

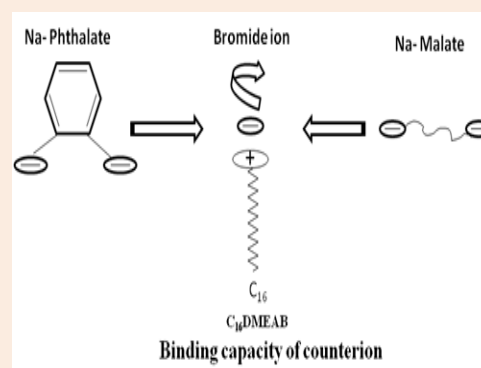
Research Article

Effect of nature of counterion on physicochemical properties of cetyl dimethyl ethanol ammonium bromide surfactant

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To study the physicochemical properties of cetyl dimethyl ethanol ammonium bromide ($C_{16}DMEAB$) surfactant in presence of bivalent counterions such as sodium salt of malate and phthalate were studied at different charge ratios by conductometric measurement. Critical micelle concentration (CMC), average degree of micelle ionization (α), binding of counterion (β), change in Gibbs's free energy of micellization (ΔG_m°) and Kraft temperature (k_T) were determined from conductance data. CMC, oil solubilization and foamability for both counterions were observed to increase at 1:0.5 surfactant to counterions charge ratio. The decrease in change in Gibbs's free energy and foam stability indicate that the micellization process is retarded at unequal surfactant to counterion charge ratio (1:0.5). The change in Gibbs's free energy is slightly more negative on addition of sodium phthalate than sodium malate at all combinations indicates that addition of sodium phthalate helps the micellization process and hence lowers the CMC.

Keywords: CMC, Foamability, Counter ion, Kraft temperature, Micelle.

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Introduction

Surfactants are used in a wide variety of industrial and commercial applications. They are exploited for their detergency, solubilization, and surface-wetting capabilities in such diverse areas as the mining, petroleum, chemical, and pharmaceutical industries, as well as in biochemical and medical research. In order to tailor the properties of the surfactant solution to best suit the desired application, one must be able to predict and manipulate (i) the tendency of the surfactant solution to form micelles as reflected by the critical micellar concentration (CMC) (ii) the shape and size distribution of the micelles that form above the CMC, and (iii) the phase behavior of the surfactant solution. Indeed, the concentration of surfactant in a solution, which is used as a cleaning detergent, should exceed the CMC to ensure the presence of micelles in which oily substances or dirt can be solubilized. The shape and size of micelles is directly related to the viscosity and other rheological features of the micellar solution, which are important in many applications involving surfactants. Ionic surfactants are the most widely used class of surfactants in industries and academic research. They are used in applications ranging from detergents, pharmaceuticals, and personal care products, to industrial applications such as coatings and lubricants. An increase in the 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 [1–3]. 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. This strategy to induce micelle growth in ionic surfactant systems, via Coulombic screening by the counterions present in the solution, has been the subject of extensive

experimental research [4–9] and is also exploited in several commercial applications involving ionic surfactants, such as the use of electrolytes as “thickeners” in shampoos, to impart increased viscosity to the product.

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 [10]. Micelles formed by the cationic surfactant cetyl trimethyl ammonium 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 [9–11].

Multivalent counterions, such as Al^{3+} and Ca^{2+} , are known to be much more effective promoters of micelle growth than monovalent counterions, such as Na^+ , at the same ionic strength [12–14]. Furthermore, lipophilic counterions, such as the aromatic salicylates, methyl-salicylic acid, chlorobenzoates, and toluic acid [15–18] as well as alkyl sulfonates [19] and quaternary ammonium ions [20, 21] strongly promote the formation of elongated rodlike or wormlike micelles in ionic surfactant solutions. The binding of counterions and their effect on the structure of ionic micelles in aqueous solution has been extensively investigated [22]. Most of the studies follow two different approaches: (a) chemical substitution of the surfactant counterion [23] (b) addition of specific counterion molecules such as malate, lactate and salicylate [24–30].

