
Chapter II

**Interfacial, Thermodynamic and Performance Properties of α - Sulfonato
Myristic Acid Methyl Ester – Hexaoxyethylene Monododecyl Ether
Mixed Surfactants**

ABSTRACT

The interfacial, thermodynamic and performance properties of the aqueous α - sulfonato myristic acid methyl ester (MES) – hexaoxyethylene monododecyl ether ($C_{12}E_6$) mixed surfactant system have been investigated. The critical micelle concentrations (cmcs) were obtained by surface tension and conductivity measurements. The maximum surface excess (Γ_{\max}) and minimum area per molecule (A_{\min}) were determined from surface tension (γ) – log concentration ($\log C$) plots. The thermodynamic parameters of micellization and adsorption were computed. Micellar aggregation numbers ($N_{agg.}$) of pure and mixed surfactant systems were evaluated by fluorescence measurements. Interaction parameters between surfactant molecules in mixed micelles were evaluated using Rubingh's approach. The performance properties of pure and mixed surfactant systems viz. foaming, detergency and viscosity were studied. Cloud point (CP) determinations of the nonionic $C_{12}E_6$ in presence of electrolytes (NaCl, NaBr and NaI) and nonelectrolytes like polyethylene glycols (MW 200, 300 & 400) was also carried out.

Keywords: Micellization, Mixed Surfactant, InteractionParameter, Foaming, Detergency

INTRODUCTION

Surfactants are versatile compounds widely used in a variety of industrial and commercial applications.^[1] The application potential of surfactants is closely related to their surface wetting capability, detergency, and solubilization in areas like mining, petroleum, chemical, and pharmaceutical industries as well as in chemical and biochemical research.^[2] Mixtures of surfactant solutions form mixed micellar aggregates that exhibit characteristic properties which are superior to those of the individual components.^[3,4] Synergistic behaviors of mixed surfactant systems may be exploited to reduce the total amount of surfactant used in particular applications resulting in reduction of cost and environmental impact.^[5] Consequently much attention has been directed towards the experimental as well as theoretical investigation of mixed surfactant system. The studies on different varieties of combinations formed by different surfactants such as nonionic-nonionic,^[6,7] nonionic-anionic,^[8-14] nonionic-cationic,^[15] etc., are reported in the literature. The α - sulfonato myristic acid methyl ester (MES) mixed with C₁₂E₆ was studied because of the good biodegradability and relatively quick availability of MES from renewable vegetable material.^[16] Fatty acid methyl ester based surfactants are readily degradable under aerobic conditions. Thus fatty acid ester based surfactants are subject of recent investigation and review.^[17,18] Gode et al.^[19] observed 99% primary degradation and 76% ultimate degradation of fatty acid ester based surfactant in two different tests.

This article deals with the physicochemical investigation of surfactants, which involves the cmc determination by surface tension and conductivity measurements and computation of standard thermodynamic parameters of micellization (ΔG_m^0 , ΔH_m^0 and ΔS_m^0). Interfacial parameters such as maximum surface excess (Γ_{max}), minimum area per molecule (A_{min}) and the standard thermodynamic parameters of adsorption at the air-water interface (ΔG_{ad}^0 , ΔH_{ad}^0 and ΔS_{ad}^0) were also computed from surface tension data. The micellar aggregation numbers (N_{agg}) were determined by fluorescence measurements. Performance properties, viz. detergency, foaming, viscosity were also studied. Cloud points (CP) of the nonionic C₁₂E₆ in the presence and absence of

electrolytes (NaCl, NaBr and NaI) and nonelectrolytes like polyethylene glycols (M.W. 200, 300 & 400) were also evaluated.

EXPERIMENTAL SECTION

Materials

Hexaoxyethylene monododecylether $[\text{CH}_3 (\text{CH}_2)_{11} (\text{OCH}_2\text{CH}_2)_6 \text{OH}]$ i.e., C_{12}E_6 , and α -sulfonato myristic acid methyl ester, $\text{C}_{12}\text{H}_{25}\text{CH}(\text{SO}_3\text{Na})\text{COOCH}_3$ (MES), of Lion Corporation, Tokyo, Japan were used without further purification. NaBr, NaI (Loba Chemie, Baroda, India) and NaCl (Qualigens, India) were used as received. Polyethylene glycols (MW 200, 300 & 400) were obtained from Merck, India. Cetyl pyridinium chloride (Loba Chemie, Baroda, India) was recrystallized twice from benzene and used. Pyrene (Fluka, Germany) was recrystallized from cyclohexane. All solutions were prepared using doubly distilled water.

