

STUDY THE MICELLIZATION BEHAVIOR OF BOTH CATIONIC AND ANIONIC SURFACTANTS IN PRESENCE OF HEN EGG YOLK

Parbhej Ahamed*, M. A. Yousuf and Md. Shahariar Imtiaj

Department of Chemistry, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh

Received: 22 March 2014

Accepted: 22 June 2014

ABSTRACT

The micellization behavior of a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB) and an anionic surfactant, sodium dodecyl sulphate (SDS) was investigated in presence of hen egg yolk. Surfactant solutions with a wide range of concentrations (2×10^{-3} to 11×10^{-3} M for SDS and 0.5×10^{-3} to 1.4×10^{-3} M for CTAB) both below and above critical micelle concentration (SDS formed CMC at 6.82×10^{-3} and CTAB at 10.34×10^{-4} M) were prepared. The change in specific conductance with the amount of added hen egg yolk was used to determine the CMC, ionization degree (α) and counterion binding of the micelles (β), to study the interaction of hen egg yolk with the surfactants in solution. It is noteworthy that egg yolk significantly influenced the CMC of both surfactants. The CMC for SDS increases strongly with the gradual addition of egg yolk. As a general rule it is believed that electrical repulsion among the ionic head groups of anionic surfactant SDS and egg yolk are responsible for the formation of micelle at higher CMC. On the other hand a decrease in CMC with the addition of egg yolk has been noted for cationic surfactant CTAB. Examination of this behavior ended strong interaction between the head groups of cationic surfactant CTAB and egg yolk fatty acids favor the micellization process.

Keywords: Anionic surfactant, Cationic surfactant, Egg yolk, Micelle.

1. INTRODUCTION

The interaction of surfactants with the presence of added electrolytes, polymers, copolymers has been studied by several groups (Goddard and Ananthapadmanaban, 1993; Kwak, 1998; Jonsson *et al.*, 1998; Zhai, *et al.*, 2005). It offers a wide range of fascinating possibilities of the complex ways in which the surfactant molecules can associate into supramolecular or nanoscale structures. The properties of the systems can be tuned simply by varying the composition, which is an attractive alternative to the synthesis of new materials (Patist *et al.*, 1998) and to carry out some organic reaction (Lipshutz and Taft, 2008) such as Heck reaction, aldol condensation reaction etc.

This is particularly true when there are attractive interactions between the surfactants, as is the case in mixtures of anionic and cationic surfactants. The picture of this interaction is supported by investigations performed by Koehler *et al.* (2000). They found that the mixing of anionic surfactant sodium oleate (NaOA) with cationic surfactants (from the family of alkyl trimethylammonium bromide) a million-fold increase in the viscosity relative to that of the single surfactant was obtained. That study illustrates how strong interactions between head groups can facilitate micellar growth and enhance the rheological properties of the system, which had a significant effect on their applications.

Penfold *et al.* investigated the structure of mixed surfactant micelles of sodium dodecyl sulfate (SDS) and hexaethylene glycol monododecyl ether ($C_{12}E_6$) in the presence and absence of hexadecane (Penfold and Staples, 2002). They have observed that solutions rich in nonionic surfactant favored the formation of small globular micelles with dramatic changes in micellar size. The solubilization of the alkane suppressed the micellar growth. It suggests that the addition of alkane changes the balance of the steric and electrostatic contributions of the headgroups to the free energy of micellization, therefore favoring the formation of short rods. Menge *et al.* also observed the latter effect in dilute solutions of pentaethylene glycol monododecyl ether ($C_{12}E_5$) upon addition of small amounts of decane, causing a transition from elongated wormlike micelles to microemulsion droplets (Meng *et al.*, 1999).

The modification of this micelle core with hydrophobic groups highlighted the importance of a hydrophobic environment for efficient catalysis in water (Mase *et al.*, 2006; Hayashi, 2006; Aratake *et al.*, 2007). It is well established that carrying out organic reactions in water based micelle nanoreactor can have advantages over that in solution or bulk (Tascioglu, 1996). Nanoreactors, can concentrate reactants through compartmentalization (Monterio, 2010), resulting in a considerable increase in the rate of product formation, faster and better controlled reactions. Furthermore, water provides an environmentally friendly medium (Butler and Coyne, 2010) with the potential to significantly reduce the amount of organic solvents in the synthesis pharmaceuticals and fine chemicals.

* Corresponding author: parbhejahamed@yahoo.com

To the best of our knowledge there are no reports of the interaction of surfactants with egg yolk components. In this work, we have first studied the interaction of hen egg yolk on the micellization of SDS and CTAB through conductivity measurement. We have determined the critical micelle concentration (cmc), ionization degree α and the counterion binding β , with the addition of different amount of egg yolk.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The surfactants SDS and CTAB were Aldrich products and were used as received. Hen eggs were collected from local shop. Deionized distilled water was used in the preparation of all the solutions.

