

**INFLUENCE OF MALATE COUNTERION ON PHYSICO-CHEMICAL PROPERTIES OF BUTANEDIYL-1,4-BIS(HEXADECYL HYDROXYETHYL METHYL AMMONIUM BROMIDE) SURFACTANT****Mahendra Sahebrao Borse<sup>a\*</sup>, Dilip Sahebrao Patil<sup>b</sup> and Anil Dharmraj Kakuste<sup>c</sup>**<sup>a\*</sup>Department of Chemistry, U.P. Arts and Science College, Dahivel, Tal.Sakri, Dist.- Dhule, North Maharashtra University, Jalgaon India.<sup>b</sup>Department of Chemistry, S.G. Patil College, Sakri, Tal.Sakri, Dist.-Dule, North Maharashtra University, Jalgaon India.<sup>c</sup>Department of Chemistry, V. U. Patil. Arts and Science College, Sakri, Tal.Sakri, Dist.-Dule, North Maharashtra University, Jalgaon India.**Corresponding Author: Dr. Mahendra Sahebrao Borse**

Department of Chemistry, U.P. Arts and Science College, Dahivel, Tal.Sakri, Dist.- Dhule, North Maharashtra University, Jalgaon India.

Article Received on 01/09/2016

Article Revised on 22/09/2016

Article Accepted on 13/10/2016

**ABSTRACT**

Influence of bivalent malate counterion on physicochemical properties of butanediyl-1,4-bis(hexadecyl hydroxyethyl methyl ammonium bromide) surfactant was studied by conductometry measurement. Critical micelle concentration, average degree of micelle ionization, kraft temperature and gibbs free energy of micellization were determined from conductivity data. Oil solubilization and foamability was observed to increase at 1:0.5 surfactant to counterion charge ratio. The decrease in change in gibbs free energy and foam stability indicate that the micellization process was retards at theoretical unequal surfactant to counterion charge ratio(1:05).

**KEYWORDS:** Surfactant, counterion, kraft temperature, cmc, oil solubilization.**INTRODUCTION**

Surfactants are the widely used in industries and academic research. They have number of applications ranging from detergents, pharmaceuticals, personal care products, and in industrial applications such as coatings and lubricants. The last decade has seen the extension of surfactant applications to high technology areas such as electronics printings, magnetic recording, biotechnology and microelectronics<sup>[1]</sup>. Therefore, a fundamental understanding of the physical chemistry of surfactants, their unusual properties and phase behaviors are essential for most industrial chemists. In ionic surfactant, ionic strength and types of ions can affect the properties of surfactant in solution, increase of ionic strength of solution leads to a lowering of the critical micelle concentration of ionic surfactants and to a transition from spherical to cylindrical (rigid rodlike or flexible wormlike) ionic micelles<sup>[1-4]</sup>. This dependence has been attributed to the screening of the electrostatic repulsion by counterions released from these surfactants and from any electrolyte added to the solution.

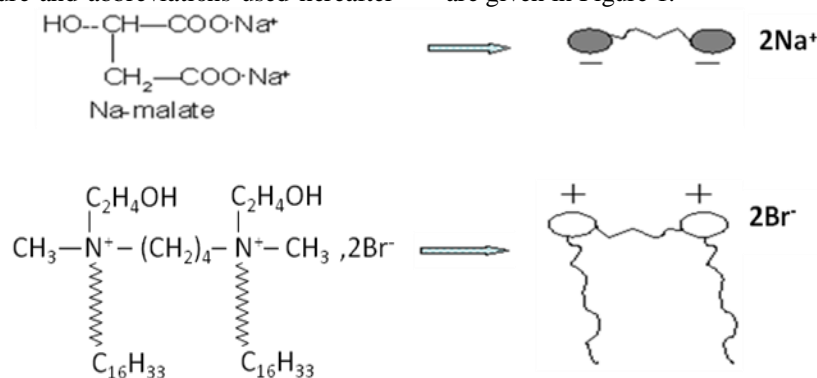
In addition, the micellar properties of ionic surfactants are strongly affected not only by the overall counterion concentration but also by the specific type of counterions released from the surfactant heads and the electrolytes added to the solution. For example, in the case of the

anionic surfactant dodecyl sulfate with associated monovalent alkali counterions, the CMC is observed to follow the sequence  $CMC_{Cs^+} < CMC_{K^+} < CMC_{Na^+} < CMC_{Li^+}$ . Critical micelle concentration is observed to increase with an increase in the size of the hydrated counterion<sup>[5]</sup>. Micelles formed by the cationic surfactant cetyl trimethylammonium bromide undergo a sphere-to-rod transition upon addition of 0.1 M NaBr, while micelles formed by its chloride analogue require addition of 1.0 M NaCl to undergo this shape transition.<sup>[6,7]</sup>