Surface Tension Measurements

The surface tension was measured by a ring method using a duNouy tensiometer – (S. C. Dey & Co., Kolkata, India) at 30°C , 35°C , 40°C and 45°C . The temperatures were maintained within ($\pm 0.1^\circ\text{C}$) by circulating thermostated water through a jacketed vessel containing the solutions. Representative plots of surface tension (γ) vs. the logarithm of surfactant concentration ($\log C$) are shown in Fig. 1. The reproducibility of (γ) measurements was within $\pm 0.1 \text{ dynes cm}^{-1}$.

Conductivity Measurements

The conductance (k) measurements were done with an Equiptronics (India) conductivity bridge. A dip type cell of cell constant 1.01 cm^{-1} was used. The conductance of different solutions, which were obtained on aliquot addition of a known concentrated surfactant solution to a given volume of the thermostated solvent, were measured. Specific Conductance (k) vs. concentration of surfactant (mole L^{-1}) plots are shown in Fig. 2 for

pure MES only, as no break in the specific conductance vs concentration plots was observed in any of the mixed surfactant systems.

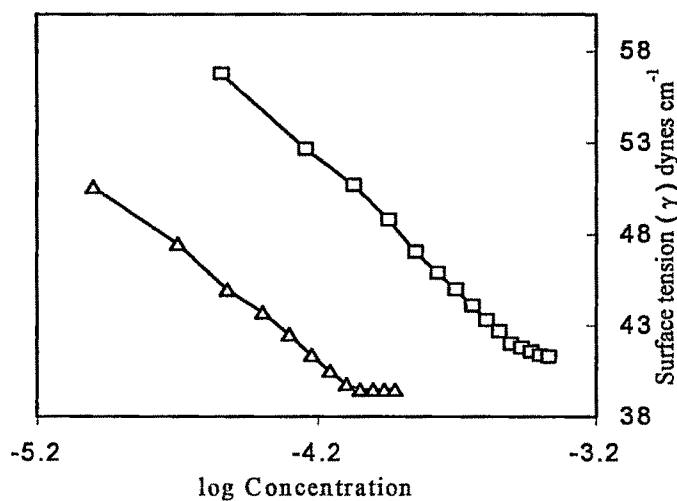


Figure 1. Representative plots of surface tension (γ) vs. log concentration ($\log C$) of surfactant. Key: Δ - 7 : 3; $C_{12}E_6$: MES at 40°C ; \square - 1 : 9, $C_{12}E_6$: MES at 45°C .

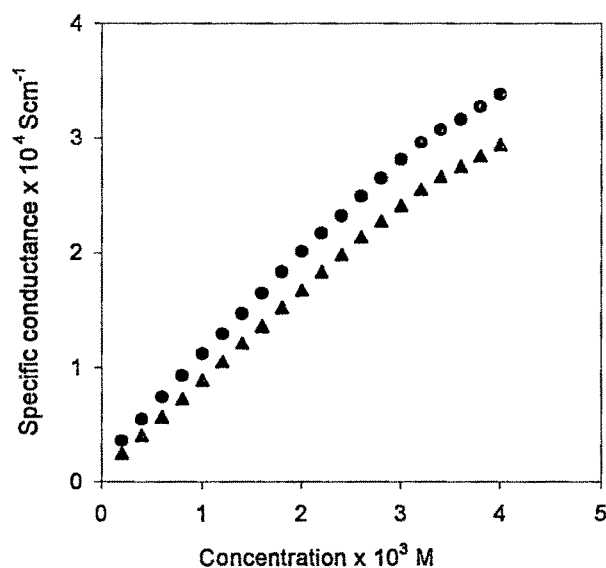


Figure 2. Representative plots of Specific conductance (κ) vs. concentration of MES. Key: \bullet - MES at 40°C ; \blacktriangle - MES at 35°C .

Viscosity

The viscosity of 0.25% (w/v) C₁₂E₆, 5%(w/v) C₁₂E₆/MES mixed surfactant solution was studied using an Ubbelohde suspended level viscometer. The effect of NaCl of different concentration on viscosity of 5%(w/v) C₁₂E₆ was also studied. The temperatures were 30°C, 35°C, 40°C, and 45°C and were maintained within (±1°C) in a thermostated bath. The intrinsic viscosity $|\eta|$ can be calculated using the relation,

$$|\eta| = \lim_{C \rightarrow 0} (\eta_r - 1)/(C) \quad (1)$$

where zero concentration limit indicates that intermolecular interactions are absent. Some researchers^[20, 21] have taken $|\eta|$ to be equal to $\eta_r - 1/C$ without the condition of limiting concentration. It has been defined as the shape factor and is expected to have a value between 2.5 and 4 cm³ g⁻¹ for globular particles.^[22] In this article we have calculated $|\eta|$ without taking the zero concentration limit.