2.2 Measurements

The CMC value of pure SDS and CTAB were determined by conductivity measurement method. A series of solution such as 2×10^{-3} , 3×10^{-3} , 4×10^{-3} , 5×10^{-3} , 6×10^{-3} , 7×10^{-3} , 8×10^{-3} , 9×10^{-3} , 10×10^{-3} , 11×10^{-3} M were prepared for SDS. The concentration of the prepared CTAB solution were 0.5×10^{-3} , 0.6×10^{-3} , 0.7×10^{-3} , 0.8×10^{-3} , 0.9×10^{-3} , 1.0×10^{-3} , 1.1×10^{-3} , 1.2×10^{-3} , 1.3×10^{-3} , 1.4×10^{-3} M. Specific conductance of this surfactant solutions were measured upon the consecutive addition of different amount of egg yolk into each surfactant solution. All measurements were carried out with the help of a digital conductometer.

3. RESULTS AND DISCUSSION

Figure 1 represents the determination of CMC of pure SDS and CTAB in water using conventional conductivity method. A break is observed in the value of conductivity of the micellar solution with the formation of the micelles. The breaks in the specific conductance vs concentration plot attributes to the beginning of micelles, i.e. to CMC. It is seen that SDS formed CMC at 6.82×10^{-3} and CTAB at 10.34×10^{-4} M.

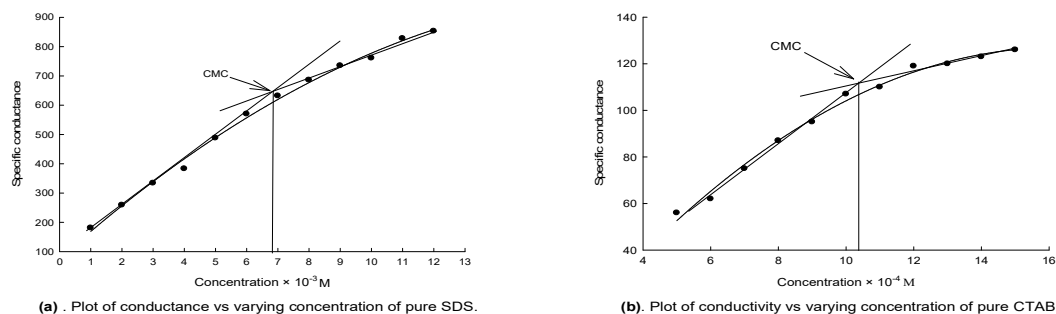


Figure 1: Determination of CMC value for the aqueous solution of (a) SDS and (b) CTAB

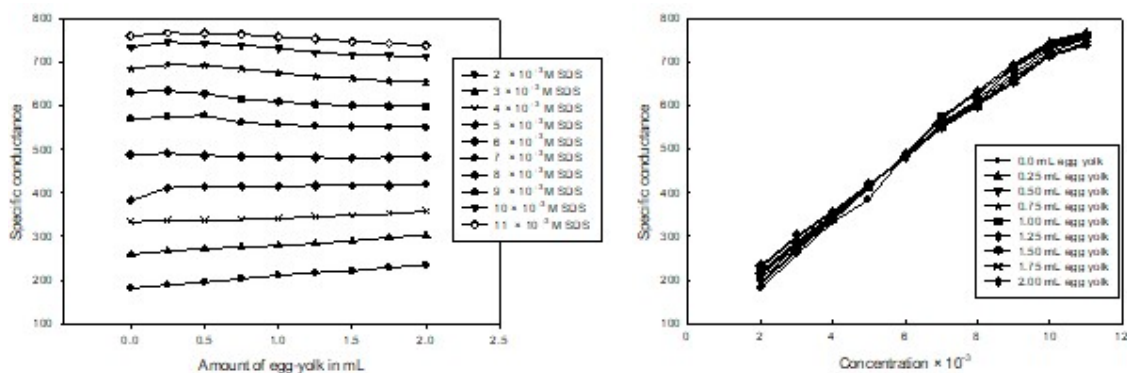


Figure 2: (a) Effect of different amount of egg yolk on the CMC, premicellar and postmicellar concentration of SDS. (b) Plot of specific conductance vs concentration of SDS in the presence of various amount of hen egg yolk.

