Chapter 6

Effect of Sodium Malate as an Additive on Aggregation Properties of Dimeric Butane-1,4-bis (dodecyl hydroxyethyl methyl ammonium bromide) and Its Monomeric Counterpart

Contents

6.1 Introduction

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 in association with 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 cetyltrimethyl 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, where the presence of these micellar structures impart viscoelasticity to the system.

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,

- chemical substitution of the surfactant counterion [23]
- 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] and Aswal et al [32] 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 various applications of novel hydroxylated bis-cationic surfactants [33-35].

Hence in this chapter a systematic study has been undertaken to examine effect of concentration of Na-malate on aggregation properties of 12-4-12 MEA and C_{12}DMEAB surfactants. The chemical structure and abbreviations used hereafter are given in Figure 6.1.

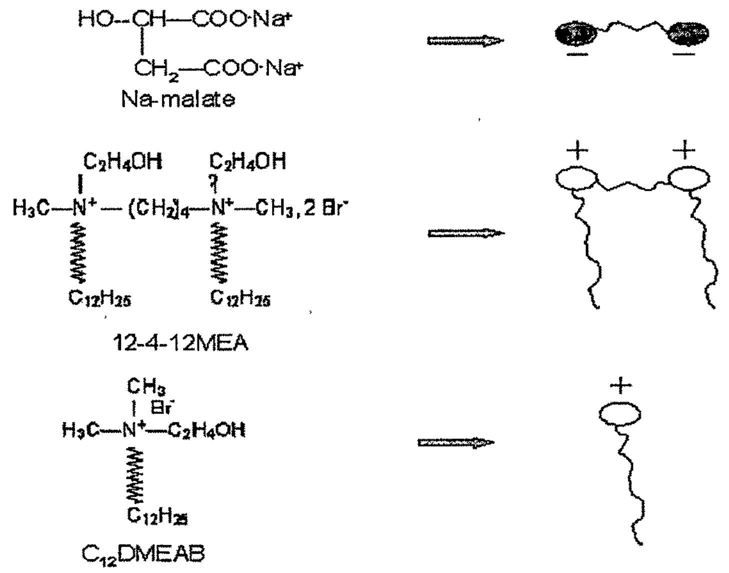

Figure 6.1 Chemical structures and schematic representation of surfactants and Na-malate under study

6.2 Experimental

6.2.1 Materials

Butanediyl-1,4-N,N'-bis(N,n-dodecyl N-hydroxyethyl N-methyl ammonium bromide) represented as 12-4-12 MEA and N,n-dodecyl hydroxyethyl dimethyl ammonium bromide (C_{12}DMEAB) were synthesized as described in section 2.2.1. Na-malate and Methyl methacrylate were purchased from Emerck (Germany) and National Chem. (India) respectively. Solutions for SANS studies were prepared in D_2O (at least 99 atom % D) obtained from Heavy Water Division, Bhabha Atomic Research Centre, Mumbai, India. Double-distilled and deionized water was used for all physicochemical studies.

6.2.2 Kraft Temperature

The kraft temperature (k_T) for 12-4-12 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.

6.2.3 Conductivity

Critical micelle concentration (CMC) of the 12-4-12 MEA surfactant in the presence of different concentrations of Na-malate was determined through conductance measurements as described earlier in section 2.23. 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 (α_{ave}) of the micelle and CMC were determined from specific conductance vs concentration plots (Figure 6.2).

6.2.4 Foamability and Foam Stability

The foamability and foam stability of 12-4-12 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 [36] and described in section 2.2.8. 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.

6.2.5 Oil Solubilization Capacity

Oil solubilization capacity of 12-4-12 MEA gemini surfactant and its monomeric counterpart C_{12}DMEAB in the presence of Na-malate was measured using MMA. A series of solutions containing 100 mM 12-4-12 MEA or 200 mM C_{12}DMEAB and 0, 50, 100 and 150 mM Na-malate was prepared. These solutions were thoroughly homogenized using a vortex mixture and kept in a thermosated water bath at accuracy of ± 0.1°C. These solutions were then titrated with methyl methacrylate (MMA) using a micro burette.

6.2.6 Small Angle Neutron Scattering

Small angle neutron scattering studies were performed as described in section 2.2.9. The scattering intensities from the solutions (surfactant + Na-malate) were corrected for detector background sensitivity, empty cell scattering and sample transmission. Scattering intensity of solvent was subtracted from that of the sample. The resulting corrected intensities were normalized to absolute cross section units, and thus $d\Sigma/d\Omega$ vs Q were obtained. This absolute calibration has an estimated uncertainty of 10 %. The experimental values were fitted using nonlinear least-square method.

