

NORMAL MICELLAR VALUE DETERMINATION IN SINGULAR AND MIXED SURFACTANT SYSTEM EMPLOYING FLUORESCENCE TECHNIQUE

Mohd Zul Helmi Rozaini^{1,2*}, Ruslimie Che Ali², Laili Che Ros^{1,2}

¹*School of Chemistry and Pharmacy, University of East Anglia, Norwich, Norfolk, NR4 7TJ, UK*

²*Department of Chemical Sciences, University Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, MALAYSIA*

(Received: May 2011 / Revised: June 2011 / Accepted: July 2012)

ABSTRACT

Studies on the determination of Critical Micelle Concentration (CMC), of mixed surfactants were carried out at 30°C for hexadecyltrimethylammonium bromide (HTAB) and polyoxyethylene sorbitan monolaurate (Tween 20), hexanol and water. From the phase diagram, a composition of 0.2 to 1.0 fraction of water is the best area for normal micelle region for HTAB and 0.3 to 1.0 fraction of water for Tween 20 with curving upward the 1-hexanol apex maximum solubility of 1-hexanol. From the fluorescence method, the CMC value for pure T20 and HTAB were 1.6293×10^{-3} M and 2.7439×10^{-3} M respectively. While for CMC₁ and CMC₁₁ value for mixed surfactant system at mole ratio 0.2: 0.8 (T20: HTAB) were CMC₁: 2.358×10^{-3} M and CMC₁₁: 7.0741×10^{-3} M. These finding were observed upon the theoretical values, which indicate the synergistic behavior between both surfactants.

Keywords: Critical Micelle Concentration (CMC); Hexadecyltrimethylammonium bromide (HTAB); Sorbitan monolaurate (Tween 20)

1. INTRODUCTION

Surfactants are among the most demanded product in the chemical industries such as the following industries: pharmaceuticals, cosmetics, detergents, paints, dye stuffs, pesticides, fibers, and plastics (Rosen, 1978). All surfactants behave like detergents, having a hydrophilic head and a hydrophobic tail. Consequently a hydrophobic molecule or compound such as, dioxins will have an affinity for the long hydrocarbon-chain tail. In industry surfactants are used either as essential additives or processing aids or in many cases as only a minor part of a system or formulation (Hamdan, 2000).

A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with the surrounding solvent, sequestering the hydrophobic single tail regions in the micelle centre (Alorgova et al., 2003). This phase is caused by the insufficient packing issues of single tailed lipids in a bilayer. The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micellae is known as micellization and forms part of the phase behavior of many lipids according to their polymorphism (Rozaini & Brimblecombe, 2009).

* Corresponding author's email: zulhelmi@ukn.edu.tw, Tel. +606683263 Ext. 3263

The addition of a second surfactant component to a single surfactant system creates mixed surfactant system, which provides a wider range of aggregates microstructures than those exhibited by single surfactant system (Minardi et al., 2002). The aggregation of pure surfactant and mixed surfactant has been compared, than it was found that mixed surfactants have the tendency to aggregate at a lower concentration (Tanford et al., 1997). This paper is a direct investigation on the ideal behaviour of mixed surfactant systems upon the addition of hexanol employing the fluorescence probing method.

2. MATERIAL AND METHODS

The fluorophore pyrene was 95% (Fluka, Buchs, Switzerland), Hexatrimethylamine Bromide (HTAB) >99% (Sigma), 1-hexanol >98% (Fluka), Polyoxyethylene (20) sorbitan monolaurate (Tween 20) > 99% (Aldrich). All the material was used without further purification. All the test tubes and glassware were rinsed with distilled water to make sure all the glassware were clean and free from contamination before using. After that the glassware was kept in an oven at 80°C to ensure that they were dry enough.

2.1. Determination of micelle region

The micelle regions were determined on a clear/turbid criteria basis by mixing components that were placed in a centrifuge for 20 min at 5000 rpm. The samples were then allowed to reach an equilibrium level in a water bath, at 30°C. The phases were inspected visually through the naked eye and observed in between crossed polarizers. An estimation of the region of the phases was made by this method by noting the turbid and clear compositions.

2.2. Fluorescence measurements

Samples for the fluorescence measurement were prepared by combining water and surfactant, at a fixed weight ratio of 9/1, with pyrene (3.0×10^{-7} M). The hexanol were incrementally added with a Hamilton syringe to the resulting samples. The fluorescence spectra were recorded on a Cary Eclipse spectrophotometer by at 335 nm. The ratio of the intensity of pyrene emissions at 373 nm and at 383 nm is defined as I_3/I_1 .

