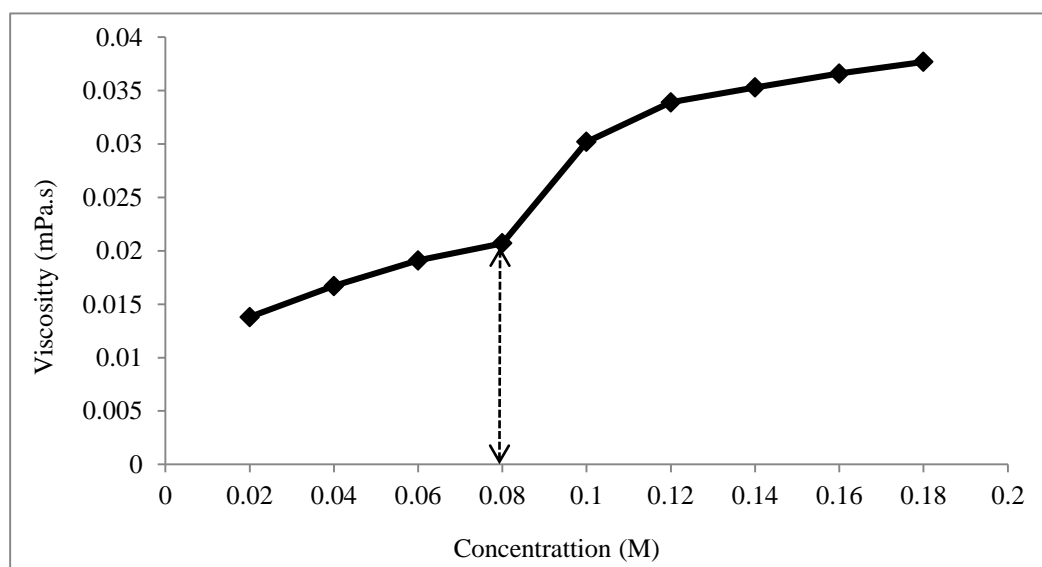


Fig. 2: Plot of viscosity as a function of concentration

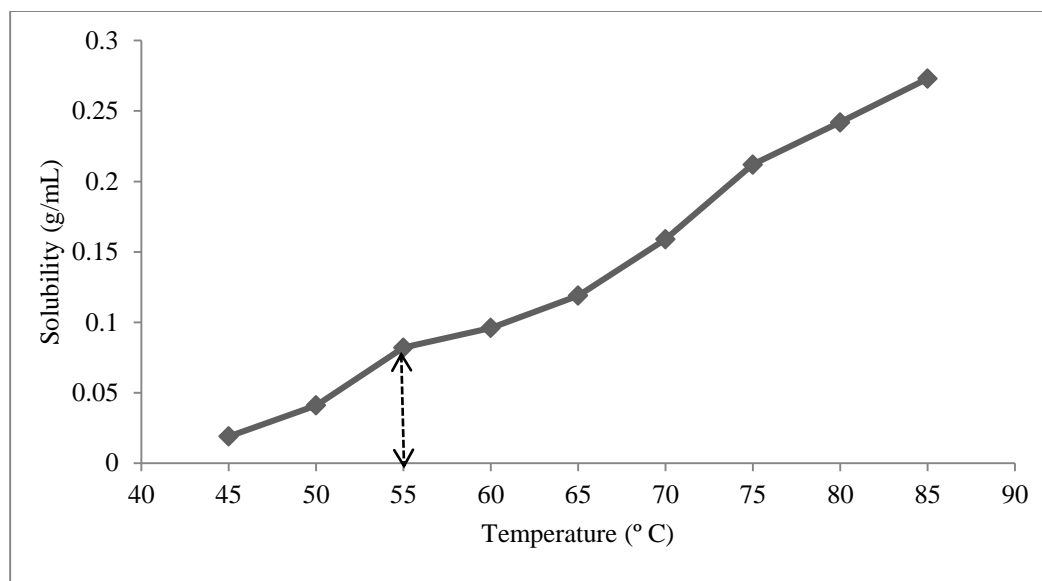


Fig. 3: Plot of solubility as a function of temperature

The result obtained revealed that the viscosity of each surfactant solution increased with an increase in its concentration. The CMC occurred where there was a sharp break as presented in Figure 2 and was found to be 0.08 M. Also, below CMC, it was clearly observed that viscosity was low; apparently as a result of the unassociated molecules in solution. At CMC, there was a sudden increase in viscosity; this could be as a result of micelle formation. Above CMC, the viscosity increased more rapidly. The suspended particles in the solution could be the reason for its higher viscosity, as the solution was not uniform and homogenous.