6.3 Results and Discussion

6.3.1 Kraft temperature

Kraft temperature of 12-4-12 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 6.1. Additions of Na-malate initially decrease the kraft temperature of 12-4-12 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 [37, 38]. 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 fractional charge, α (Table 6.3) 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 (Table 6.1). On further increase in Na-malate (1:1, & 1: 1.5) concentration, charge on micelle decreases (Table 6.3).This results in the increase in the stability of surfactant monomer and hence increase in kraft temperature.

Table 6.1 Effect of concentration of Na-malate on kraft temperature of 12-4-12 MEA surfactant

12-4-12 MEA to Na-malate mole ratio	kraft Temperature (k_T) (°C)
1:0.0	30
1:0.5	22
1:1.0	36
1:1.5	38

6.3.2 Critical Micelle Concentration (CMC)

The plots for the determination of CMC of 12-4-12 MEA surfactant in the presence of Na- malate (bivalent counterion) from conductance measurement are given in Figure 6.2. The CMC, average degree of ionization of micelle (α_{ave}) and Gibb's free energy change of micellization (ΔG^o_m) were determined from conductance data and results are given in Table 6.2.

Table 6.2 Effect of Na-malate concentration on critical micellar concentration (CMC), average degree of micelle ionization (α_{ave}) and Gibb's free energy(ΔG^o_m) change of micellization of 12-4-12 MEA gemini surfactant at 30°C.

12-4-12 MEA to Na-malate mole ratio	CMC ($x10^{-5}$M)	α_{ave}	($-\Delta G^o_m$) KJ.Mol^{-1}
1: 0.0	2.80	0.26	32.74
1.0.5	3.48	0.29	31.29
1:1.0	2.49	0.25	33.37
1:1.5	1.74	0.23	35.05

It was observed that addition of Na-malate to 12-4-12 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 [40, 41]. 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 (ΔG^{o}_{m}) at 1:0.5 mole ratio.

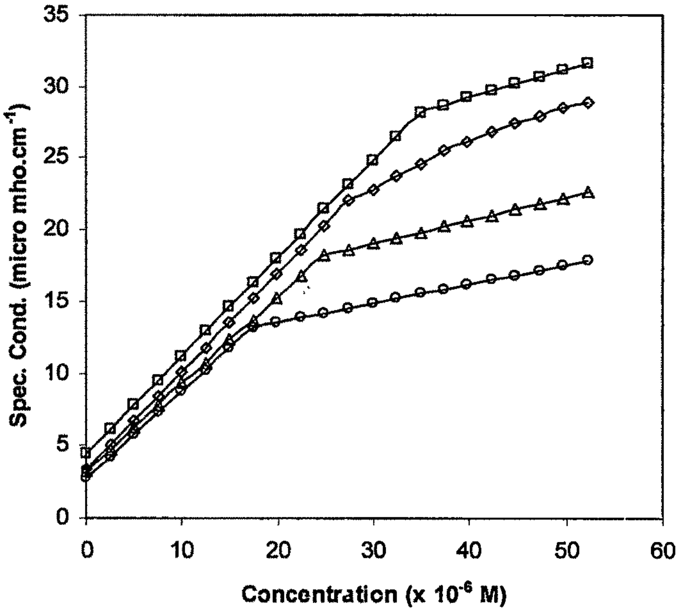

Figure 6.2 Effect of concentration of Na-malate on critical micelle concentration of 12-4-12 MEA gemini surfactants. 12-4-12 MEA : Na-malate mole ratios; 1:0(◇),1:0.5(□),1:1(△),1:1.5(o)

6.3.3 Foamability and Foam Stability

The results obtained in the study of foamability and foam stability of 12-4-12 MEA dimeric surfactant in the presence of different concentration of Na-malate are given in Figure 6.3. With addition of Na-malate to 12-4-12 MEA foamability decreases and foam stability increases except at mole ratio 1:0.5.

This fact can be explained in terms of CMC, aggregation number 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 [42]. 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 a 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.