3. RESULT AND DISCUSSIONS

3.1. Micelle region

The partial phase diagrams exhibiting the micelle region for the individual HTAB/1-hexanol/water systems at 30°C are shown in Figure 1. The micellar region was appointed with the existence of two regions of homogenous isotropic solution. The V pattern, was higher with the alcohol content (1-Hexanol) which is what we called the inverse micellar region and the other parts were nourished with aqueous content and determined as a micelle region (small V pattern). The limits of these areas were determined by titration to the turbidity with the smallest amount of one component to the homogenous solution.

In this system, the inverse micellar region covered between 80 wt% to 100 wt% of water while the micelle region covered about 1 wt% to 50 wt% of alcohol. The addition of the third component (1-Hexanol) not only affected the critical micelle concentration (CMC) and the aggregation number of micelle, but also the microenvironments of the micellar itself.

The liquid crystal region has been divided into two parts, one of which is a lamellar liquid crystal and the other is a hexagonal liquid crystal. Hexagonal liquid crystals were covered by the phase diagram between 38 wt% to 48 wt% of water. While the lamellar liquid crystals were covered up to the point of 75 wt% water, 12 wt% HTAB and 13 wt% 1-Hexanol to point 20 wt% water, 48 wt% HTAB and 32 wt% of 1-hexanol.

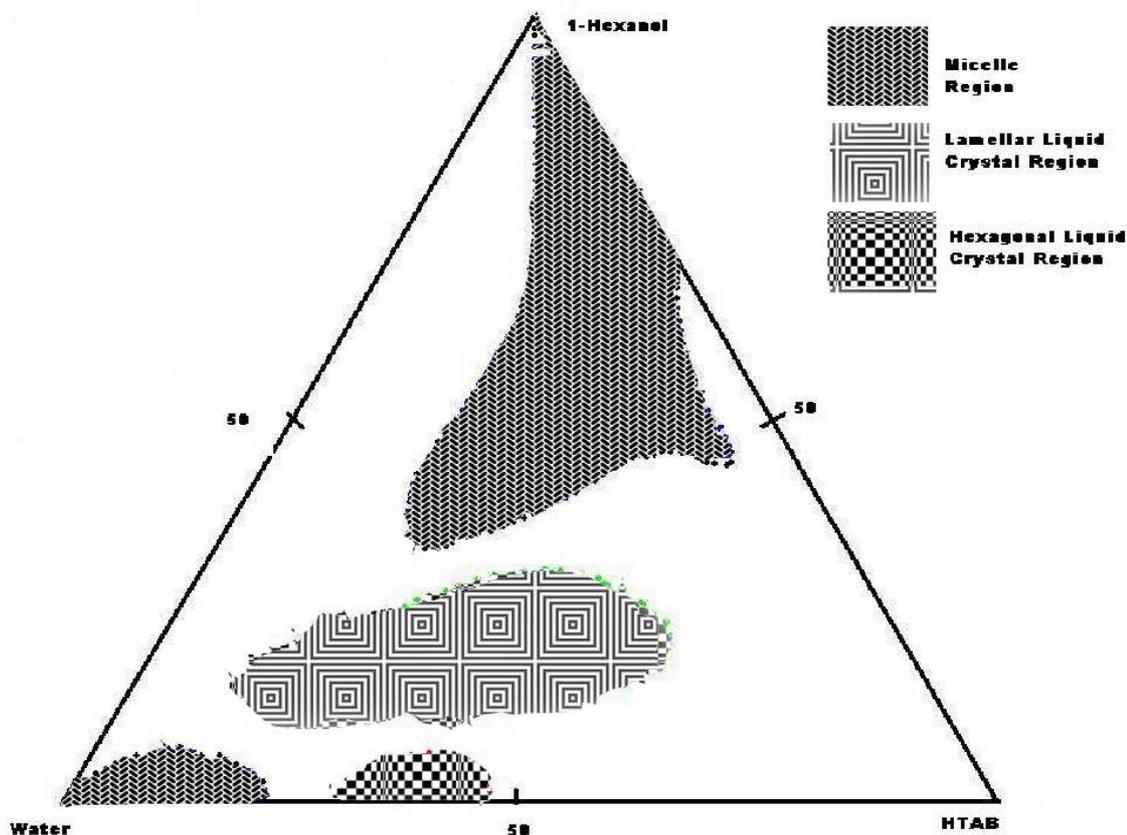


Figure 1 Phase Diagram for Pure Surfactants (HTAB)/1-hexanol/water

The partial phase diagram for mixed surfactants T20 /HTAB/water system at 30°C is shown in Figure 2. The micelle region has emerged as a bigger size than in Figure 1. It covered almost of the diagram due to the mixing of two types of surfactants. Previous work discovered that, when two or more surfactants are present in a water solution, a complex balance of intermolecular forces will be formed (Holland et al., 1992). In fact the mix of surfactants results in the disappearance of the hexagonal liquid crystal region from Figure 1. It has been observed that when the percentage of T20 decrease and percentages of HTAB increase, the micelle region becomes smaller, but the liquid crystal region becomes larger (Clint, 1992).