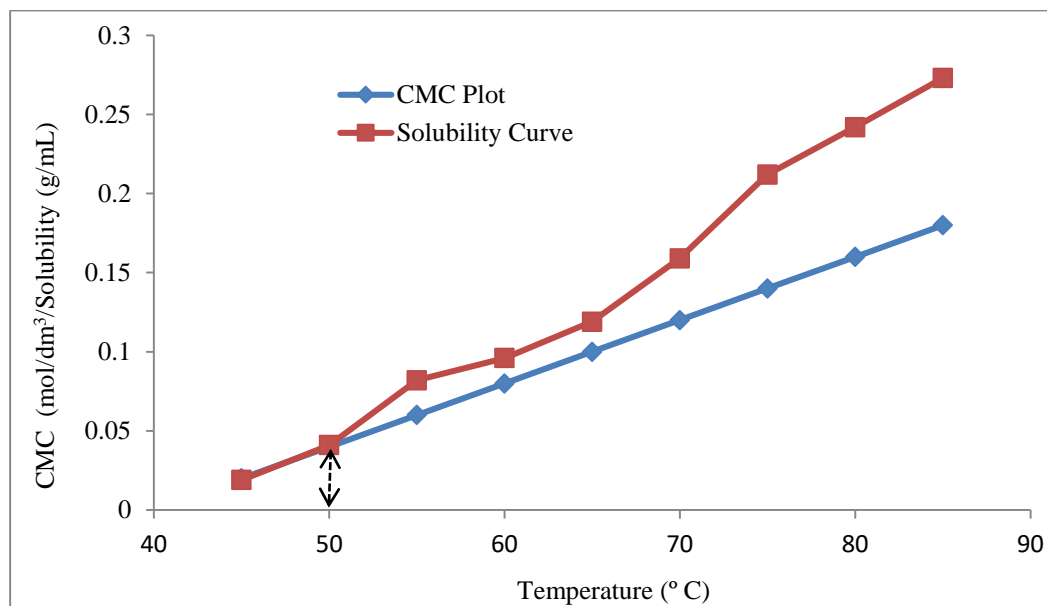


Fig. 4: Variation of CMC and solubility as a function of temperature

From the data shown in Figure 3, it was observed also that the solubility of each surfactant solution increased with increase in temperature. Below the Krafft temperature, there was a slight increase in solubility of the surfactant concentration with temperature. At Krafft temperature, there was a sharp break followed by slow solubility increase; but above the Krafft temperature, a rapid increase in solubility at higher temperatures was observed. From the solubility test, it was noticed that at low temperatures, a small mass of 1-hexadecanol in 10 ml of distilled water was required to dissolve it. But as the temperature increase progressed, more mass of 1-hexadecanol in 10 ml of distilled water was required to dissolve. This finding supports the fact that as temperature increases, solubility increases (Black and Muller, 2010). The Krafft temperature occurred at the point of intersection between CMC plot and solubility curve as shown in Figure 4 and it was found to be 50°C. This experimental temperature was in close agreement with the literature (Rosen, 2004). This temperature influences the relative solubility of surfactant in an aqueous solution. Below this temperature, no level of solubility will be sufficient to form aggregates due to minimal movement of particles in solution (Carolina and Barney, 2003). As the system temperature increased, the CMC showed a corresponding decrease, and micellization occurred at lower concentration. Additional increase in temperature also caused an increase in the breakdown of the structured water surrounding the hydrophobic groups, which was unfavorable to micellization (May and Dhafer, 2013). 1-hexadecanol which was insoluble in water, showed a gradual increase in solubility with increase in temperature up to its Krafft temperature (melting point) of approximately 50°C. The above observation showed that the solubility of surfactants is dependent on temperature.

Determination of Thermodynamic Parameters

The following equations 3, 4 and 5 were used for the calculation of the thermodynamic parameters; the results are presented in Table 1

$$\Delta G_{\text{CMC}}^{\circ} = -RT \ln [\text{CMC}] \quad (3)$$

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (4)$$

$$\Delta S_{\text{CMC}}^{\circ} = \frac{\Delta H^{\circ} - \Delta G_{\text{CMC}}^{\circ}}{T} \quad (5)$$

Where, $\Delta G_{\text{CMC}}^{\circ}$ = standard Gibb's free energy of CMC; R = gas constant; T = absolute temperature; K_c = equilibrium constant; ΔS° = standard entropy change; ΔH° = standard enthalpy change.