The effect of egg yolk on the CMC value of SDS and CTAB were studied by preparing a range of premicellar and postmicellar concentration solutions. It was observed that the successive addition of different amount of egg yolk into each solution of SDS and CTAB provided conductance variation. Figure 2(a) represents the dependence of conductance at CMC, premicellar and postmicellar aqueous solution of 2×10^{-3} , 3×10^{-3} , 4×10^{-3}

$3, 5 \times 10^{-3}, 6 \times 10^{-3}, 7 \times 10^{-3}, 8 \times 10^{-3}, 9 \times 10^{-3}, 10 \times 10^{-3}, 11 \times 10^{-3}$ M solutions of SDS with the addition of different amount of egg-yolk.

Surprisingly, two different trend of conductivity was obtained at premicellar and postmicellar solutions. At premicellar concentration the conductivity always increased with increasing the amount of egg-yolk. It varies slightly at CMC, but always decreased at postmicellar concentration with increasing the amount of egg yolk. Then the Figure 2(b) used for determining the CMC value, ionization degree (α) and counterion binding of the micelles (β), of different solution of SDS. Ionization degree of the micelles α , has been calculated as the ratio of the slopes of the two intersecting lines as in Figure 1 and then β has been calculated using the formula $\beta = 1 - \alpha$ (Dominguez *et al.*, 1997). The results are presented in Table-1.

Table 1: Increase in CMC, degree of surfactant ionization (α) and counterion binding (β) for micellization of surfactant SDS with the addition of egg yolk.

Amount of egg yolk added (in mL)	Critical micelle concentration (M)	Ionization degree of the micelle, α	Counterion binding, β
0.00	6.82×10^{-3}	0.21	0.79
0.25	7.39×10^{-3}	0.50	0.50
0.50	7.77×10^{-3}	0.71	0.29
0.75	7.80×10^{-3}	0.73	0.27
1.00	7.81×10^{-3}	0.66	0.34
1.25	8.32×10^{-3}	0.54	0.46
1.50	8.45×10^{-3}	0.53	0.47
1.75	8.52×10^{-3}	0.58	0.42
2.00	8.53×10^{-3}	0.49	0.51

These results suggest that there is a electrical repulsion between the polar head groups of SDS and egg yolk fatty acid during micelle formation. Electrical repulsion among the ionic head groups of the same charge results an increase in the CMC value of SDS with increasing the amount of egg yolk.

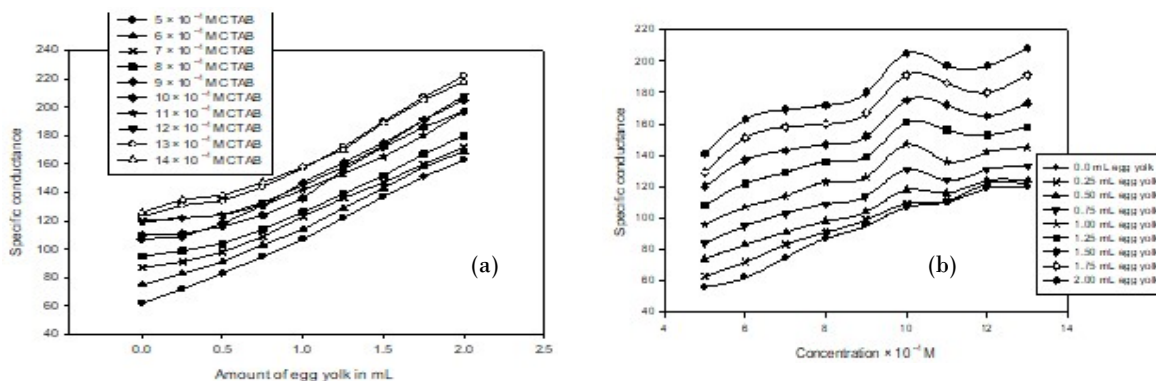


Figure 3: (a) Effect of different amount of egg yolk on the CMC, premicellar and postmicellar concentration of CTAB. (b) Plot of specific conductance vs concentration of CTAB in the presence of various amount of hen egg yolk.

Table 2: Increase in CMC, degree of surfactant ionization degree (α) and counterion binding (β) for micellization of surfactant CTAB with the addition of egg yolk.

Amount of egg yolk added (in mL)	Critical micelle concentration (M)	Ionization degree of the micelle, α	Counterion binding, β
0.00	6.82×10^{-3}	0.21	0.79
0.25	7.39×10^{-3}	0.50	0.50
0.50	7.77×10^{-3}	0.71	0.29
0.75	7.80×10^{-3}	0.73	0.27
1.00	7.81×10^{-3}	0.66	0.34
1.25	8.32×10^{-3}	0.54	0.46
1.50	8.45×10^{-3}	0.53	0.47
1.75	8.52×10^{-3}	0.58	0.42
2.00	8.53×10^{-3}	0.49	0.51

Similarly, the variation of conductance with the addition of different amount of egg yolk at CMC, premicellar and postmicellar concentrations of CTAB is depicted in Figure 3(a). A completely different trend of conductivity pattern is observed compare to SDS. It is observed that the conductivity always increased at all concentration of aqueous solution of CTAB. The changed CMC value, ionization degree (α) and counterion binding of the micelles (β) were calculated from Figure 3(b).

