Study of Physico-Chemical Properties of Glycerol Ester Based Non-Ionic Gemini Surfactant

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Abstract: *Gemini or dimeric surfactants can be viewed as two conventional surfactants connected via a spacer at the level of the polar head groups. Various Physico-chemical properties of synthesized glycerol based non-ionic gemini surfactant synthesized by using 1,2,7,8 -diepoxideoctane as spacer has been studied. The surface active properties such as surface tension, critical micelle concentration and effectiveness were determined. The value of surface tension and critical micelle concentration were found to be 30.5mN/m and 0.005mMol/L respectively. The foam production and stability was studied by measuring the volume of foam produced after 30 second and 300 second by varying concentration. The result shows that foaming power and stability is quite low. The investigation showed that synthesized surfactant has good emulsifying power as it promotes emulsion formation at both low and high concentration. The wetting power of synthesized surfactant is quite low. The dispersion power of synthesized non-ionic gemini surfactant was found to be 35%. The synthesized surfactant can be used as emulsifier and dispersing agent.*

Keywords: Gemini Surfactant, Surface Tension, Critical Micelle Concentration, Effectiveness, Foaming Power and Stability, Wetting Power, Dispersing Power.

1. Introduction

Surfactants are well known materials generally described as compounds bearing a hydrophobic and hydrophilic group per molecule. They are referred to as surface active agents that lower surface tension and they may act as emulsifier, detergents, dispersants and solubilizing agent in the field of cosmetic, textile treatment, industrial and personal cleaning operation. Surfactant molecules will diffuse in water and concentrate at interface between air and water, in case where water is mixed with oil, or form aggregates in water such as micelles [1]. Today, new surfactants should be milder, safer, and efficient with a minimal impact on the environment. Environmental awareness and protection have led to the development of more environmentally benign surfactant. There is trend toward replacing petrochemicals by renewable raw materials [2].

Gemini surfactants, sometimes called dimeric surfactants have two hydrophilic head groups and two hydrophobic groups in the molecules, in contrast to conventional surfactants that generally have a single hydrophilic head group and a single hydrophobic group in the molecule. Gemini surfactants can be ten to a thousand times more surface active than conventional surfactants with similar but single hydrophilic and hydrophobic groups in the molecule. Gemini surfactant is very attractive for catalysis and adsorption applications, nanoscale technology, biotechnology and enhanced oil recovery. They also have good emulsifying behaviour when compared with the conventional singled-head-group surfactants. They are also applicable in the textile industry and gene therapy [1], [3]. These advantages of gemini surfactants reduces the over dependence and excessive consumption of conventional surfactant and are considered environment friendly. Due to their high molecular weight, skin penetration of gemini surfactant is expected to be low, which is one of the desirable properties of a surfactant to be used in body care products such as soaps, shampoos and cosmetics [1].

There are several research publications on Gemini surfactants and their potential applications. Aratani et al have synthesized Gemini surfactants from tartaric acid and studied properties. Anno Wagennaar et al have synthesized non-ionic reduced-sugar based bola amphiphiles and gemini surfactants with an α, ω-diamino-(oxa) alkyl spacer. Wenjian Zhang et al, synthesized non-ionic gemini surfactant Di-Glycerol 2, 9-Dihexyldecanedioate and studied the physico-chemical and performance properties [4]-[6].

In previous paper [7], we have described synthesis, characterization and some performance properties of glycerol based non-ionic gemini surfactant by using 1,2 7,8-diepoxideoctane as spacer. In this paper, various physico-chemical properties of synthesized glycerol based non-ionic gemini surfactant have been studied. The surface active properties of synthesized surfactant such as surface tension, critical micelle concentration and effectiveness were determined. The performance properties such as foaming power and stability, emulsifying power, wetting power, dispersion power were studied in details.

2. Materials and Methods

2.1 Material

Non-ionic gemini surfactant was prepared from methods developed previously [7]. Light Paraffin oil, sodium stearate were purchased from sigma aldrich. Doubly distilled water was used all through the study.

2.2 Evaluation of Surfactant Properties

2.2.1 Surface Tension
The surface tension of different concentrations of surfactants aqueous solution were measured using Du Nouy Tensiometer equipped with platinum-iridium ring at 25^{0}C. The tensiometer was calibrated using doubly distilled water [8].The average value of three measurements of the surface tension data was used.