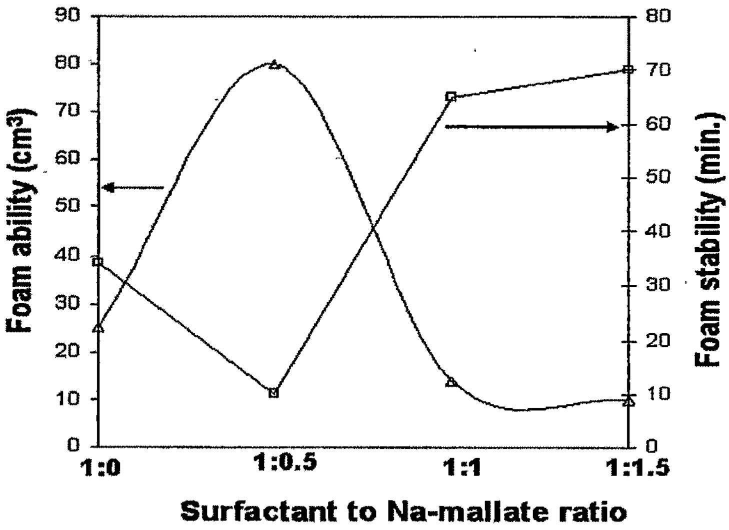

Figure 6.3 Foamability and foam stability of 12-4-12 MEA surfactant in presence of Na-malate at 30 °C.
Δ Foamability, □ Foam stability

6.3.4 Oil Solubilization

Oil solubilization capacity of 12-4-12 MEA gemini surfactant and its monomeric counterpart C_{12}DMEAB 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 6.4(a) and 6.5(a). The oil solubilization capacity of 12-4-12 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. This can be explained on the basis of number density of micelles per unit volume. From SANS data (Table 6.3) it was observed that, the number density of micelle is more at 50 mM Na-malate concentration than at 0, 100 and 150 mM concentration of Na-malate. This result indicates that, at 50mM Na-malate concentration, more number of micellar templates are available for solubilization. The oil solubilization was also observed to increase with increase in temperature as shown in Figure 6.4(b). No significant change was observed in oil solubilization capacity for C_{12}DMEAB surfactant on addition of Na-malate. This statement can also be explained on the basis of number density of micelle as shown in Figure 6.5(a). Oil solubilization capacity for C_{12}DMEAB surfactant system was observed to increase only at high temperature (70°C) as shown in Figure 6.5(b).

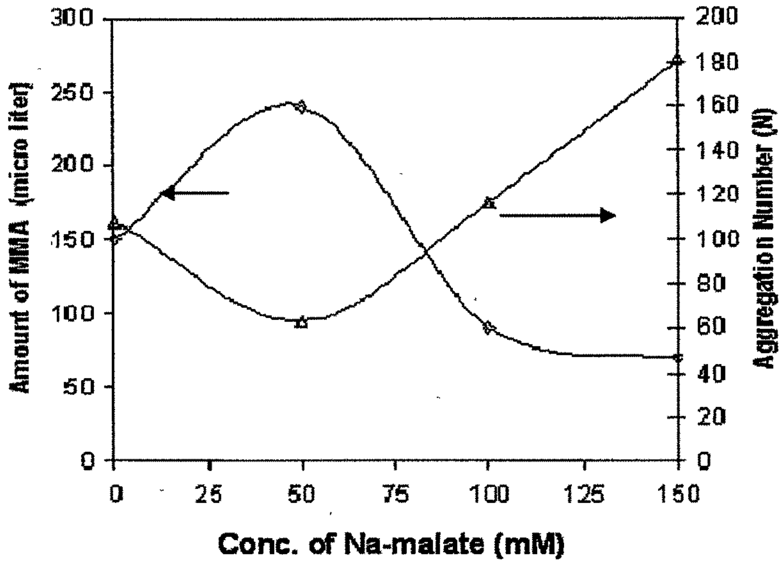

Figure 6.4(a) Effect of Na-malate on oil solubilization capacity and Aggregation number(N) of 12-4-12 MEA(100 mM) at 30°C.