Foaming

Foam height was measured using a variation of Ross-Miles method.²³ Surfactant solution (200 mL) of known concentration (5.8 mM) was allowed a free fall into 50 mL of the same solution through a tube 90 cm long (1.5cm internal diameter). The reproducibility of initial foam height values was within ± 2%.

Fluorescence Measurements

The micellar aggregation number of surfactant solutions were determined by steady state fluorescence measurements. Pyrene was used as a probe and cetyl pyridinium chloride as quencher. The excitation and emission wavelengths were 335 and 385 nm, respectively. All the measurements were carried out at room temperature (~25°C) using a Hitachi F-4010 fluorescence spectrophotometer. Each spectrum had one to five vibronic peaks from shorter to longer wavelengths (Fig. 3). The fluorescence intensities were monitored at 385 nm.

An aliquot of the stock solution of pyrene in ethanol was transferred into a flask and the solvent was evaporated with nitrogen. The surfactant solution (10 mM) was added and concentration of pyrene was kept constant at 10^{-6} M. The quencher concentration was varied from 0 to 12×10^{-5} M. The aggregation number ($N_{agg.}$) was deduced from the equation,²⁴

$$\ln I = \ln I_0 - \frac{N_{agg.}[Q]}{[S] - cmc} \quad (2)$$

where $[Q]$ and $[S]$ are the concentrations of quencher and total surfactant, respectively. The I_0 & I are the fluorescence intensities in the absence and presence of quencher, respectively.

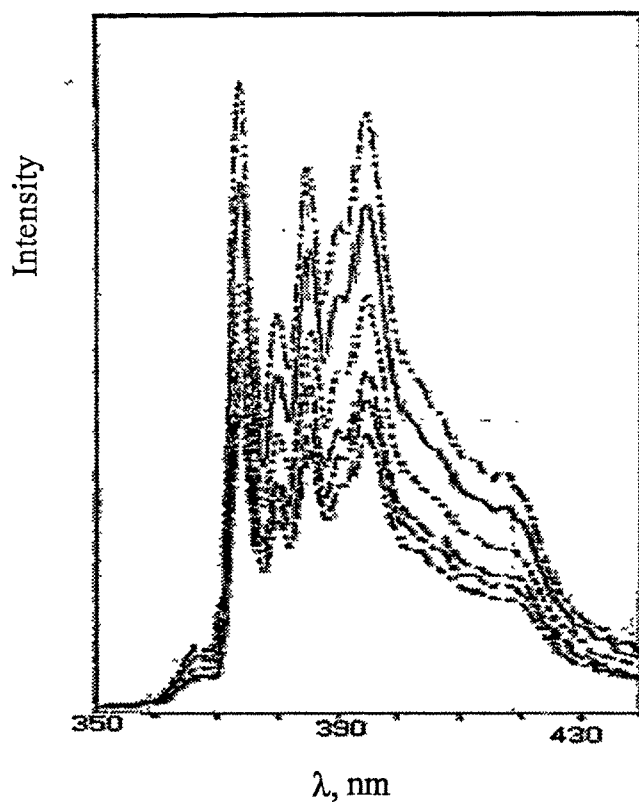


Figure 3: Representative emission fluorescence spectra of 10^{-6} M pyrene in aqueous micellar solution of $C_{12}E_6$: MES (5 : 5).

I_0 & I values can also be used to calculate the Stern-Volmer binding constant K_{SV} by using the following relation,

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \quad (3)$$

Microenvironment

The intensity ratio of the first (I_1) & and third (I_3) vibronic peaks i.e., I_1/I_3 of the pyrene spectrum in presence of surfactants is taken to be the index of micropolarity of the system i.e., it gives an idea of microenvironment and solubilization site.^[25] A low value of this ratio (< 1) is generally taken as that the pyrene has nonpolar surroundings whereas higher value (> 1) is taken as that the pyrene has polar surroundings.

Detergency

The detergency efficiency of the surfactant solutions was evaluated by a dye solubilization/dye removal method. A known amount of shoe polish (0.05 gm.) was dissolved in a fixed amount of chloroform. This dye solution was applied to cotton and terylene fabrics and dried thoroughly. The fabric was then placed in 50 ml of known concentration of surfactant solution and kept under constant stirring. This surfactant solution (3 mL) was withdrawn at regular intervals. The absorbance of these solutions were determined at λ_{\max} of 440 nm using a Bausch and Lomb Spectronic-20 spectrophotometer. The temperatures of the systems were kept constant.