3.2. Fluorescence Intensity

The ratio of fluorescence intensity, I_3/I_1 versus the concentration of HTAB at 25°C is shown in Figure 3. The intensity values, I_3/I_1 of HTAB were increased between 0 to 10.474 before they reached a break point at an 11.0676 ratio intensity and became constant. This break point corresponds to the formation of Critical Micelle Concentration (CMC) and the value is 2.7439×10^{-3} M.

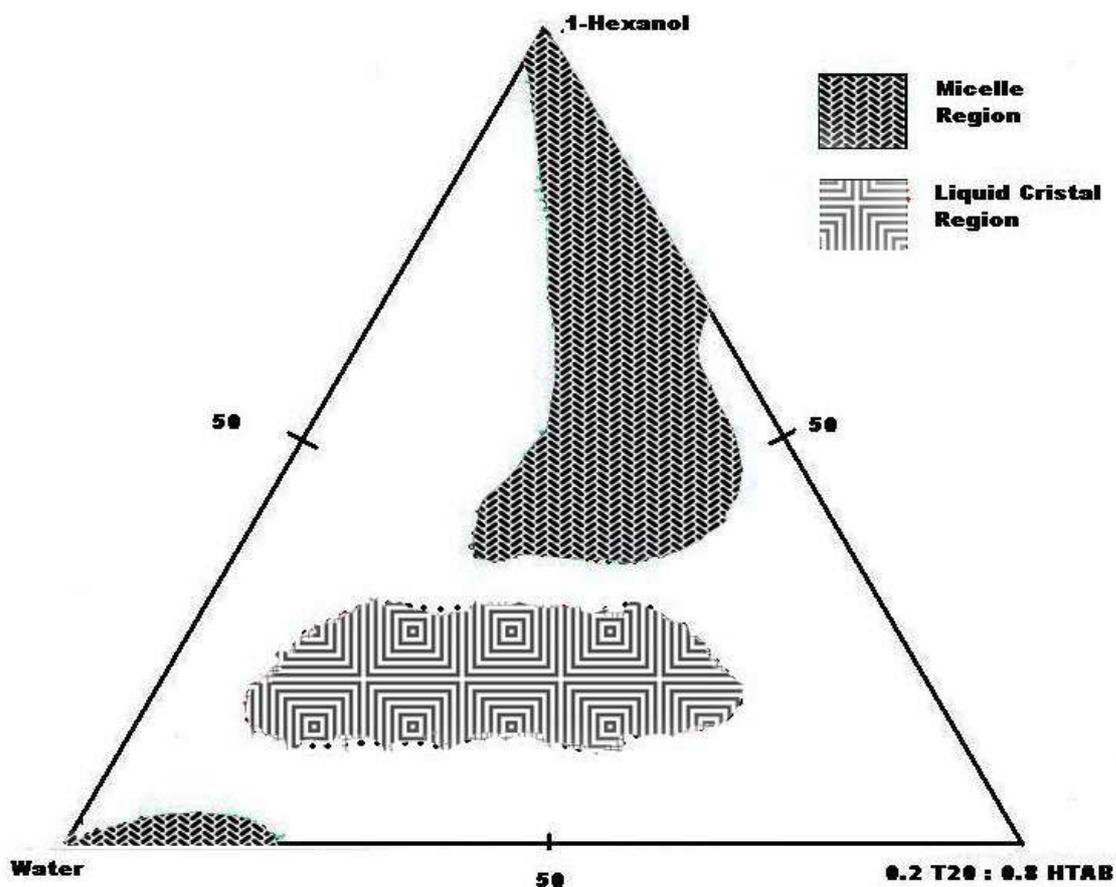


Figure 2 Phase diagram for mixed surfactants (HTAB:T20)/1-hexanol/water

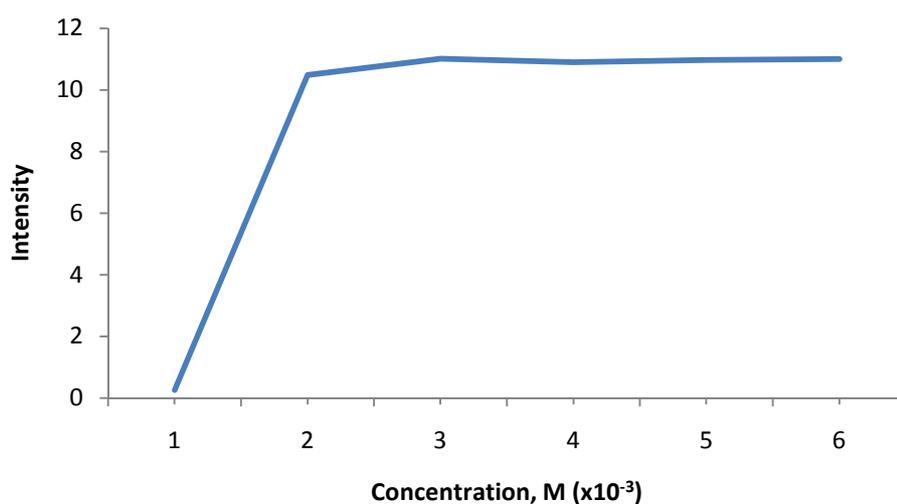


Figure 3 Intensity (I_3/I_1) versus concentration, of pure HTAB