In the second case binding affinity of counterion in solution seems to be the main driving force to significantly change the micellar microstructure and intermicellar interactions. Imae [31] reported that micelles of cationic surfactant grow rapidly from globular to wormlike on the addition of small amount of sodium salicylate. Recently we have reported synthesis, characterization and physicochemical properties newly synthesized CTAB derivatives [32].

Hence in continuation of this work a systematic study has been undertaken to examine effect of various counterions like sodium phthalate and sodium malate on physicochemical properties of C_{16} DMEAB surfactants. The chemical structure and abbreviations used hereafter are given in **Figure 1**.

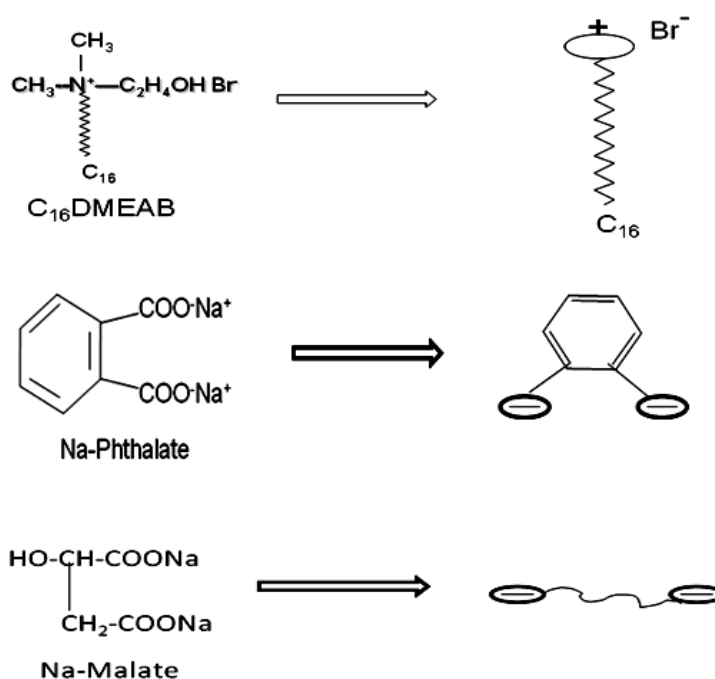


Figure 1 Chemical structures and schematic representation of surfactants and Na- phthalate and Na-malate under study

Experimental

Materials

Cetyl dimethyl ethanol ammonium bromide (C₁₆DMEAB) was synthesized in our laboratory [32]. Na-phthalate, Na-malate and Methyl methacrylate were purchased from Emerck (Germany) and National Chem. (India) respectively. Double-distilled and deionized water was used for all physicochemical studies.

Methods

Kraft Temperature

The kraft temperature (k_T) of C₁₆DMEAB in the presence of Na-phthalate and Na-malate at different charge 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 of surfactant to counterions charge ratios 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 specific conductance (k) versus 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.

Conductance measurements

Critical micelle concentration (CMC) of the C₁₆DMEAB surfactant in the presence of sodium phthalate and sodium malate at various surfactant to counterions charge ratios was determined through conductance measurements using Digital Conductivity Meter-EQ664 (Equiptronics, Mumbai, India) with cell constant 1.01 cm⁻¹, at 30.0 \pm 0.1 °C. The stock solutions for CMC measurement were prepared at four different surfactant to counterion charge 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 measurements were done for all solutions. The average degree of dissociation of counter ions (α) of the micelle and CMC were determined from specific conductance verses concentration plots and values are given in **Tables 1** and **2** for both systems.