2.2.2 Foaming Ability

Foaming power and stability of aqueous solution of Gemini surfactant of different concentrations were studied according to DIN-53902-1 method [9]. For the measurement, 200 ml of the aqueous solution of Gemini surfactant was poured into a graduated 1 liter measuring cylinder. The solution was manually beaten with a perforated disc with a frequency of 60 beats per minute. The volume of the foam produced was measured after 30 seconds (foaming ability) and after 300 seconds (foam stability). Each of which was repeated three times and the average value was used for estimating the foam ability and foam stability of the surfactant.

2.2.3 Emulsifying Ability

Emulsifying power of the aqueous solutions of product was determined for water/liquid paraffin system. Aqueous solutions of the product at different concentrations were prepared. 20 ml of aqueous solution of product was taken in a100 ml stoppered graduated measuring cylinder and 20 ml of paraffin was poured into it from the side of the wall. The entire cylinder was kept at room temperature (25^OC). After sufficient time the cylinder containing solution was turned upside down for 30 times at the rate of 1 turn per 2 seconds. The time of separation of a aqueous phase for 20 ml was noted [10].

2.2.4 Microscopic Examination of the Emulsions

Water-in-oil type of emulsion was prepared by mixing coconut oil, surfactants and water. Oil and water were taken in 3:1 ratio and 0.6% (by weight) of the prepared surfactant. The mixture was stirred for 30 minutes at 3000 rpm by a magnetic stirrer to prepare the emulsion. The emulsion stability was monitored by microscope. The images were snapped with a camera installed on the microscope and the diluted emulsions were observed [11].

2.2.5 Wetting Ability

The wetting ability of the different concentrations of surfactants solution in distilled water onto canvas were determined using the canvas disc method [12]. The time for a canvas wafer from immersion to starting to sink in the surfactant solution was measured. This was repeated five times and the average time was defined as the wetting time. Then the curve of wetting time vs surfactant concentrations was drawn.

2.2.6 Dispersing Capability

First aqueous solution (0.25 ± 0.01 wt%) of the surfactant were prepared. Secondly 5 mL of aqueous solution (0.5 ± 0.01 wt %) of sodium stearate and 10 mL of „„hard water‟‟ were mixed in a 100-mL stoppered graduated measuring cylinder. Then a certain amounts of the aqueous solution (0.25 ± 0.01 wt %) of surfactant were added to the cylinder. The cylinder was turned upside down for a total of 20 times at a rate of 1 turn per 30s. Increasing the dosage of aqueous solution of surfactants gradually until the coagulation in the cylinder had disappeared and the measuring cylinder mixture was translucent. At that time the added amount of surfactant solution was recorded and this was repeated three times and average value was defined as V_1 [13].

Lime-Soap Dispersion Requirement (LSDR)

$$= \frac{V_1 \text{ X } 0.25 \text{ X } 100}{V_2 \text{ X } 0.5 \text{ \%}}$$

Where V_1 is the amount of surfactant solution (mL) and V_2 is the amount of sodium stearate solution (5 mL).

3. Result and Discussion

3.1 Surface Activity

Surfactant form aggregates of molecules called micelles, which are formed when the concentration of surfactant solute in the bulk of the solution exceed a limiting value, called critical micelle concentration (CMC), which is the fundamental characteristic of each solute-solvent system. If the interfacial properties of a surfactant solution are plotted as a function of the concentration of the solution, the interfacial properties vary linearly with the concentration up to the CMC, at which point there is a break in the curve as shown in fig.1.
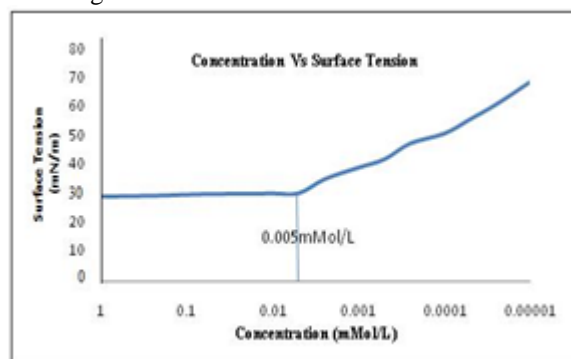

Figure 1: Variation of surface tension versus concentration at 25^0C.

