

Determination of Critical Micelle Concentration and Thermodynamic Evaluations of Micellization of GMS

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Abstract

The uncontrolled distribution of surfactants which are commonly used as household and industrial products like soaps, lubricants and detergents in the global market have provoked this study. The determination of critical micelle concentration (CMC) of glycerol monostearate surfactant (GMS) was evaluated using Conductivity and UV-Visible Spectroscopic techniques respectively. The effect of solubility was quantified and the Krafft temperature was obtained. The thermodynamic feasibility parameters were evaluated using Eyring and Vant Hoff's equations. The CMC values were taken from the sharp breaks in the plots of absorbance versus surfactant concentrations and conductivity versus surfactant concentration respectively. The result showed that as the temperature increases, the CMC initially decreases and then followed by slight increase owing to the smaller probability of hydrogen bond formation at higher temperatures. The result showed that the critical micelle concentration of GMS obtained using Conductivity and UV-Visible techniques were 4.50×10^{-2} and 2.40×10^{-2} moldm⁻³ respectively and the Krafft temperature (K_T) was obtained at 50°C. The Gibbs free energy change of micellization (ΔG° CMC) was found to decrease as temperature increases over the whole temperature range. The entropy change of micellization (ΔS° CMC) showed positive values throughout the temperature range tested while the large enthalpy change, ΔH° (CMC) means that in the micellization process, the attractive interaction among hydrophobic chains was opposed by the strong interaction of the oxyethylene chains of glycerol monostearate with water molecules. The study revealed that the use of UV-Visible Spectroscopy technique was a very good and easy way of determining the critical micelle concentration of GMS. This study is also a valuable industrial tool for the production of soap related products and its applications in domestic and industrial processes.

Keywords: Solubilization; Critical micelle concentration; Glycerol monostearate; Krafft temperature

Introduction

The concept of surfactants has been described by many researchers as a surface active agent which is composed of a hydrophilic head and hydrophobic tail found at the boundary between two components (one may be air) [1,2]. However, surfactants can be viewed as encompassing organic compounds with enormous applications in the areas of soaps, detergents, emulsions, paints, organic synthesis, froth flotation, drug formulations, petroleum recovery, lubricants and as membrane mimics. The applications of surfactants are also useful in chemistry and chemical engineering, thermodynamics and catalysis evaluations [3].

The global developmental and industrial changes have provoked many researchers in the study of different kinds of surfactants that constitute the micellar environment.

The hydrophilic region (head) which is polar in nature may be anionic, cationic, neutral or zwitterionic. On the other hand, the hydrophobic region (tail) is usually composed of hydrocarbons of one or more chains with varying length.

In water, these surface-active agents dissolve completely at very low concentrations but above a certain limit referred to as the critical micelle concentration (CMC), the molecular species form an organized molecular enclavage called micelles. The formation of

micelle is temperature dependent and therefore the temperature at which micelles are observed is known as the Krafft temperature or the melting point. The formation is such that the hydrophobic tails groups in association create a non-polar interior with the hydrophilic heads located at the inter-phase between the aqueous medium and air.

The micelles formed vary in size and shapes depending on the number of aggregation (N). It has been shown that the order of numbers of aggregation is in the range of 50-100 [4]. The value of the CMC can be evaluated by the change in the physicochemical properties of the surfactant solutions as the concentration of the amphipatic molecules is increased. The determination of the CMC can be achieved by the use of ultraviolet-visible (UV) spectroscopy, fluorescence technique, surface tension, nuclear magnetic resonance (NMR) and electrical conductivity techniques [5].

In addition, the introduction of insoluble dyes has helped in the determination of the CMC. In this study, methylene blue dye was used. Studies have equally shown that the presence of non-transition metal salts decrease the CMC i.e., making it faster for micelles to be formed. However, the presence of transition metal salts prolonged the formation of CMC or sometimes the CMC does not reach which invariably means that micelle does not form. The presence of these counter ions not only affects the CMC; it significantly influences the properties of micelle size, micellar catalytic activity, etc. The extent of decrease or increase in the surfactant solutions depend on the polarizability and valence of the counter ions [6].

The mechanism of surfactants in a detergent or soap is to mix completely in both the aqueous and hydrocarbon phases where their surfaces are in contact and hence the solubilization of the hydrocarbon phase (hydrophobic tail) will lead to washing away of dirt, oily substances and grease.

The thermodynamics of micelle formation reflects the contributions of interactions between micelle chains within the micelles and between the polar head groups and the surrounding medium. Related works have shown that the process exhibits both endothermic and exothermic reactions with positive entropy [7,8]. This depends on the type of surfactant used. The increase in free energy when polar groups cluster together and the reduction of their structural demands on the solvent is the origin of the hydrophobic interaction and other models that tend to stabilize groupings of hydrophobic character in biological macromolecules. However, this hydrophobic interaction is an example of an ordering process that is stabilized by a tendency toward greater disorder of the solvent.