It is clear from the results that the addition of egg yolk lowers the CMC value of CTAB. The CMC value decreased with increasing the amount of egg yolk. The trend of this behavior could be explained in terms of strong interaction between the polar head groups of egg yolk fatty acid and CTAB. Strong ion-pairing may occur between the oppositely charged counter ions of CTAB and fatty acids. The electrostatic attraction among the ionic head groups may enhance the micellization process.

4. CONCLUSION

The micellization behaviors of anionic surfactant SDS and cationic surfactant CTAB have been examined separately by adding different amount of egg yolk in succession. It was found egg yolk significantly influences the micellization process of both surfactants. In case of SDS the addition of egg yolk retards micellization process which leads to an increase in the CMC. On the other hand, micellization process of the aqueous solution of CTAB favors with the addition of egg yolk. The obtained results can be represented by the following Figure 4.

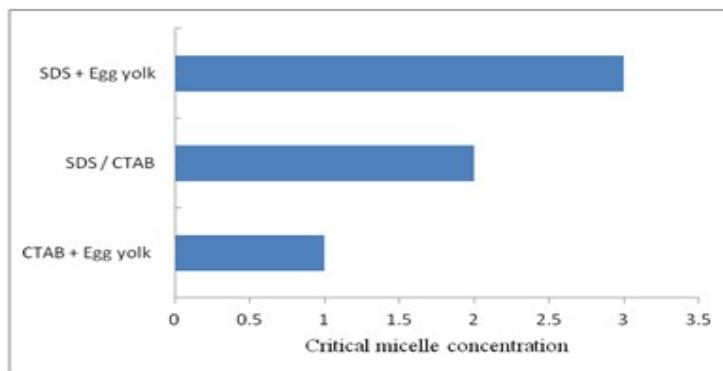


Figure 4: Graphical representation for observed CMC values of surfactant, SDS-Egg yolk & CTAB-Egg yolk by conductivity

Hence the final trend of critical micelle concentration for the present work is: Cationic surfactant-Egg yolk < Surfactant < Anionic surfactant-Egg yolk.

REFERENCES

- Aratake, S., Itoh, T., Okano, T., Nagae, N., Sumiya, T., Shoji, M., and Hayashi, Y., 2007. *Chem.-Eur. J.*, 13(36), 10246–10256.
- Butler, R. N., and Coyne, A. G., 2010. *Chem. Rev.* 110, 6302.
- Dominguez, A. Fernandez, A. Gonzalez, N. Iglesias, L. Montenegro, J., 1997. Determination of critical micelle concentration of some surfactants by three techniques. *J. Chem. Educ.* 74, 1227-1231.
- Goddard, E. D. and Ananthapadmanaban, K. P., 1993. *Interactions of Surfactants with Polymer and Proteins*, CRC Press: Boca Raton, FL.
- Hassan, P. A; Fritz, G; and Kaller, E. W. J., 2003. *Colloid Interface Science*, 257, 154-158.
- Hayashi, Y., 2006. *Angew. Chem., Int. Ed.* 45(48), 8103–8104.
- Jonsson, B.; Lindman, B., 1998. Holmberg, K.; Kronberg, B. *Surfactants and Polymers in Aqueous Solution*; John Wiley & Sons: London.
- Koehler, R. D; Raghavan, S. R; and Kaller, E. W., 2000. *J. Phys. Chem. B* 104, 11035.
- Kwak, J. C. T., 1998. *Surfactant Science Series Volume 77: Polymer- Surfactant Systems*; Marcel Dekker: New York.
- Lipshutz B. H., and Taft, B. R., 2008. *Org. Lett.* 10, 1329.
- Mase, N.; Nakai, Y.; Ohara, N.; Yoda, H.; Takabe, K.; Tanaka, F.; Barbas, C. F.; III *J. Am. Chem. Soc.* **2006**, 128(3), 734-735.
- Menge, U., Lang, P., and Findenegg, G. H., 1999. *J. Phys. Chem. B* 103, 5768.
- Monteiro M. J., 2010. *Macromolecules* 43, 1159.
- Patist A., T. Axelberd and D-O. Shah, J., 1998. *Colloid and Interface Science*, 208, 259.
- Penfold, J; Staples, E., 2002. *J. Phys. Chem. B* 106, 8891.
- Tascioglu S., 1996. *Tetrahedron* 52, 11113.
- Zhai L., Zhao M., Sun D., Hao J, and Zhang L., 2005. *J. Phys. Chem. B*, 109, 5627-5630.