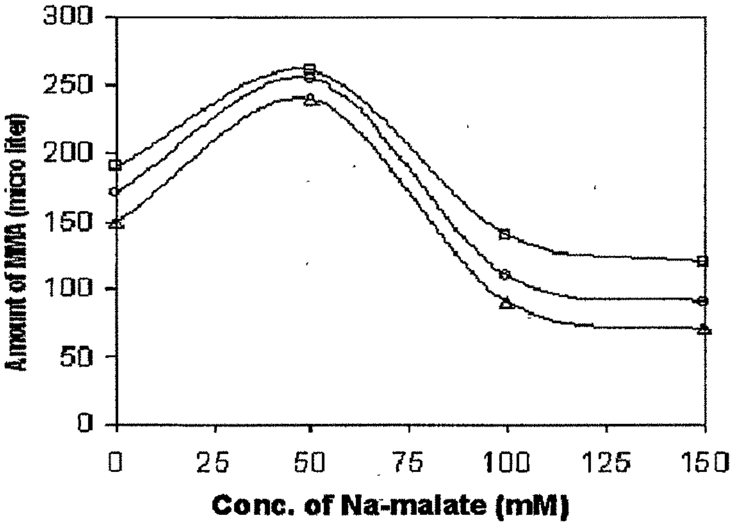

Figure 6.4 (b) Effect of temperature on oil solubilization capacity of 12-4-12 MEA and Na-malate mixed system.

30 (△), 50(o) and 70°C (□)

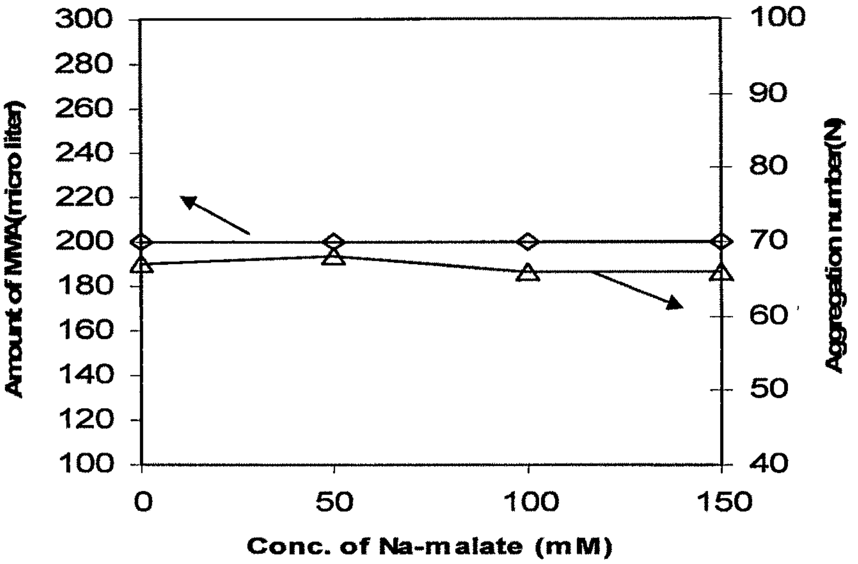

Figure 6.5(a) Effect of Na-malate on oil solubilization capacity and aggregation number (N) of C_{12}DMEAB (200mM) at 30°C.

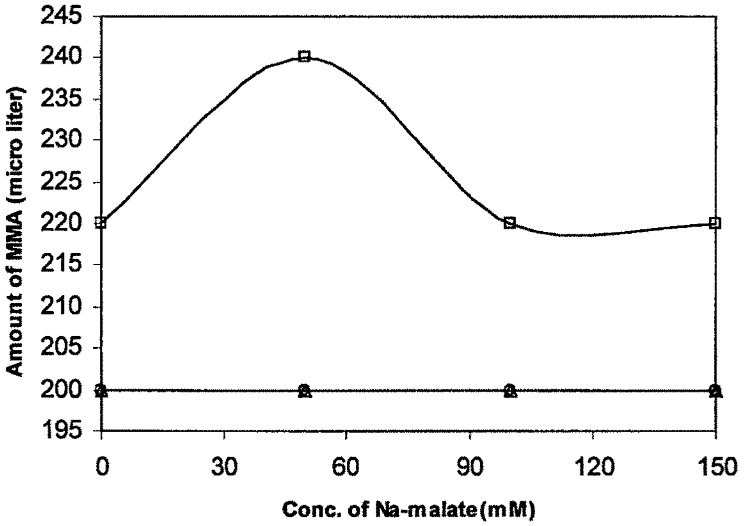

Figure 6.5(b) Effect of temperature on oil solubilization capacity of C_{12}DMEAB and Na-malate mixed system

30 (△), 50(o) and 70°C (□)

6.3.5 Shape, Size and Aggregation Number

To understand the effect of Na-malate (bivalent counterion) on aggregation behavior of 12-4-12 MEA gemini surfactant and its monomeric counterpart C_{12}DMEAB, SANS studies were undertaken. The SANS measurements were made at 100 mM aqueous solution of 12-4-12 MEA and at 200 mM C_{12}DMEAB in the presence of 0, 50, 100 and 150 mM concentration of Na-malate at 30°C as shown in Figure 6.6 and Figure 6.7 respectively.