The surface tension of water (72 mN/m at 25^0C) is normally reduced to a value 30-40 mN/m at the cmc of surfactant. Gemini surfactant is generally superior over conventional surfactant in term of surface activity. This is due to the distortion of water by hydrophobic groups. In Gemini surfactant two hydrophobic groups in single molecules are more disruptive than individual chain in conventional surfactant. The variation in the surface tension values versus concentration for solutions of surfactant at 25^0C are represented in fig. 1. Effectiveness is determined by the difference between interfacial tension values at CMC (Υ_{CMC}) and the interfacial tension values measured for pure water at the appropriate temperature (Υ_0). The most effective surfactant gives the greatest lowering of surface tension for given CMC. The values of surface tension at CMC, Critical micelle concentration and effectiveness are shown in table 1.

Table 1: Surface active properties of the synthesized non-ionic Gemini surfactant at temperature 25^oC

Sr. No.	Parameters	Values
1	Surface Tension	30.5 mN/M
2	Critical Micelle concentration	0.005 mMolL^{-1}
3	Effectiveness (π_{cmc})	41.5 mN/M

3.2 Performance Properties

Among the performance properties we have studied emulsifying power, wetting power, foaming power and stability of the product synthesized at different concentration.

3.2.1 Emulsifying Power

Emulsifying power of the aqueous solutions of product was determined for water/liquid paraffin (light) system. Stable emulsion was formed using surfactant solution to oil in a ratio of 1:1 (volume: volume). At different concentration of the synthesized Gemini surfactant, a creamy emulsion of oil in water was observed. The more is the time required for clearing the two layers, the higher is the emulsifying power of the surfactant [10]. On storage during the steady state, it was observed that the creamy stability gradually decreases. This may be result of droplet break and not droplet formation. The emulsifying power of surfactant at different concentrations is shown in table 2. The variation of emulsifying power with concentrations is represented in fig. 3.

3.2.1.1 Microscopic Examination of the Emulsions:

It has been demonstrated that the optical microscope can be an alternative method for the characterization of emulsions [11]. The photos of the emulsion droplets of synthesized Gemini surfactant are shown in fig. 2. It is important to note that the emulsion with smaller droplets in the photos is more stable than with bigger droplets.

Figure 2: Microscopic image of the emulsions formed by using synthrsized non-ionic gemini surfactant and coconut oil.

3.2.2 Wetting Performance

The wetting behaviors of the synthesized product using the canvas disc method were studied. The time required to sink the canvas disc in surfactant solution is measured as wetting time. The minimum is the time required for sinking the disc, higher is the wetting power of surfactant [14]. The wetting time decreases with increase in concentration as shown in table 2.

Table 2: Emulsifying power and wetting time of synthesized Gemini surfactant at different concentrations.

Sr. No.	Concentration of surfactant (gm/100ml)	Emulsifying Power (minute)	Wetting time (second)
1	0.1	6	228
2	0.2	9	142
3	0.3	11	87

A surfactant can adsorb at the solid–liquid and liquid–gas interface when it is added to the solution. The adsorption leads to the solid surface wetting due to the hydration of surfactant. The more surfactant adsorbs onto the solid surface, stronger is the wetting ability. An aqueous solution of a surfactant can wet a solid surface due to the adsorption and hydration of the surfactant. The wetting ability mainly depends on the interaction between the solid surface and the surfactants. The variation of wetting time versus surfactant concentration for prepared surfactant is shown in Fig.3.
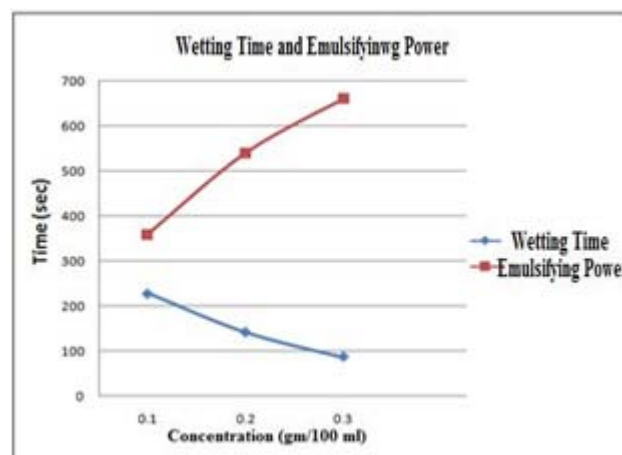