Foamability and Foam Stability

The foamability and foam stability of C₁₆DMEAB surfactant in the presence of both counterions Na-phthalate and Na-malate at various surfactant to counterions charge ratios; 1:0, 1:0.5, 1:1 and 1:1.5 were studied as per the method reported by Shah [33]. A graduated glass cylinder of 100 cm³ volume was used for the measurement of the foam

Table 1 Effect of concentrations sodium phthalate on critical micellar concentration (CMC), average degree of micelle ionization (α), binding of counterion (β) and Gibb's free energy (ΔG_m°) change of micellization of C₁₆DMEAB surfactant at 30°C

C ₁₆ DMEAB to Na-phthalate charge ratio	CMC ($\times 10^{-3}$ M)	α	$\beta = (1-\alpha)$	$-\Delta G_m^\circ$ (KJ mol ⁻¹)
1:0.0	0.21	0.276	0.724	36.79
1:0.5	0.27	0.336	0.664	34.46
1:1.0	0.17	0.267	0.733	37.90
1:1.5	0.11	0.260	0.740	39.97

Table 2 Effect of concentrations sodium malate on critical micellar concentration (CMC), average degree of micelle ionization (α), binding of counterion (β) and Gibb's free energy (ΔG°_m) change of micellization of C16DMEAB surfactant at 30°C

C ₁₆ DMEAB to Na-malate charge ratio	CMC (x 10 ⁻³ M)	α	$\beta = (1-\alpha)$	$-\Delta G^\circ_m$ (KJ mol ⁻¹)
1:0.0	0.21	0.276	0.724	36.79
1:0.5	0.35	0.345	0.655	33.19
1:1.0	0.19	0.270	0.730	37.36
1:1.5	0.18	0.267	0.733	39.66

stability and foamability. Twenty cubic centimeter 1 % (w/v) solution (surfactant + counterions) was poured into the calibrated cylinder. The solution was given 10 uniform jerks within 10s. 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 three times.

Oil Solubilization Capacity

Oil solubilization capacity of C₁₆DMEAB surfactant in the presence of various counterions Na-phthalate and Na-malate was measured using methyl methacrylate oil (MMA). A series of solutions containing C₁₆DMEAB and counterions at different charge ratios (1:0, 1:0.5, 1:1 and 1:1.5) 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 methyl methacrylate (MMA) oil using a micro burette.

Results and Discussion

Kraft temperature

Kraft temperatures of C₁₆DMEAB surfactant in the presence of Na-phthalate and Na-malate at different surfactant to counterion charge ratios (1:0, 1:0.5, 1:1 and 1:1.5) were determined (**Figures 2 and 3**) and the results are given in **Tables 3 and 4**. Additions of counterions initially decrease the kraft temperature of C₁₆DMEAB. Further increase in the concentration of counterion 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 [34–35]. 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 counterion charge ratio is due to the theoretical larger value of fractional charge 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 (**Figures 2 and 3**). On further increase in counterions (1:1 and 1:1.5) concentration, charge on micelle decreases. This result in the increase in the stability of surfactant monomer and hence increase in kraft temperature. The kraft temperature in presence of sodium malate is less than sodium phthalate at all combinations. This is may be due to the binding of counterion from sodium phthalate is more than that of the counterion from sodium malate is shown in **Tables 1 and 2**.

Critical Micelle Concentration (CMC)

The plots for the determination of CMC of surfactant C16DMEAB in the presence of sodium phthalate (aromatic bivalent counterion) and sodium malate (aliphatic bivalent counterion) from conductance measurement at 1:0, 1:0.5, 1:1, 1:1.5 charge ratios are given in **Figures 4 and 5**.

The CMC, average degree of ionization of micelle (α) and Gibb's free energy change of micellization (ΔG°_m) were determined from conductance data [36–37] and results are given in **Table 1**.