The SANS distribution spectra of 12-4-12 MEA surfactant show well defined correlation peaks at 0 and 50 mM Na-malate concentration and peak intensity was observed to decrease at 50 mM Na-malate concentration indicating the decrease in aggregation number and increase in effective fractional charge per head (Table 6.3). The correlation peak disappeared at 100 and 150 mM Na-malate concentration, indicating the complete neutralization of micellar charge due to addition of equivalent (100 mM) or excess (150 mM) amount of Na-malate.

Table 6.3 Effect of Na-malate concentration on aggregation parameters of 12-4-12 MEA gemini surfactant at 30 °C from SANS

Concentration of Na-Malate (mM)	Agg. Nos. (N)	Frac^{nal} charge (α)	Semi-major axis (b) (Å)	Semi-minor axis (a) (Å)	Axial ratio (b/a)	Equi^{m} dist. between charged head (d) (Å)
0	108	0.06	75.2	19.0	4.0	7.2
50	63	0.10	33.9	15.6	2.2	8.9
100	116	0.00	98.4	17.3	5.7	7.2
150	181	0.00	171.5	16.3	10.5	6.7

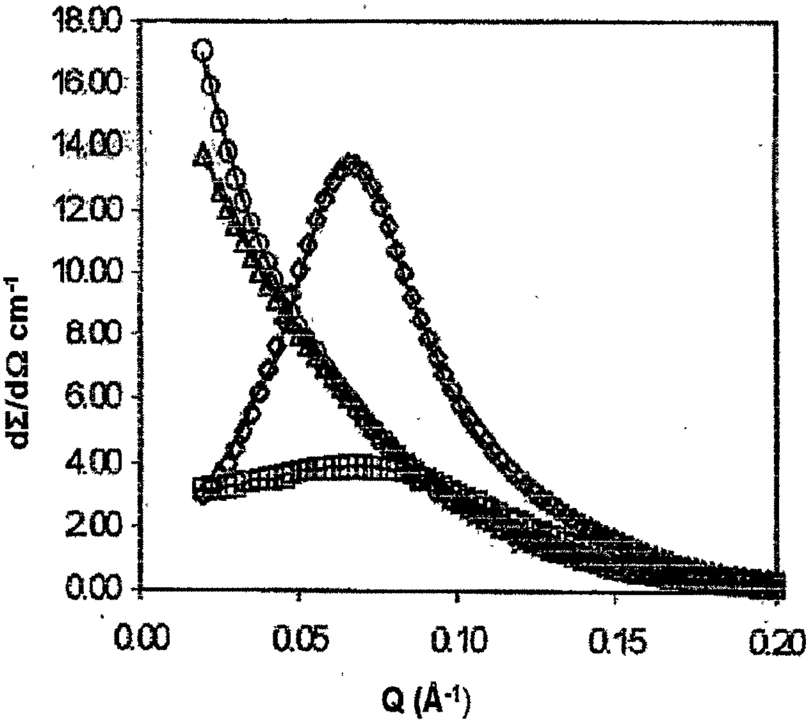

Figure 6.6 SANS spectra for 12-4-12 MEA (100 mM) in the presence of various concentrations of Na-malate at 30°C.

Solid lines represent theoretical fits and symbols are experimentally determined values.

0 mM (◇), 50 mM (□), 100 mM (Δ), 150 mM (o)

The SANS distribution spectra of C_{12}DMEAB surfactant show well defined correlation peak but no significant change was observed in peak position and peak intensity (Figure 6.7). The extracted micellar parameters from SANS data for 12-4-12 MEA and C_{12}DMEAB are given in Table 6.3 and Table 6.4 respectively. From the Table 6.3 the aggregation number (N) and dimension of micelle (b/a) was observed to decrease from 108 to 63 and 4.0 to 2.2 respectively on addition of 50 mM Na-malate. Further addition of 100 and 150 mM of Na-malate to surfactant system showed sharp increase in N and b/a (Table 6.3). The effective fractional charge per head was observed to increase from 0.06 to 0.11 on addition of 50 mM Na-malate to 12-4-12 MEA surfactant system. Further addition of 100 mM and 150 mM of Na-malate the complete neutralization of charged micelle was observed (Table 6.3). The significant decrease in aggregation number was observed for 12-4-12 MEA surfactant system on addition of 50 mM Na-malate which can explained on the basis of effective fractional charge per head of surfactant molecule. In aqueous solution of surfactant Na-malate was observed to completely dissociate and gives bivalent malate anions which act as bivalent counterions. The binding tendency of bivalent counterion was observed to be more than that of monovalent Br^- ion. Addition of 100 and 150 mM Na-malate gives respectively equivalent and excess malate counterion and hence complete neutralization of charged micelles takes place. But 50 mM Na-malate gives unequivalent malate counterions, resulting into more fractional charge per head or more Columbic repulsion between charged heads. This results in decrease in aggregation number and increase in equilibrium distance between charged heads(Table 6.3). No significance difference was observed by addition of Na-malate on micellar parameters of C_{12}DMEAB surfactant (Table 6.4)