The fluorescence intensity ratio (I_3/I_1) versus the concentration of Tween 20 was observed at Figure 4. The results showed that the intensity ratio (I_3/I_1) values were increased up to 5.6737 before reached 8.827 at CMC value of 1.6293×10^{-3} M.

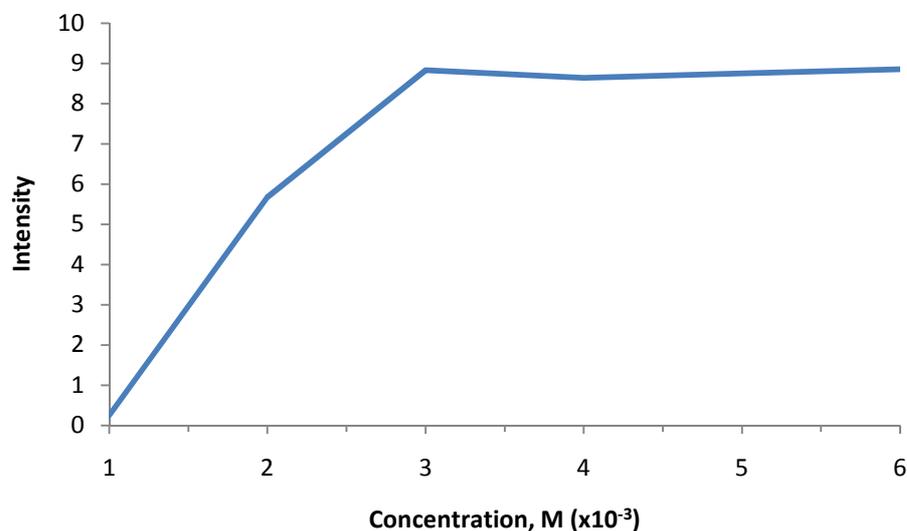


Figure 4 Intensity (I_3/I_1) versus concentration, of Tween 20

For mixed surfactants, 0.2 T20: 0.8 HTAB the fluorescence intensity ratios were also observed in Figure 5

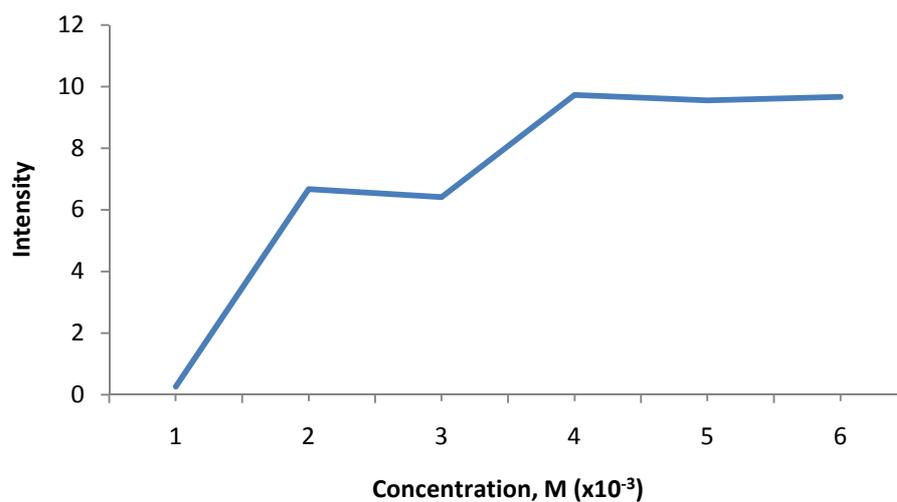


Figure 5 Intensity (I_3/I_1) versus concentration, of mixed surfactant HTAB and Tween20