Glycerol monostearate commonly referred to as GMS, is an organic molecule used as an emulsifier. GMS is a white, odorless, and sweet-tasting flaky powder that is hygroscopic. It is a glycerol ester of stearic acid. The International Union of Pure and Applied Chemistry (IUPAC) represent it as 2, 3-dihydroxypropyl octadecanoate. GMS appears in white to yellowish solid and is insoluble in water. GMS is largely used in baking preparations and is responsible for giving ice cream and whipped cream its smooth texture. It is an environmentally friendly surfactant, hence the choice as surfactant in this study.

The need to manufacture soaps, detergents and emulsifiers that can withstand hard water problems, remove stains or dirt and save cost has provoked this study.

The aim is therefore to determine the critical micelle concentration of glycerol monostearate (GMS) using Conductivity and UV-Visible Spectroscopic techniques and ultimately determine the thermodynamic feasibility possibilities.

Materials and Methods

Analytical grades of glycerol monostearate (GMS), methylene blue dye and ethanol (99.7%) were purchased from Joechem Ventures Co. Port Harcourt.

UV-Visible spectrophotometer (721,18TS201407023 Germany), electronic scale (JJ500), heating mantle (ZDHW-1000 USA), digital

conductivity meter, thermometer, measuring cylinder, volumetric flask, beakers, pipette, and stirring rod were used for this study.

Experimental Procedures

Aqueous stock solutions of 0.04 M glycerol monostearate were prepared by dissolving 0.71 g in deionized water up to 50 ml mark of volumetric flask. Methylene blue dye was prepared by dissolving 1.0 g of solute in 30 ml of 99.7% ethanol and diluted with 70 ml distilled water. De-ionized water (25 ml) was pipetted into a 200 ml beaker and the conductivity of the de-ionized water measured and recorded using Conductivity meter. GMS stock solution (2 ml) was pipetted into water and stirred. The solution was placed on a heating mantle and as the temperature varied, the conductivity of this solution was recorded. This step was repeated until all the GMS have been added into the beaker. This step was also repeated for UV-Visible Spectroscopic 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.

Determination of CMC of GMS

The critical micelle concentration values were determined from the break point in the plots of conductivity versus surfactant concentration (C) and absorbance (A) versus surfactant concentration respectively. The CMC was measured in mol dm^{-3} .

Effect of temperature on the CMC of GMS

The GMS stock solution (2 ml) was added to de-ionized water and the solution was placed on the heating mantle as the temperature varied. This was repeated for all GMS solution added to de-ionized water. The CMC was determined; a plot of CMC of GMS versus temperature was carefully examined and studied in order to understand and evaluate the thermodynamic properties of micellization.

Results and Discussion

Evaluation of conductivity and absorbance of GMS

The GMS conductivity and absorbance were measured as a function of their concentrations at various temperatures as shown in Table 1.

Table 1: Volume of stock solution added, concentration of stock solution, conductivity, absorbance and temperature.

S/N	Volume of stock solution added (ml)	Concentration of stock solution (mol/dm^3)	Conductivity ($\mu\text{S/cm}$)	Absorbance (nm)	Temperature ($^{\circ}\text{C}$)
1	0	0	0	0.127	10
2	2	0.0029	0	0.208	12.8
3	4	0.0055	10	0.241	15.6
4	6	0.0077	10	0.264	18.4
5	8	0.0096	10	0.405	21.2
6	10	0.0114	10	0.467	24
7	12	0.0129	10	0.491	26.8
8	14	0.0143	20	0.529	29.8

9	16	0.0156	20	0.543	32.4
10	18	0.0167	20	0.588	35.2
11	20	0.0177	20	0.59	38
12	22	0.0187	30	0.622	40.8
13	24	0.0195	30	0.639	43.6
14	26	0.0203	30	0.79	46.4
15	28	0.0211	40	1.091	49.2
16	30	0.0218	40	1.362	52
17	32	0.0224	40	1.452	54.8
18	34	0.023	50	1.662	57.6
19	36	0.0236	60	1.615	60.4
21	38	0.0241	60	1.548	63.2
22	40	0.0246	70	1.438	66
23	42	0.025	70	1.349	68.8
24	44	0.0255	80	1.351	71.6
25	46	0.0259	100	1.366	74.4
26	48	0.0263	150	1.44	77.2
27	50	0.0266	250	1.53	80