Figure 3: A plot of wetting time and emulsifying power at different concentration of synthesized non- ionic gemini surfactant at 29°c

3.2.3 Foaming power and stability

The most widely appreciated property of surface active substances in aqueous solution is their ability to promote the formation of foam and bubbles. The gas is dispersed in the liquid to form the foam which is a thermodynamically unstable system. Surfactants can reduce the interfacial tension between the gas and liquid to form stabilized foam. These behaviors could be attributed to the physical nature and bubble formation. The results obtained for synthesized Gemini surfactant shows low quality foam production. The foam produced from synthesized surfactant has thicker nature with small bubbles throughout the experimental period. The foaming power and stability increases with increase in concentration of synthesized surfactant as shown in table 3.

Table 3: Foaming power, foaming stability of synthesized non-ionic Gemini surfactant at different concentrations.

Sr No	Concentration of surfactant (gm/100ml)	Foam volume(ml) at 30seconds	Foamvolume(ml) at 300 seconds
1	0.1	15 ml	12 ml
2	0.2	28 ml	20 ml
3	0.3	40 ml	35 ml

The main factor that can affect the formability and stability of surfactants are the interfacial tension and the properties of interfacial film. When generating foam of same total surface area, lower surface tension system needs less work. This means that lower surface tension is good for the foam production. The stability IJof foam is mainly depends on the drain speed and intensity of the interfacial film and also on the solution viscosity. Viscosity can increase the strength of the liquid film and increase the stability of the foam. The foam producing ability of prepared compound is quite low.
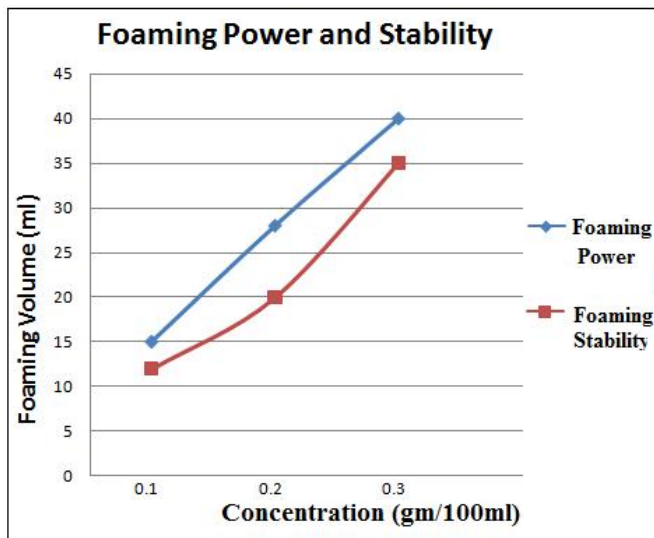
Figure 4: A plot of foam production and stability at different concentration of synthesized non-ionic gemini surfactant at room temperature (29°c).

3.2.4 Dispersing capability [13]:

A surfactant possesses the ability to disperse the agglomerative solid particle and this is called dispersibility. Generally, dispersibility is measured by its lime-soap dispersion ability. The lime soap dispersion capability of the synthesized gemini surfactant was measured as 35%. The smaller the LSDR %, the better is the dispersibility. It was found that the dispersion capability of synthesized surfactant is quite good.

4. Conclusion

The various physicochemical properties of a novel class of gemini surfactants with two glycerol moieties as the polar head group has been studied. Surface tension of synthesized non-ionic gemini surfactant is low. The critical micelle concentration has remarkable low value so the quantity of synthesized gemini surfactant required for application would be less in amount. Effectiveness of synthesized surfactant is good. The study investigated foam production and stability of synthesized surfactant. The foam production and stability was studied by measuring the volume of foam produced after 30 seconds and 300s second and by varying concentration. The result showed that foam production was quite low. Foaming power of synthesized gemini surfactant increases with increase in the concentration. The investigation showed that synthesized surfactant is good emulsifier as it promotes emulsion formation at both low and high concentration. On varying concentrations it was observed that emulsion capacity of synthesized surfactant decreases with increase in storage time. The wetting power and dispersion power were studied. The wetting power of synthesized surfactant increases with concentrations. It can be concluded that synthesized surfactant can be used as good emulsifying and dispersing agent.

5. Acknowledgment

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