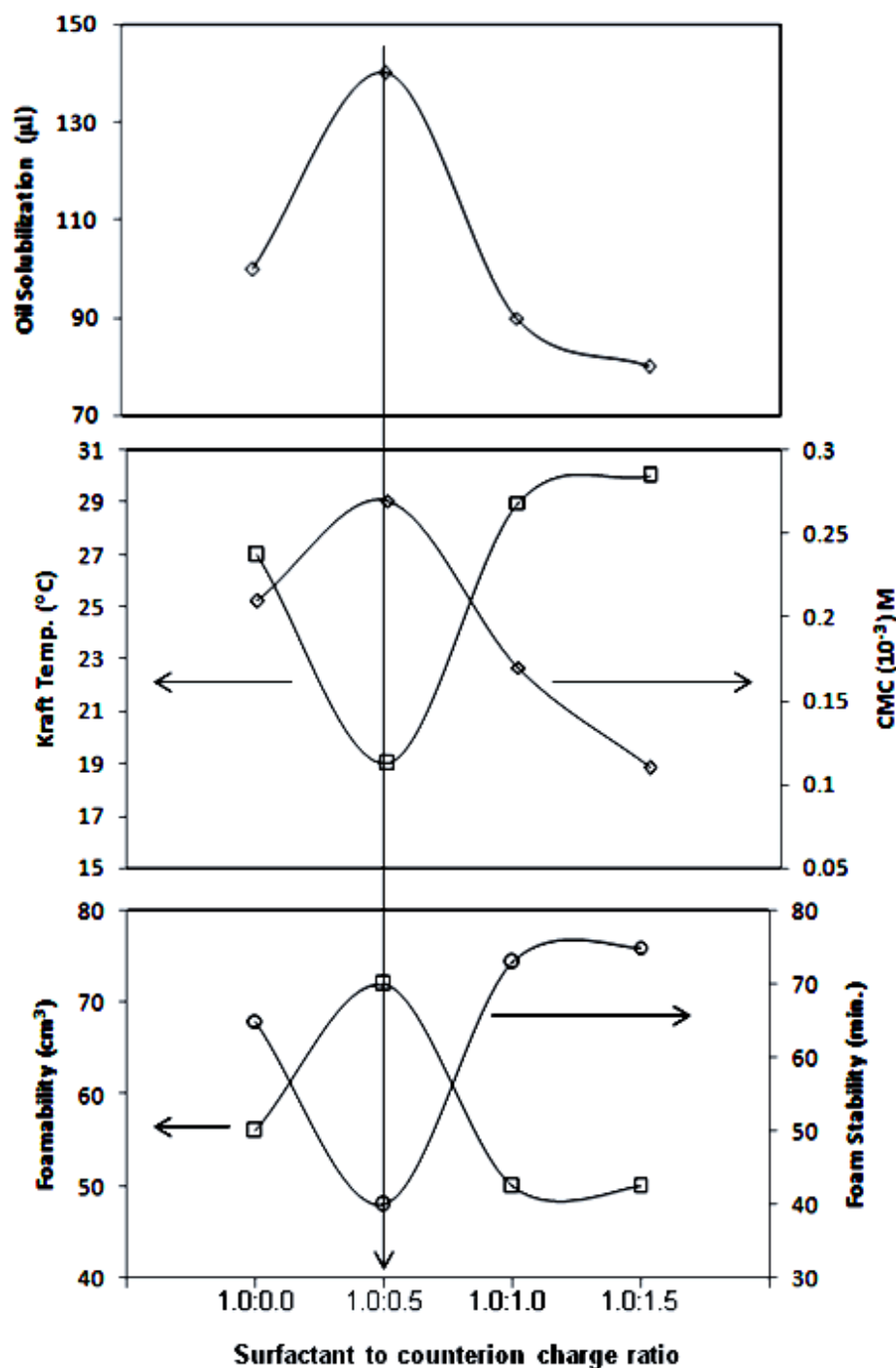


Figure 2 Effect of oil solubilization capacity, Kraft temperature, CMC, foamability and foam stability of $C_{16}DMEAB$ surfactant on Na-phthalate at $30^{\circ}C$.

It was observed that addition of sodium phthalate to $C_{16}DMEAB$ (1:0.5) initially CMC and average degree of micelle ionization (α) increases up to the unequivalent surfactant to counterion charge ratio and further increase in sodium phthalate concentration CMC as well as average degree of micelle ionization (α) was observed to decrease. Similar trends were observed in presence of Na-malate at all combinations and the results are given in Table 2.