There were two break points formed in this observation. The graph intensity value was increased up to 6.415 and 10.000. As previous mentioned by Cabral and Smith (1992), it was

reported that the first break point was attributed to the micelle formation and the concentration corresponding to this point was named CMC_1 (first CMC) while the second one was interpreted as being caused by the change in micelle shape and the corresponding concentration was named CMC_2 (second CMC). While Basu et al., (2005) assumed that this second CMC corresponds to the formation of rodlike micelles. The CMC values were determined in this investigation are $CMC_1: 2.358 \times 10^{-3}$ M and $CMC_2: 7.0741 \times 10^{-3}$ M, respectively.

An interesting observation was found in CMC value at a ratio 0.2 T20:0.8 HTAB. The CMC value for mixed surfactants is still less than those from pure surfactants. According to Sharma et al. (2003), the CMC value in a mixed surfactant system at any mole ratio is less than those of either pure surfactant, which indicates a synergistic behaviour.

4. CONCLUSION

The investigation of several of the ratios of pure and mixed surfactants is summarized to indicate that the mixed surfactants formed a bigger micelle region (normal and inverse micellar) compared to a single combination. In addition, the combination of surfactants has blocked the formation of hexagonal liquid crystals and remains in the smaller region of lamellar liquid crystals. From the fluorescence method, the CMC value for pure T20 and HTAB were 1.6293×10^{-3} M and 2.7439×10^{-3} M respectively. While for CMC_1 and CMC_{11} value for mixed surfactant system at mole ratio 0.2: 0.8 (T20: HTAB) were $CMC_1: 2.358 \times 10^{-3}$ M and $CMC_{11}: 7.0741 \times 10^{-3}$ M.

5. ACKNOWLEDGEMENTS

The authors are indebted to the Physical Chemistry Research Group and also staff members of Chemical Sciences Department East Anglia, UK for providing the daily observation on tensiometer value. They also acknowledge their sincere appreciation to the reviewer for their comments and suggestions. This research was funded by University Malaysia Terengganu.

6. REFERENCES

- Alorgova, R. G., Petskov, J. T., Petsev, D. N., 2003. Micellization and interfacial Properties of alkyloxyethylene sulfate surfactants in the presence of multivalent counterions. *Journal of Colloid Interface Science*, Volume:261:1-11.
- Basu, R. G., Chakraborty, I., Ghosh S., Moulik S. P., 2007 On mixed binary surfactant systems comprising MEGA 10 and alkyltrimethyl ammonium bromide: A detailed physicochemical with a critical analysis. *Journal of Colloid and Interface Science*, Volume: 307:456-462
- Cabral, J., P., S., Smith, A. R. W., 1992 Determination of the critical micelle concentration of Dodecylguanidine Monoacetate (dodine). *Journal of Colloid and Interface Science*, Volume: 149:567-673
- Clint, J.H., 1992. Surfactant Aggregation. pp:130-139. New York: Blackie & Son Ltd.
- Hamdan, S., 2000. Into The Wonders of Surfactant Behavior. Siri Syarahan Inaugural. Kolej Universiti Terengganu. 3, 9-11. ISBN:0-8247-8796. Penerbit Universiti Malaysia Terengganu.
- Holland P. M., Rubingh D. N., 1992. Mixed surfactant system, pp:123-152. Marcel dekker, inc Washington, D. C.
- Minardi, R. M, Schulz, P. C., Vuano, B., 2002. Triangular phase diagram of the cationic system dodecyltrimethylammonium bromide-disodium dodecanephosphonate water. *Colloid Surface A: Physicochem. Eng. Aspects*, Volume:197: 167-172.
- Rosen, M. J, 1989. Surfactants and Interfacial Phenomena. 2nd ed. pp 3-7. New York: John Wiley & Sons, Inc.

- Rozaini, M.Z.H., Brimblecombe, P., 2009. The solubility of dicarboxylic acid. *Journal of Chemical Thermodynamic*, Volume: 41:980-986.
- Sharma K. S, Christoper R., Rama M. Palepu, A. K. Rakshit., 2003. Studies of Mixed surfactant solution of cationic dimeric (Gemini) Surfactant with nonionic surfactant C12E6 in aqueous medium. pp 178-193. New York: Blackie & Son Ltd.
- Tanford, C.,1995. Hydrophobic free energy, micelle formation and association of proteins with amphiphiles. *Journal of Molecular Biology*, Volume: 67:56-64.