Table 1: Thermodynamic Parameters of 1-Hexadecanol at different Temperatures

S/N	Temperature (K)	ΔH°_{CMC} (kJ/mol)	ΔS°_{CMC} (J K ⁻¹ mol ⁻¹)	ΔG°_{CMC} (kJmol ⁻¹)
1	318.00			- 6.68
2	323.00			- 6.78
3	328.00			- 6.89
4	333.00			- 6.99
5	338.00	- 2.31	273.70	- 7.10
6	343.00			- 7.21
7	348.00			- 7.31
8	353.00			- 7.41
9	358.00			- 7.52

It was found that ΔG°_{CMC} decreased monotonically as the temperature increased over the whole temperature range (318 – 358) K. The standard entropy change ΔS°_{CMC} appeared to show an increase and decrease over the temperature range. The large enthalpy change means that in the micellization, the attractive interaction among hydrophobic chains was opposed to the strong interaction of the oxyethylene chains of 1-hexadecanol surfactant with water molecules.

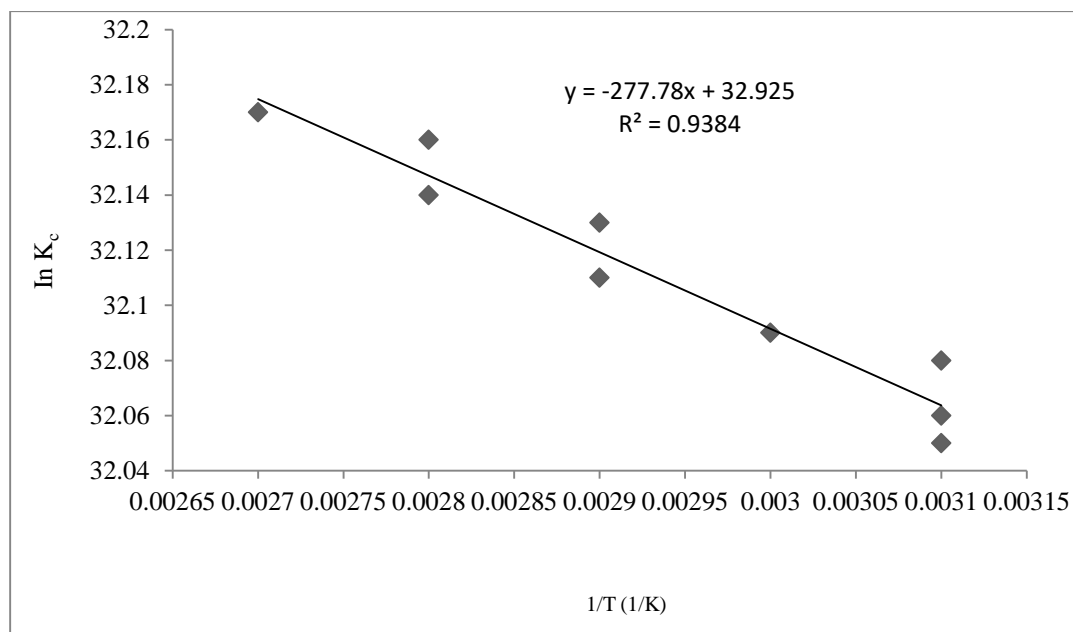


Fig. 5: Plot of $\ln K_c$ against $1/T$

CMC of 1-Hexadecanol with respect to Conductivity and Absorbance

The surfactant's conductivity and absorbance were measured as a function of the concentration as shown in Figures 6 and 7.