Table 6.4 Effect of Na-malate concentration on aggregation parameters of C_{12}DMEAB monomeric surfactant at 30°C from SANS

Concentration of Na-Malate (mM)	Agg. Nos. (N)	Frac^{nal} charge (α)	Semi-major axis (b) (Å)	Semi-minor axis (a) (Å)	Axial ratio (b/a)	Equi^{m} dist. bet^{n} charged head (d) (Å)
0	67	0.07	34.7	15.2	2.3	8.7
50	68	0.09	36.9	15.4	2.4	8.7
100	66	0.08	34.4	15.5	2.2	8.8
150	66	0.07	33.9	15.6	2.2	8.8

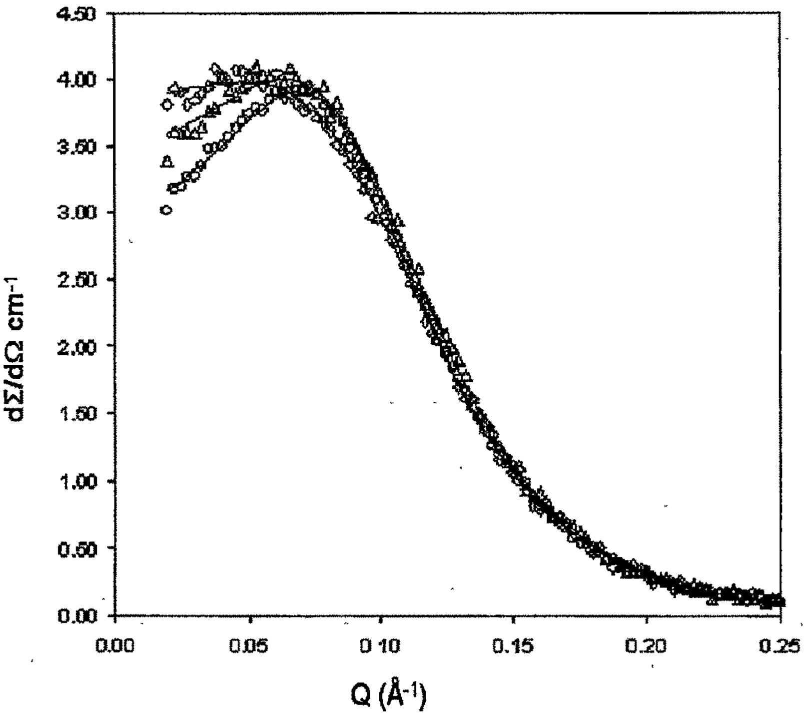

Figure 6.7 SANS spectra from C_{12}DMEAB (200 mM) in the presence of various concentrations of Na-malate at 30°C. Solid lines represent theoretical fits and symbols experimentally determined values.
50mM (◇),100 mM(Δ), 150 mM(o)

6.4 Conclusions

- Varying ratios of surfactant and counterion concentration is very convenient tool for controlling and directing self assembly of bis-cationic surfactants at molecular scale.
- Influence of Na-malate on aggregation behavior of 12-4-12 MEA surfactant was observed to be more sensitive than that of C_{12}DMEAB.
- Critical micelle concentration (CMC), average degree of micelle ionization (α_{ave}) and Gibb's free energy change of micellization (ΔG^{o}_{m}) of 12-4-12 MEA surfactant is strongly influenced by Na-mallate.
- Kraft temperature (k_T) of bis-cationic surfactant 12-4-12 MEA can be monitored by adding specific amount of Na-malate.
- The foamability of 12-4-12 MEA surfactant system was observed to decrease by adding equivalent moles of Na-malate.
- The solubilization capacity of surfactant system was observed to increase by adding unequivalent (50 mM) moles of Na-malate.
- The dimension (b/a) of 12-4-12 MEA micelle was observed to increase 2.2 to 10.5 on addition of 150 mM of Na-malate.

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