Multivalent counterions, such as  $Al^{3+}$  and  $Ca^{2+}$ , are known to be much more affects the properties of surfactants than monovalent counterions, such as  $Na^+$ , at the same ionic strength<sup>[8-12]</sup>. Furthermore, lipophilic counterions, such as the aromatic salicylates, methyl-salicylic acid, chlorobenzoates, and toluic acid<sup>[13-15]</sup> as well as alkyl sulfonates<sup>[16]</sup> and quaternary ammonium ions,<sup>[17,18]</sup> strongly promote the formation of elongated rodlike or wormlike micelles in ionic surfactant solutions, where the presence of these micellar structures impart viscoelasticity to the system.

Hence in this paper we have undertaken the influence of bivalent malate counterion on physicochemical properties of butanediyl-1,4-bis(hexadecyl hydroxyethyl methyl ammonium bromide) surfactant.

The chemical structure and abbreviations used hereafter



**Figure 1: Chemical structures and schematic representation of surfactants and Na-malate under study**

## MATERIAL AND METHODS

### Materials

Butanediyl-1,4-N,N'-bis(N,n-hexadecyl N-hydroxyethyl N-methyl ammonium bromide) represented as 16-4-16 MEA was synthesized<sup>[19]</sup>. Na-malate and Methyl methacrylate was purchased from Emerck (Germany) and National Chem. (India) respectively. Double-distilled and deionized water was used for all physicochemical studies.

### Kraft Temperature

The kraft temperature ( $k_T$ ) for 16-4-16 MEA in the presence of Na-malate at different molar ratios, 1:0, 1:0.5, 1:1 and 1:1.5 respectively was determined through conductance measurements as well as through visual observation of the transparency of the surfactant system. Aqueous one percent(w/v) true solutions were prepared and placed in refrigerator at a temperature of about 1 - 2°C for at least 24 h till precipitate of the hydrated surfactant crystal appeared. The precipitated system was introduced in conductivity cell and temperature of the system was gradually increased using water bath of accuracy  $\pm 0.2^\circ\text{C}$ . The conductance was measured as the temperature was progressively increased until the turbid solution became clear. The Kraft temperature was taken as the temperature where the conductance ( $k$ ) vs temperature plot showed break. This break usually coincided with the temperature where complete dissolution of hydrated solid surfactant resulted into transparent solution. The measurements were repeated at least three times and reproducibility in  $k_T$  values was observed within  $\pm 0.3^\circ\text{C}$ .

### Critical Micelle Concentration (CMC)

Critical micelle concentration (CMC) of the 16-4-16 MEA surfactant in the presence of different concentrations of Na-malate was determined through conductance measurements using Digital Conductivity Meter-664 (Equiptronic, Mumbai, India) with cell constant  $1.01\text{ cm}^{-1}$ , at  $30.0 \pm 0.1^\circ\text{C}$ . The stock solutions for CMC measurement were prepared at four different surfactant to malate molar ratios; 1:0, 1:0.5, 1:1 and 1:1.5. The conductance was measured on addition of an aliquot of a known concentration of a stock solution to a given volume of the thermostated solvent. The average

are given in Figure 1.

degree of dissociation of counter ions ( $\alpha_{ave}$ ) of the micelle and CMC were determined from specific conductance vs concentration plots (Figure 2).

### Foamability and Foam Stability

The foamability and foam stability of 16-4-16 MEA surfactant in the presence of Na-malate (at surfactant to malate molar ratios; 1:0, 1:0.5, 1:1 and 1:1.5 respectively) were studied as per the method reported by Shah<sup>[20]</sup>. A graduated glass cylinder of  $100\text{ cm}^3$  volume was used for the measurement of the foam stability and foamability. Twenty centimeter cubic 1 % (w/v) solution (surfactant + Na-malate) was poured into the calibrated cylinder. The solution was given 10 uniform jerks within 10 s. The volume of the foam generated was measured as foamability and the time required for the collapse of the foam to half of its initial height was taken as a measure for the foam stability. The experiments were repeated at least five times.