This effect is explained on the basis of surfactant to 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 [38–39]. In the present system, addition of sodium phthalate to aqueous surfactant solution, gives aromatic bivalent phthalate as counterions and addition of sodium malate to aqueous surfactant solution, gives aliphatic bivalent malate as counterion. However, at 1:0.5 surfactants 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 change in Gibb's free energy of micellization (ΔG_m°) at 1:0.5 charge ratio.

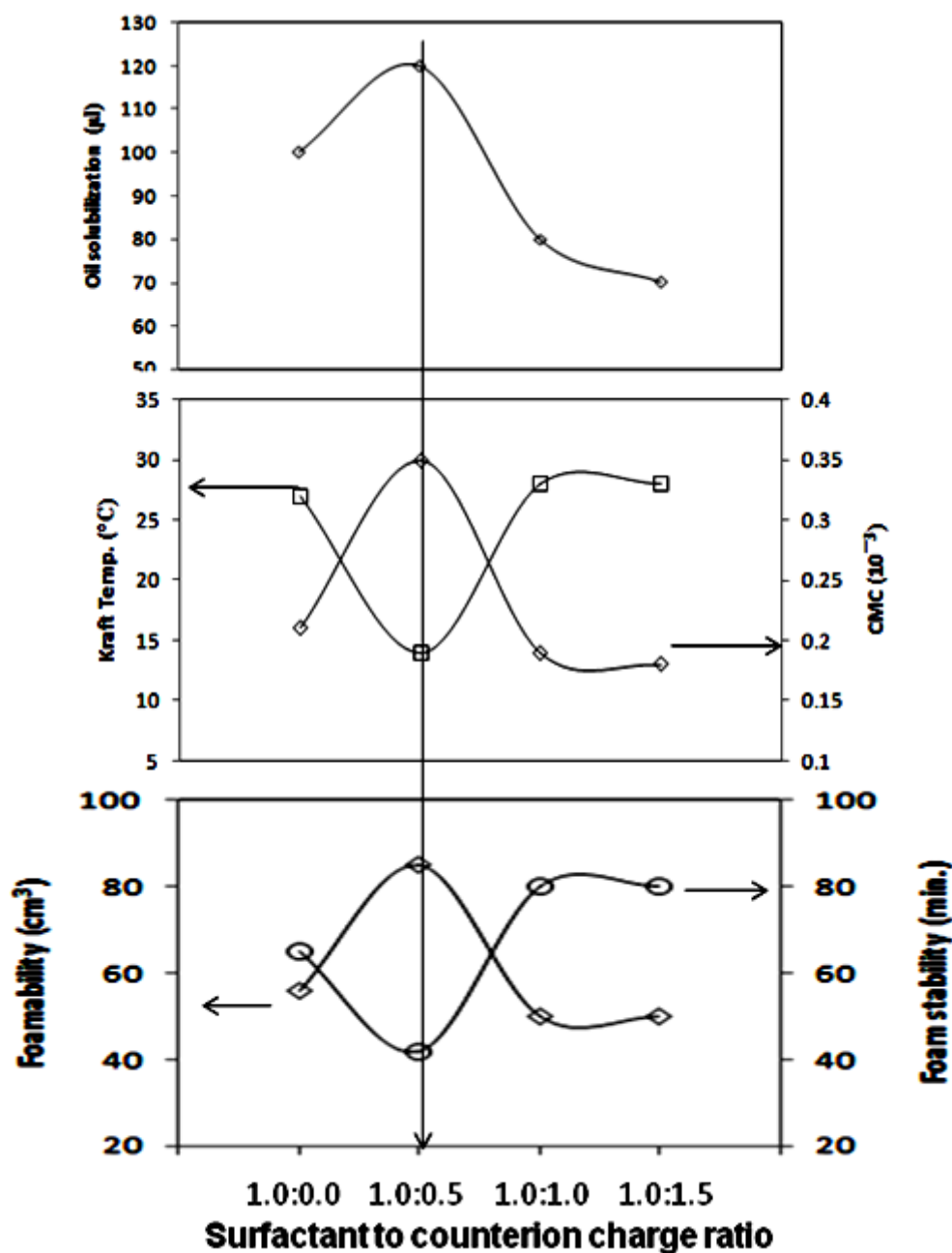


Figure 3 Effect of oil solubilization capacity, Kraft temperature, CMC, foamability and foam stability of C_{16} DMEAB surfactant on Na-malate at 30°C

Table 3 Effect of concentrations sodium phthalate on kraft temperature (k_T), foamability and foam stability and oil solubilization of micellization of C_{16} DMEAB surfactant at 30°C

C_{16} DMEAB to Na-phthalate charge ratio	Kraft temperature (°C)	Foamability (Cm^3)	Foam stability (min.)	Oil solubilization (μ l)
1:0.0	27	56	65	100
1:0.5	19	72	40	140
1:1.0	29	50	73	90
1:1.5	30	50	75	80

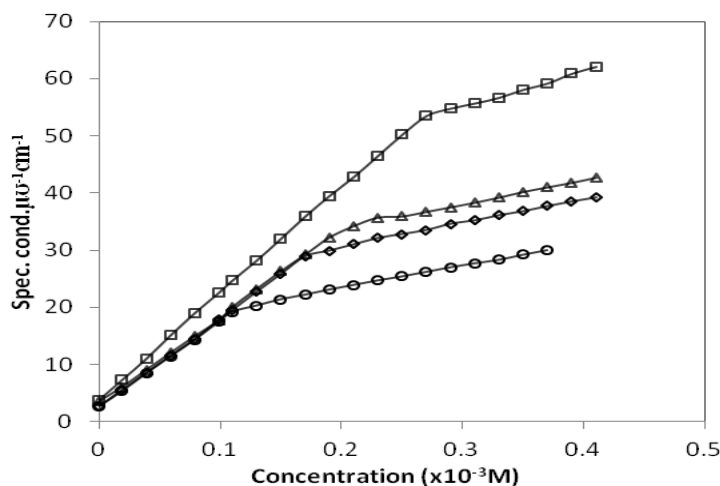
Table 4 Effect of concentrations sodium malate on kraft temperature (k_T), foamability and foam stability and oil solubilization of micellization of C_{16} DMEAB surfactant at 30°C

C_{16} DMEAB to Na-malate charge ratio	Kraft temperature (°C)	Foamability (Cm^3)	Foam stability (min.)	Oil solubilization (μ l)
1:0.0	27	56	65	100
1:0.5	14	85	42	120
1:1.0	28	50	80	80