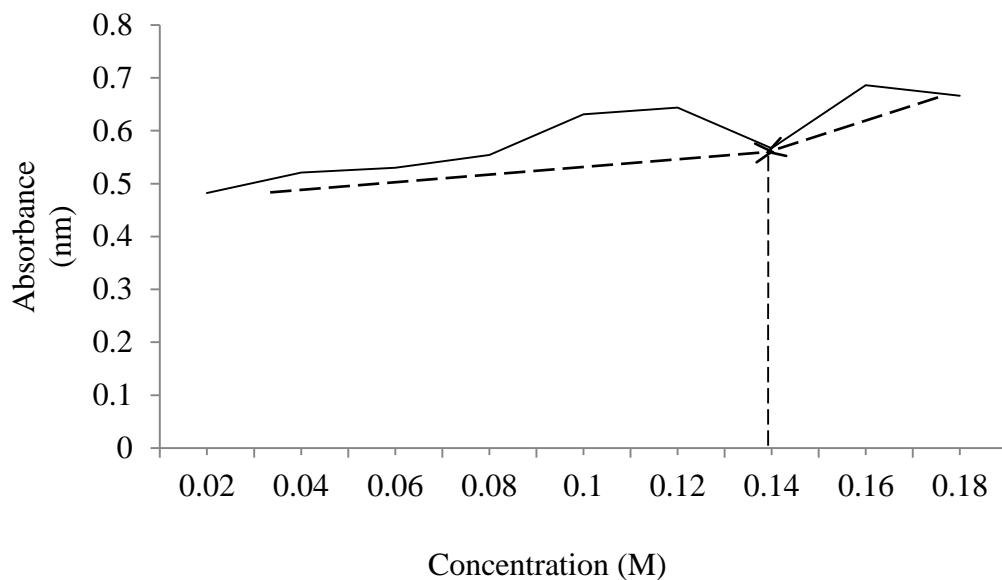


Fig. 6: Plot of absorbance as a function of concentration

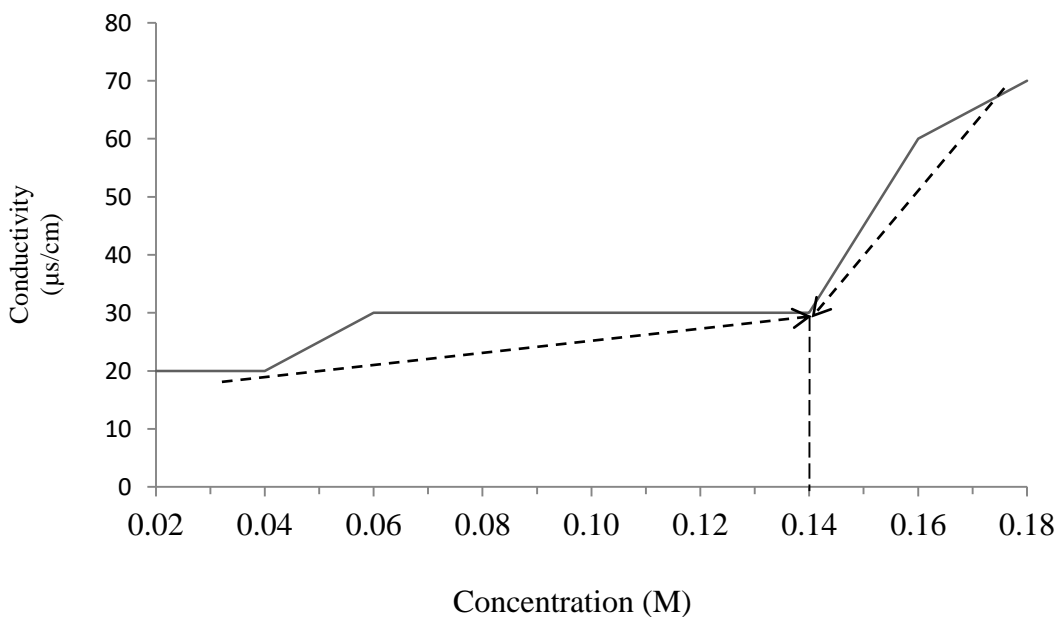


Fig. 7: Plot of conductivity as a function of concentration

The result revealed that at concentration below the CMC, the solution's absorbance and conductivity were low. At CMC there was a sudden increase in absorbance and conductivity, which could be as a result of micelle formation (Elisabet *et al.*, 2005). Above the CMC, the absorbance of the solution increased linearly with increasing concentration, and later showed a steep decrease while conductivity showed a linear increase with slight decrease above the CMC. The CMC occurred where there was a sharp break; and the CMC of 1-hexadecanol was found to be 0.14 M for the absorbance and conductivity measurements. The CMC obtained by means of absorbance and conductivity measurements showed the approximate value for the CMC of non-ionic surfactant (Mondal and Ghosh, 2012).

Conclusion

The use of the Ostwald viscometer technique in determining the critical micelle concentration of non-ionic surfactants was good, easy and reliable. More so, absorbance and conductivity measurements using UV-Visible Spectrophotometer and conductivity meter respectively gave accurate methods of scientific determination of the critical micelle concentration of non-ionic surfactants. The negative values of Gibbs free energy change of micellization (ΔG°_{CMC}) obtained from the CMC value show that micellization process was spontaneous. The results of this study provide useful information for users in production of foods such as ice cream, baked fillings, snack glazes and cakes.