### Oil Solubilization Capacity

Oil solubilization capacity of 16-4-16 MEA gemini surfactant in the presence of Na-malate was measured using methyl methacrylate (MMA). A series of solutions containing 100 mM 16-4-16 MEA and 0, 50, 100 and 150 mM Na-malate was prepared. These solutions were thoroughly homogenized using a vortex mixture and kept in a thermostated water bath at accuracy of  $\pm 0.1^\circ\text{C}$ . These solutions were then titrated with MMA using a micro burette.

## RESULT AND DISCUSSION

### Kraft temperature

Kraft temperature of 16-4-16 MEA surfactant in the presence of Na-malate at different mole ratios of surfactant to malate; 1:0, 1:0.5, 1:1 and 1:1.5 were determined and are given in Table 1. Additions of Na-malate initially decrease the kraft temperature of 16-4-16 MEA. Further increases in the concentration of Na-malate shows increase in kraft temperature. This can be explained in terms of electrostatic interaction. It is reported that kraft temperature of ionic surfactant increases with increased binding of counterions, or with increase in branching of the hydrocarbon chain<sup>[21,22]</sup>. The kraft temperature is also a reflection on the stability of

surfactant monomers in the presence of hydrated crystal. The observed lower  $k_T$  value at 1:0.5 surfactant to Na-malate mole ratio is due to the larger value of average degree of ionization charge,  $\alpha_{ave}$  indicating stronger Coulombic repulsion between the charged heads of surfactant. This results in destabilization of the hydrated crystal leading to decrease in the kraft temperature. On further increase in Na-malate (1:1, and 1:1.5) concentration, charge on micelle decreases (Figure 3). This results in the increase in the stability of surfactant monomer and hence increases in kraft temperature.

**Table 1: Effect of concentration of Na-malate on kraft temperature of 16-4-16 MEA Surfactant**

16-4-16 MEA to Na-malate mole ratio	kraft Temperature ( $k_T$ ) ( $^{\circ}$ C)
1:0.0	38
1:0.5	25
1:1.0	40
1:1.5	42

**Table 2: Effect of Na-malate concentration on critical micellar concentration (CMC), average degree of micelle ionization ( $\alpha_{ave}$ ) and Gibb's free energy ( $\Delta G_m^{\circ}$ ) change of micellization of 16-4-16 MEA gemini surfactant at 30 $^{\circ}$ C.**

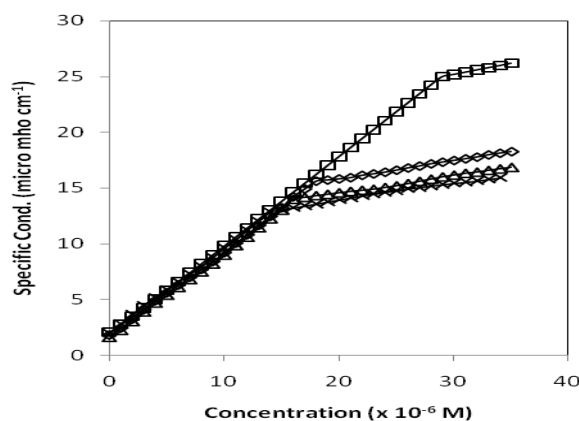
16-4-16 MEA to Na-malate mole ratio	CMC ( $\times 10^{-6}$ M)	$\alpha_{ave}$	( $-\Delta G_m^{\circ}$ ) KJ.Mol $^{-1}$
1: 0.0	$1.8 \pm 0.1$	0.21	42.98
1.0.5	$2.9 \pm 0.1$	0.25	40.14
1:1.0	$1.6 \pm 0.1$	0.20	43.70
1:1.5	$1.5 \pm 0.1$	0.19	44.25

It was observed that addition of Na-malate to 16-4-16 MEA initially increases CMC and average degree of micelle ionization. But further increase in Na-malate concentration decreases CMC as well as average degree of micelle ionization. This effect is explained on the basis of surfactant and counterion, charge ratio. It is well reported that the ionic strength of solution and charge on counterion strongly influence properties and solution behavior of surfactant molecules<sup>[23]</sup>. In the present system, addition of Na-malate to aqueous surfactant solution, gives bivalent malate as counterions. The