Cloud Point Measurement

Cloud Points are the manifestations of the solvation/desolvation phenomena in nonionic surfactant solutions.^[26,27] Cloud Points of $C_{12}E_6$ (1%, w/v) solutions were determined by visually noting the temperature at which the turbidity was observed when the surfactant solutions were slowly heated under constant stirring.^[28] The temperature at which the turbidity disappeared on slow cooling was also noted. The cloud points

presented are the averages of appearance and disappearance temperatures, which did not differ by more than 0.4°C.

RESULTS AND DISCUSSIONS

The micellization of surfactants is dependent on temperature, additives and solvent.^[29] Intramicellar interactions in mixed surfactants are studied at the cmc, where their effect on mixed micelle formation can be measured.^[30] In our present study, the cmcs of C₁₂E₆/MES mixed surfactant system, where the mole ratio of the two components were varied, were determined at different temperatures. The cmc data are presented in Table 1.

Table 1. Critical micelle concentration, (mM) values of C₁₂E₆/MES mixed surfactant system in aqueous media at different temperatures.

N_{MES}	Temperature (K)			
	303	308	313	318
0.0	0.071	0.062	0.051	0.047
0.1	0.065	0.062	0.053	0.048
0.3	0.093	0.086	0.080	0.075
0.5	0.120	0.096	0.079	0.062
0.7	0.129	0.122	0.115	0.110
0.9	0.365	0.338	0.322	0.315
	2.39	2.51	2.63	3.16
1.0	3.16 ^b	3.24	3.32	3.48
	(0.634) ^a	(0.641)	(0.646)	(0.656)

^aValues in parenthesis are the degree of ionization of micelle of MES.

^bConductivity data.

The cmcs of ionic and nonionic surfactants are functions of temperature. For the nonionic surfactant, the cmc decreases with increasing temperature as has generally been observed in literature.^[31,32] In the case of MES, with increasing temperature (30–45°C), the cmc increases. The cmc values of MES obtained by conductivity are in good agreement with those reported in literature.^[16] The hydrophobic interactions are responsible for micelle formation. The hydration of hydrophobic groups in nonionic surfactant decreases as the temperature increases and thus the disturbance of water structure around the hydrophobic group results in increasing hydrophobic interaction and consequently the cmc decreases. Moreover, the hydration of oxyethylene groups also decreases as temperature increases resulting in lower cmc. The ionic repulsive forces are responsible for higher values of cmc for ionic surfactants.^[29] In the case of C₁₂E₆/MES mixed systems, the cmc values were evaluated by surface tension measurements only, as conductance did not show any break. We have failed to understand the reason. Thus we decided that this nonionic-anionic surfactant mixture behaves as a nonionic one. i.e mixed micelles are nonionic in nature. The cmc's of binary combinations of C₁₂E₆ & MES fall between the individual cmc values of the components (C₁₂E₆ & MES). The cmc values of MES obtained by surface tension and conductance do differ at low temperature (Table 1). Repeated experimentation confirmed the result. However no explanation is forthcoming. The standard thermodynamic parameters of micellization can be determined from the temperature dependence of the cmc.^[33] The standard free energy of micellization for a nonionic surfactant is given by the relation^[31]

$$\Delta G_m^0 = RT \ln X_{cmc} \quad (4)$$

where X_{cmc} is the cmc in mole fraction scale.

The ΔG_m^0 values are presented in Table 2. It is evident from Table 2 that the ΔG_m^0 values become more and more negative with increasing temperature, suggesting spontaneity in micelle formation with rising temperature. The standard enthalpy ΔH_m^0 and standard entropy ΔS_m^0 of micellization were evaluated from ΔG_m^0 to T plots. The slope and intercept gave ΔS_m^0 and ΔH_m^0 , respectively. The micellization process is endothermic, except for MES, where it is exothermic. This indicates that the micellization process is

purely entropy dominated for $C_{12}E_6$ and mixed systems though not exactly so for MES; that is, micellization is specific to surfactants and temperature.^[34-36] The entropy of micellization ΔS_m^0 values are positive and large values of entropy are obtained which is seen quite often.^[37] The entropy changes are so large that it may be considered as a change of phase.

Table 2. The thermodynamic parameters of micellization of $C_{12}E_6$ /MES mixed surfactant systems.