1:1.5	28	50	80	70

The CMC values in presence of phthalate counterion are less than that of malate counterion indicates that binding tendency of aromatic bivalent phthalate counterion is more than that of aliphatic bivalent malate counterion.

Foamability and Foam Stability

The results obtained in the study of foamability and foam stability of C_{16} DMEAB monomeric surfactant in the presence of different counterions at different surfactant to counterion charge ratios (1:0, 1:0.5, 1:1 and 1:1.5) are given in **Figures 2 and 3**. With addition of sodium phthalate to C_{16} DMEAB, foamability decreases and foam stability increases except at charge ratio 1:0.5. Similar trend in results were obtain on addition of Na-malate to C_{16} DMEAB and the results are given in Tables 3 and 4.

**Figure 2** Effect of concentration of Na-phthalate on critical micelle concentration of C_{16} DMEAB surfactant. C_{16} DMEAB: Na-phthalate charge ratio; 1:0.0 (Δ), 1:0.5 (\square), 1:1.0 (\diamond), 1:1.5 (\circ)

This fact can be explained in terms of CMC and micellar stability. It is well reported that binding of counterion strongly influences the critical micelle concentration, micellar size, aggregation number and molecular packing at interface [40]. The degree of binding of counterion was observed to decrease at 1:0.5 surfactants to sodium phthalate and sodium malate charge ratio, due to theoretical 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 phthalate and surfactant to malate charge ratio.