### Critical Micelle Concentration (CMC)

The plots for the determination of CMC of 16-4-16 MEA surfactant in the presence of Na-malate (bivalent counterion) from conductance measurement are given in Figure 2. The CMC, average degree of ionization of micelle ( $\alpha_{ave}$ ) and Gibb's free energy change of micellization ( $\Delta G_m^{\circ}$ ) were determined from conductance data and results are given in Table 2.

binding tendency of these bivalent malate ions is more than that of monovalent ( $Br^{-}$ ) counterion. However at 1:0.5 surfactants to malate mole ratio, surfactant charge to counterion charge ratio is unequal, resulting into more electrostatic repulsion between head groups of surfactants. This results in the increase in the CMC and decrease in micellization tendency indicated by higher Gibb's free energy change of micellization ( $\Delta G_m^{\circ}$ ) at 1:0.5 mole ratio.



**Figure 2: Effect of concentration of Na-malate on critical micelle concentration of 16-4-16 MEA gemini surfactants.**

16-4-16 MEA : Na-malate mole ratios; 1:0( $\diamond$ ), 1:0.5( $\square$ ), 1:1( $\Delta$ ), 1:1.5( $\times$ )

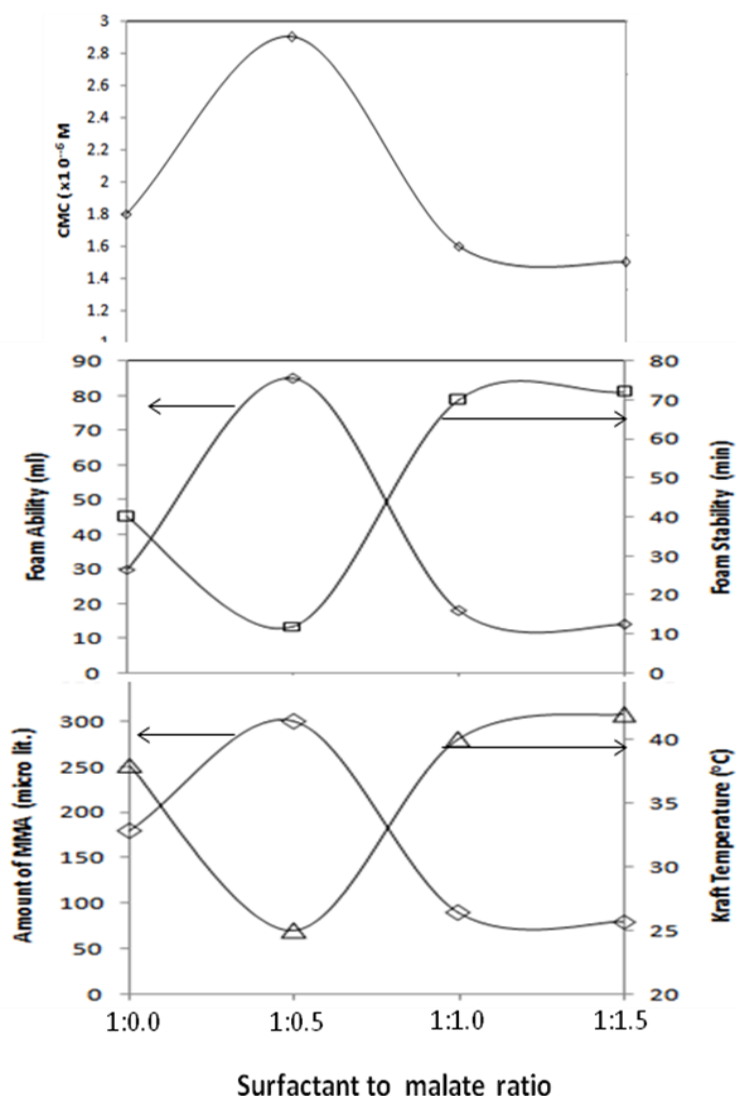
### Foamability and Foam Stability

The results obtained in the study of foamability and foam stability of 16-4-16 MEA dimeric surfactant in the presence of different concentration of Na-malate are given in Figure 3. With addition of Na-malate to 16-4-16 MEA foamability decreases and foam stability increases except at mole ratio 1:0.5. This fact can be explained in terms of CMC, aggregation tendency and micellar stability. The degree of binding of counterion was observed to decrease at 1:0.5 surfactants to Na-malate mole ratio, due to unequal surfactant ions to counterions charge ratio. This results in increase in the repulsion between adjacent surfactant head groups, causing loosely packed micelles and hence providing more monomer

flux to stabilize the new air/water interface. This results in more foamability and less foam stability at 1:0.5 surfactants to Na-malate mole ratio.

