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[1]. 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[1-4]. This dependence has been attributed to the screening of the electrostatic repulsion between the charged ionic heads at the micelle surface 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 CMCNa⁺ < CMCLi⁺ < CMCK⁺ < CMCCa⁺. Critical micelle concentration is observed to increase with an increase in the size of the hydrated counterion[5]. 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.[6,7]

Multivalent counterions, such as Al³⁺ and Ca²⁺, are known to be much more affects the properties of surfactants than monovalent counterions, such as Na⁺, at the same ionic strength[8-12]. Furthermore, lipophilic counterions, such as the aromatic salicylates, methylsalicylic acid, chlorobenzoxates, and toluic acid[13-15] as well as alkyl sulfonates[16] and quaternary ammonium ions[17,18] 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 are given in Figure 1.

Figure 1: Chemical structures and schematic representation of surfactants and Na-malat 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\(^{[19]}\). 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 ± 0.2°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 ± 0.3°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 (Equipnic, Mumbai, India) with cell constant 1.01 cm\(^{-1}\), at 30.0±0.1°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 degree of dissociation of counter ions (\(\alpha_{\text{ave}}\)) 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\(^{[20]}\). A graduated glass cylinder of 100 cm\(^2\) volume was used for the measurement of the foam stability and foambility. Twenty centimeter cubic 1 % (w/v) solution (surfactant + Na-malate) was poured into the calibrated cylinder. The solution was given 10 uniform jerks within less than 10 s. The volume of the foam generated was measured as foambility 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 ± 0.1°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 molar 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\(^{[21,22]}\). 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

<table>
<thead>
<tr>
<th>16-4-16 MEA to Na-malate mole ratio</th>
<th>kraft Temperature (( k_T )) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.0</td>
<td>38</td>
</tr>
<tr>
<td>1:0.5</td>
<td>25</td>
</tr>
<tr>
<td>1:1.0</td>
<td>40</td>
</tr>
<tr>
<td>1:1.5</td>
<td>42</td>
</tr>
</tbody>
</table>

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\(^23\). In the present
system, addition of Na-malate to aqueous surfactant
solution, gives bivalent malate as counterions. The
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 (\( \Delta G_m^o \)) at
1:0.5 mole ratio.

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 (\( \Delta G_m^o \)) were determined from conductance
data and results are given in Table 2.

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

<table>
<thead>
<tr>
<th>16-4-16 MEA to Na-malate mole ratio</th>
<th>CMC (x10^-3 M)</th>
<th>( \alpha_{ave} )</th>
<th>(( \Delta G_m^o )) KJ.Mol^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.0</td>
<td>1.8 ± 0.1</td>
<td>0.21</td>
<td>42.98</td>
</tr>
<tr>
<td>1.0.5</td>
<td>2.9 ± 0.1</td>
<td>0.25</td>
<td>40.14</td>
</tr>
<tr>
<td>1:1.0</td>
<td>1.6 ± 0.1</td>
<td>0.20</td>
<td>43.70</td>
</tr>
<tr>
<td>1:1.5</td>
<td>1.5 ± 0.1</td>
<td>0.19</td>
<td>44.25</td>
</tr>
</tbody>
</table>

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(◊),1:0.5(□),1:1(△),1:1.5(χ)
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.

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 (\(\Delta G_m^{°}\)) 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.

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REFERENCES