References

- Andrew, P.S. & Athanassios, Z.P. (2016). Determination of the critical micelle concentration in simulations of surfactant systems. *Journal of Chemical Physics*, 144(4): 1-9.
- Ankur, C. (2008). Determination of Viscosity by using Ostwald-type, Suspended-level and Rotating Viscometer, 1st edition, Pharmaceutical guideline, India, p.8.
- Black, M. & Muller, F. (2010). Technical note on the effect of temperature on aqueous solubility of organic solids. *Organic Process Research and Development*, 14(3): 661-665.
- Carolina, V.G. & Barney, L.B. (2003). Estimate of the ionization degree of ionic micelles based on Krafft temperature measurements. *Journal of Physical Chemistry B*, 107: 5398-5403.
- David, L.D. & Maria, M.V. (2007). Variation of critical micelle concentration with surfactant structure: A simple method to analyze the role of attractive-repulsive forces on micellar association. *The Chemical Educator*, 12: 1-4.
- Elisabet, F., Marti, R., Clara, R., Elisabeth, F., Marti, R., Clara, R. & Elisabeth, B. (2005). Critical micelle concentration in aqueous buffered and unbuffered systems. *Analytical Chimica Acta*, 548(1-2): 95-100.
- Gregory, N.S., Paul, B., Sarah, E.R. & Julian, E. (2013). Evidence for CMC of surfactants in hydrocarbon solvents. *Langmuir*, 29(10): 3252-3258.
- Helena, M.R., Gillian, M.E. & Jose, A.G.M. (2004). Structure and rheology of semi-solid o/w creams containing cetyl alcohol non-ionic surfactant mixed emulsifier and different polymers. *International Journal of Cosmetic Science*, 26(2): 47-59.
- Holmberg, K., Jonsson, B., Kronberg, B. & Lindman, B. (2002). Surfactants and Polymers in Aqueous Solution, 2nd edition, John Wiley and Sons, New York, p. 99.
- Jones, G.P., Regismond, S., Kwetkat, K. & Zana, R. (2001). Micellization of non-ionic surfactant dimers and the corresponding surfactant monomers in aqueous solution. *Journal of Colloid and Interface Science*, 243: 496-502.

- Mahmood, M.E. & Al-Koofee, D.A.F. (2013). Effect of temperature changes on critical micelle concentration for tween series surfactant. *Global Journal of Science Frontier Research Chemistry*, 13(4): 1-7.
- Malica, L., Snezana, S. & Ivana, P. (2016). An overview of novel surfactants for formulation of cosmetics with certain emphasis on acidic active substances. *Tenside Surfactants Detergents*, 53(1): 7-19.
- May, E.M. & Dhafer, A.F. (2013). Effect of temperature changes on the critical micelle concentration for Tween series surfactant. *Global Journal of Science Frontier Chemistry*, 13: 249-496.
- Mohajeri, E. & Noudeh, G.D. (2012). Effect of temperature on the critical micelle concentration and micellization thermodynamic of non-ionic surfactants: Polyoxyethylenesorbitan fatty acid esters. *E-Journal of Chemistry*, 9(4): 2268-2274.
- Mondal, S. & Ghosh, S., (2012). Role of curcumin on the determination of the critical micellar concentration by absorbance, fluorescence and fluorescence anisotropy techniques. *Journal of Photochemistry and Photobiology B: Biology*, 115:9-15.
- Moroi, Y., (1992). *Micelle, Theoretical and Applied Aspects*. Plenum Press, New York and London, p.7.
- Ottaviani, G., Wendelspiess, S. & Alvarez-Sanchez, R. 2015. Importance of critical micellar concentration for the prediction of solubility enhancement in biorelevant media. *Molecular Pharmaceutical*, 12(4): 1171-1179.
- Richard, J.F. (2006). *Chemistry and Technology of Surfactants*, 1st Ed., Blackwell Publishing, UK, p. 2.
- Rosen, M.J. (2004). *Surfactants and Interfacial Phenomena*, 3rd Ed., John Wiley and Sons Inc., New Jersey, p. 82.
- Percival, S.I., Mayer, D., Malone, M., Swanson, T., Gibson, D. & Shulta, G. (2017). Surfactants and their roles in wound cleansing and biofilm management. *Journal of Wound Care*, 26(11): 680-690.
- Saliva, M.I.M (2014). Role of surfactants in nanotechnology and their applications. *International Journal of Current Microbiology and Applied Sciences*, 3(5): 237-260.
- Schramm, L.L. (2000). *Surfactants: Fundamentals and Applications in Petroleum Industry*, 2nd Ed., Cambridge University Press, Cambridge, p. 55.
- Sonalika, V. & Ashok, K.G. (2019). Microemulsion methods for synthesis of nanostructural materials. *Comprehensive Nanoscience and Nanotechnology*, 2: 1-12.