Determination of critical micelle concentration

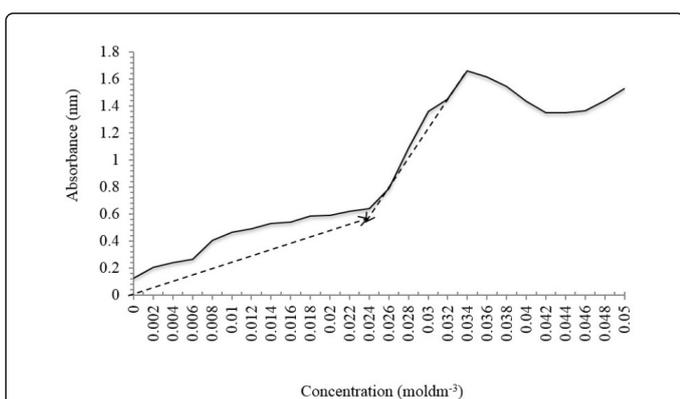


Figure 1: Plot of absorbance as a function of GMS concentration.

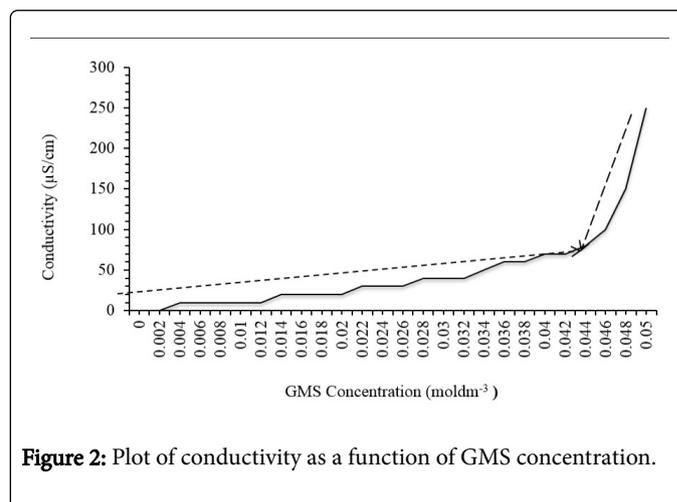


Figure 2: Plot of conductivity as a function of GMS concentration.

Absorbance and conductivity measurements were carried out at various temperatures; it was clearly observed that at concentrations below the CMC, the solution's absorbance and conductivity were low. At CMC, there is a sudden increase in absorbance and conductivity; this could be a result of micelle formation. Above the CMC, the absorbance of the solution increases linearly with increasing concentration, and later showed a minute decrease, while conductivity shows a linear increase above the CMC. The CMC occurs where there is a sharp break. Looking at Figures 1 and 2, the CMC of glycerol

monostarate determined were approximately 0.024 and 0.045 mol/dm³ respectively. The CMC obtained by absorbance showed a more actual value for the CMC of non-ionic surfactant; since the CMC of non-ionic surfactants are lower than that of ionic surfactant [9]. Conductivity method by review, have shown to be more suitable for determination of CMC of ionic surfactant [10]. Therefore, the CMC obtained by absorbance measurement would be used for further determination of thermodynamic properties.

Effect of temperature on the critical micelle GMS concentration

As the system temperature increases, the CMC shows an initial decrease and then slightly increases, as shown in Figure 3 which corresponds to reported review of non-ionic surfactant [4]. The initial decrease in CMC with temperature is as a result of the decreased hydrophilicity of the surfactant molecules. In addition, the increase in temperature causes the reduction in hydration of the hydrophilic oxyethylene group, which favors the formation of micelles. Consequently, as temperature increases, the micellization process occurs at lower concentrations. Additional increase in temperature also causes an increase in the breakdown of the structured water surrounding the hydrophobic groups, which disfavors micellization process. However, the slight increase can be attributed to the smaller probability of hydrogen bond formation at higher temperatures. Glycerol monostrate which is insoluble in water, showed a gradual increase in solubility with increase in temperature up to its krafft temperature (melting point) of approximately 50°C where rapid solubility was observed. Above the krafft temperature, no possible micelles will be formed. The above observation showed that the solubility of GMS was dependent on temperature.

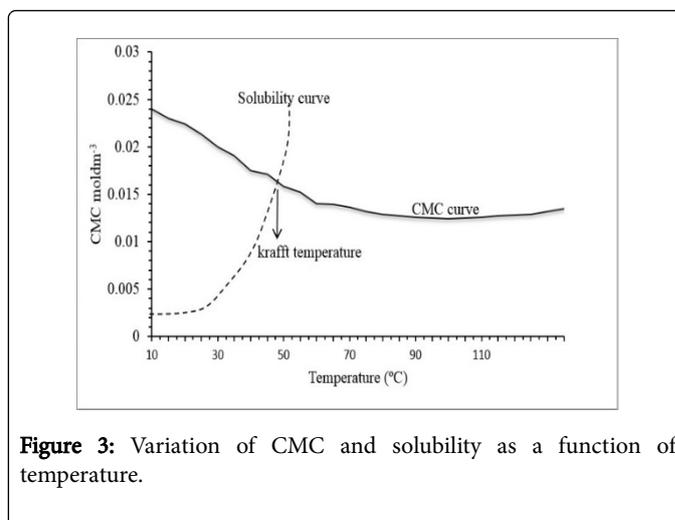


Figure 3: Variation of CMC and solubility as a function of temperature.