### Oil Solubilization

Oil solubilization capacity of 16-4-16 MEA gemini surfactant in the presence of various concentrations (0, 50, 100 and 150 mM) of Na-malate at three different temperatures were measured. Amount of methyl methacrylate solubilized in given micellar system is given in Figure 3. The oil solubilization capacity of 16-4-16 MEA surfactant was observed to be more in the presence of 50 mM Na-malate than that at 0, 100 and 150 mM Na-malate.



**Figure 3: Variation of CMC, Kraft Temperature, Oil solubilization, Foamability and Foam stability of 16-4-16 MEA surfactant on addition of Na-malate at 30°C.**

### CONCLUSIONS

In this paper we report the physicochemical properties of novel hydroxylated 16-4-16 MEA surfactant in presence of Na-malate. Malate anion acts as bivalent counterion for dimeric surfactant in aqueous solution. The change in concentration of surfactant and counterion is very

convenient tool for controlling properties of surfactant. Critical micelle concentration (CMC), average degree of micelle ionization ( $\alpha_{ave}$ ) and Gibb's free energy change of micellization ( $\Delta G_m^0$ ) of 16-4-16 MEA surfactant is strongly influenced by concentration of Na-malate. Kraft temperature ( $k_T$ ) and foamability, foamstability of bis-

cationic surfactant 16-4-16 MEA can be monitored by adding specific amount of Na-malate. The solubilization capacity of surfactant system was observed to increase by adding unequivalent moles (50 mM) of Na-malate concentration.

#### ACKNOWLEDGEMENT

The authors are grateful to UGC-WRO, Pune for providing financial support to this research work.

#### REFERENCES

1. Tanford C, *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; John Wiley: New York, 1980.
2. Zana R, Benrraou M, Bales BL, *J. Phys. Chem. B*, 2004; 108: 18195.
3. Hayashi S, Ikeda S, *J. Phys. Chem.* 1980; 84: 744.
4. Porte G, J Appell, *J. Phys. Chem.* 1981; 85: 2511.
5. Imae T, Kamiya R, Ikeda S, *J. Colloid Interface Sci.* 1985; 108: 215.
6. Rosen MJ, *Surfactants and Interfacial Phenomena*, John Wiley, New York, 1989.
7. Dorshow RB, Bunton CA, Nicoli DF, *J. Phys. Chem.* 1983; 87: 1409.
8. Alargova RG, Ivanova VP, Kralchevsky PA, Mehreteab A, Broze G, *Colloids Surf. A* 1998; 142: 201.
9. Alargova R, Petkov J, Petsev D, Ivanov IB, Broze G, Mehreteab A, *Langmuir*, 1995; 11: 1530.
10. Alargova RG, Danov KD, Kralchevsky PA, Broze G, Mehreteab A, *Langmuir*, 1998; 14: 4036.
11. Rehage H, Hoffmann H., *Mol. Phys.*, 1991, 74, 933.
12. Lin Z, Cai JJ, Scriven LE, Davis HT, *J. Phys. Chem.* 1994; 98: 5984.
13. Kumar S, Aswal VK, Goyal PS, Kabirud Din, *J. Chem. Soc., Faraday Trans.*, 1998; 94: 761.
14. Hunter RJ, *Foundation of Colloid Sci., Oxford Sci. Publications*, Clarendon Press Vol.1, Oxford, UK, 1987.
15. Liu YC, Baglioni P, Teixeira J, Chen S.H., *J. Phys. Chem.*, 1994; 98: 10208.
16. Shinoda K, Halo M, Hayashi T, *J. Phys. Chem.*, 1972; 76: 909.
17. Borse MS, Sharma V, Aswal VK, Pokhariyal NK, Joshi JV, Goyal PS, Devi SG, *Phys. Chem. Chem. Phys.*, 2004; 6: 3508.
18. Shah DO, *J. Colloid and Interface Sci*, 1971; 37: 744.
19. Yang PW, Mantsch HH, *J. Colloid Interface Sci.*, 1986; 113: 218.
20. Mukerjee P, *Adv. Colloid Interface Sci.*, 1967; 1: 24.
21. Pandey S, Bagwe RP, Shah DO, *J. Colloid and interface Sci.*, 2003; 267: 160.