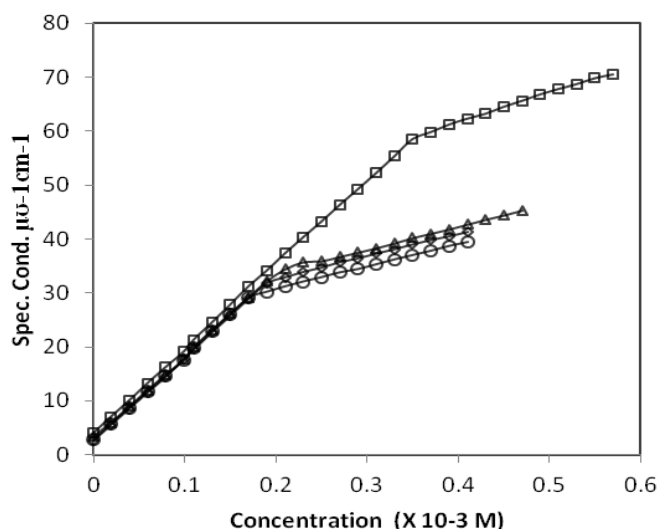


Figure 3 Effect of concentration of Na-malate on critical micelle concentration of C₁₆DMEAB surfactant. C₁₆DMEAB: Na-malate charge ratio; 1:0.0 (Δ), 1:0.5 (□), 1:1.0 (◇), 1:1.5 (○).

Oil Solubilization

Oil solubilization capacity of C₁₆DMEAB monomeric surfactant in the presence of various surfactant to counterions charge ratios (1:0, 1:0.5, 1:1 and 1:1.5) were measured and the results are given in Tables 3 and 4. Amount of methyl methacrylate (MMA) oil solubilized in given micellar system as shown in Figures 2 and 3.

The oil solubilization capacity of C₁₆DMEAB surfactant was observed to be more at 1:0.5 than at 1:0, 1:1 and 1:1.5 surfactant to counterions charge ratio for both C₁₆DMEAB: phthalate and C₁₆DMEAB: malate system. This result indicates that, at 1:0.5 surfactant to counterions charge ratio, more numbers of micellar templates are available for solubilization. In comparison, on addition of sodium phthalate, surfactant system shows more oil solubilization than that in presence of sodium malate. This may be due to the phthalate counterion is more hydrophobic than that of malate counterion, hence shows more oil solubilization in presence of phthalate.

Conclusion

By knowing the factors that governs the formation of amphiphilic association provides tools for manipulating and guiding the process in desired path. In this paper we present the effect of aromatic bivalent phthalate and aliphatic bivalent malate anionic counterions on physicochemical properties of hydroxylated cationic surfactant C₁₆DMEAB. From this we can draw the following conclusions:

- Varying ratios of surfactant to counterion concentration is very convenient tool for controlling and directing self assembly of cationic surfactants at molecular scale.
- Critical micelle concentration (CMC), average degree of micelle ionization (α) and Gibb's free energy change of micellization (ΔG_m°) of C₁₆DMEAB surfactant is strongly influenced by bivalent counterions.

- Kraft temperature (k_T) of cationic surfactant C_{16} DMEAB can be controlled by adding specific amount of counterions such as phthalate and malate.
- The foamability of C_{16} DMEAB surfactant system was observed to decrease by adding equivalent moles of sodium phthalate or sodium malate.

The solubilization capacity of C_{16} DMEAB surfactant system was observed to increase by adding unequivalent amount (unequal charge ratios) of sodium phthalate and sodium malate. In comparison, the solubilization capacity of C_{16} DMEAB was observed to be more in presence of phthalate counterion than that of malate counterion.

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