Determination of thermodynamic parameters

The Thermodynamic parameters obtained from the equations below are presented in Table 2.

$$\Delta G^{\circ}(\text{CMC}) = RT \ln [\text{CMC}] \quad 1$$

$$\ln K(\text{CMC}) = \frac{\Delta H^{\circ}}{RT} - 2$$

$$\Delta S^{\circ}(\text{CMC}) = \frac{\Delta H^{\circ} - \Delta G^{\circ}(\text{CMC})}{T} \quad 3$$

Table 2: Thermodynamic parameters.

S/N	Temperature	$\Delta G^{\circ} \text{ CMC}$	$\Delta H^{\circ} (\text{CMC})$	$\Delta S^{\circ} (\text{CMC})$
	(K)	(kJmol ⁻³)	(kJmol ⁻³)	(kJmol ⁻³)
1	283	-8775.5	2655.8	40.4
2	285.8	-8862.3	2715.3	40.5
3	288.6	-8949.1	2552.3	39.9
4	291.4	-9035.9	2051.8	38
5	294.2	-9122.8	2572	39.8
6	297	-9209.6	2419.5	39.2
7	299.8	-9296.4	2873.5	40.6
8	302.6	-9383.2	2730.7	40
9	305.4	-9470.1	2619.8	39.6
10	308.2	-9556.9	2537	39.2
11	311	-9643.7	2473.7	39
12	313.8	-9730.5	2424.8	38.7
13	316.6	-9817.4	2522.6	39
14	319.4	-9904.2	2480.8	38.8
15	322.2	-9991	2565.7	39

16	325	-10077.8	2672.2	39.2
17	327.8	-10164.7	2495.2	38.6
18	330.6	-10251.5	2700.6	39.2
19	333.4	-10338.3	2664.1	39
20	336.2	-10425.1	2726.7	39.1
21	339	-10511.9	2694.5	39
22	341.8	-10598.8	2666.9	38.8
23	344.6	-10685.6	2722.2	38.9
24	347.4	-10772.4	2697.3	38.8
25	350.2	-10859.3	2675.8	38.6
26	353	-10946.1	2657.2	38.5

The thermodynamic parameter obtained for micelle formation as shown in Table 2 revealed that ΔG° (CMC) decreases monotonically as the temperature increases over the whole temperature range (283-353) K. The entropy change ΔS° (CMC) appears to show an increase and decrease over the temperature range (fluctuation). The large enthalpy change means that in the formation of micelles, the attractive interaction among hydrophobic chains was opposed by the strong interaction of the oxyethylene chains of glycerol monostearate surfactant with water molecules.

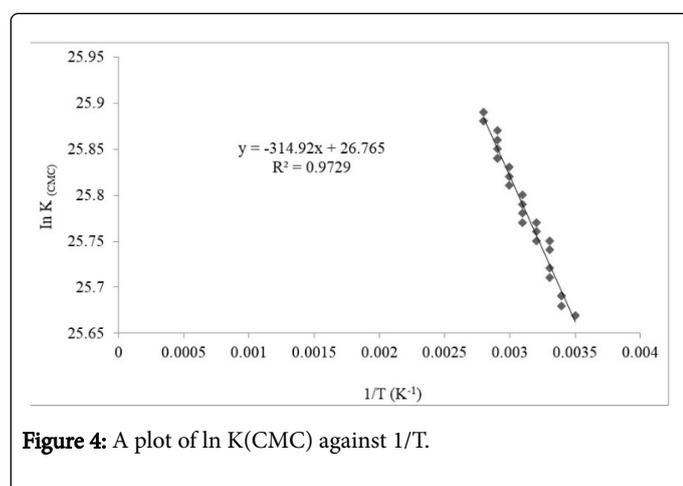


Figure 4: A plot of $\ln K(\text{CMC})$ against $1/T$.

From Figure 4 above, it is clearly seen that $\ln k\text{CMC}$ versus $1/T$ showed a linear decrease with a correlation coefficient (R^2) of 0.972.

Conclusion

The use of UV-Visible Spectroscopy technique was a very good and easy way of determining the critical micelle concentration of GMS. The increase in temperature causes the reduction in the hydration of the hydrophilic oxyethylene group, which favors micellization and has a severe effect on the CMC.

A significant application of this research work is the process of emulsion polymerization. It is a technologically and commercially important reaction that can be used to synthesize alternatives to natural latex rubber.

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