N_{MES}	$-\Delta G_m^0$ (kJmol ⁻¹)				ΔH_m^0 (kJmol ⁻¹)	ΔS_m^0 (Jmol ⁻¹ K ⁻¹)
	303 K	308 K	313 K	318 K		
0.0	34.2	35.1	36.1	36.9	21	182
0.1	34.4	35.1	36.1	36.9	17.2	170
0.3	33.5	34.3	35	35.7	10.7	146
0.5	32.9	34	35	36.2	33.2	218
0.7	32.7	33.4	34.1	34.7	7.9	134
0.9	30	30.7	31.4	31.9	6.2	120
1.0	33.6	33.9	34.3	34.4	-16.7	56

The surface excess concentration under the conditions of surface saturation, Γ_{max} , can be used as a measure of maximum extent of adsorption of surfactants at the air/water interface using the Gibbs adsorption equation.^[7,38] The Γ_{max} and A_{min} values thus calculated are presented in Table 3. It is observed that Γ_{max} increases with increasing temperature for $C_{12}E_6$, whereas it decreases with increasing temperature for MES.

The increase in Γ_{\max} for $C_{12}E_6$ is due to decreasing hydration of ethoxy segments, leading to greater tendency to locate at the air/water interface.

Table 3. Maximum Surface Excess (Γ_{\max}) and limiting surface area per molecule ($A_{\min.}$) of $C_{12}E_6$ /MES mixed surfactant system.

N_{MES}	$\Gamma_{\max.} \times 10^{10} \text{ mol cm}^{-2} \text{ at}$				$A_{\min.} (\text{nm}^2)$			
	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K
0.0	2.48	2.71	2.86	2.98	0.67	0.61	0.58	0.55
0.1	2.66	2.6	2.5	2.46	0.62	0.64	0.66	0.67
0.3	2.3	2.22	2.12	2.02	0.72	0.75	0.78	0.81
0.5	2.25	2.4	2.73	3.04	0.74	0.70	0.61	0.55
0.7	2.84	2.82	2.92	3.06	0.58	0.59	0.56	0.54
0.9	2.07	2.4	2.5	2.52	0.80	0.72	0.66	0.66
1.0	1.25	1.16	1.08	1.06	1.33	1.43	1.53	1.57

The decrease in $\Gamma_{\max.}$ with rising temperature for MES may be due to higher solubility of MES in water, which opposes adsorption of surfactants at the air/water interface. The thermodynamic parameters of adsorption of surfactants at the air/water interface, evaluated using the relation,^[39]

$$\Delta G_{ad}^{\circ} = RT \ln_{cmc} - N \Pi_{cmc} A_{cmc} \quad (5)$$

are presented in Table 4, where N , Π_{cmc} and A_{cmc} are Avogadro's number, surface pressure at cmc ($\gamma_0 - \gamma_{cmc}$) and area per molecule at cmc, respectively. The second term in Eq. (5) represents surface work involved in going from zero surface pressure to surface pressure at cmc (Π_{cmc}) at constant minimum surface area per molecule. The ΔH_{ad}° and ΔS_{ad}° values were evaluated from a ΔG_{ad}° to T plot.

Table 4. The thermodynamic parameters of adsorption of C₁₂E₆/MES mixed surfactant system.

N_{MES}	$-\Delta G_{ad}^0$ (kJmol ⁻¹)				ΔH_{ad}^0 (kJmol ⁻¹)	ΔS_{ad}^0 (Jmol ⁻¹ K ⁻¹)
	303 K	308 K	313 K	318 K		
0.0	44.5	44.7	45.3	45.5	-22.6	72
0.1	40.3	40.9	42.3	44.1	37.6	256
0.3	43.2	44.7	46.0	47.1	35.5	260
0.5	41.9	43.3	43.4	44.1	-1.6	134
0.7	41.1	43.1	44.3	45.4	44.1	282
0.9	38.2	39.9	40.8	42	36.2	246
1.0	48.4	50.3	52.3	53.3	52.6	334

It is clear from Table 4, that ΔG_{ad}^0 values are negative throughout, indicating that adsorption at the air/water interface takes place spontaneously in pure and mixed surfactants. The ΔG_{ad}^0 values are more negative in comparison to ΔG_m^0 values suggesting that, when a micelle is formed, more work has to be done to transfer the surfactant molecules in its monomeric form at the surface to the micellar stage in bulk. The ΔH_{ad}^0 values in most cases are positive suggesting adsorption of surfactants is an endothermic process. The standard entropy of adsorption ΔS_{ad}^0 values are largely positive reflecting greater freedom of movement of hydrocarbon chains at the air/water interface. However the study of adsorption of surfactants has proven not to be straightforward,^[40] as can be seen from our results where any regularity is difficult to observe.

A linear correlation between ΔS_m^0 & ΔH_m^0 (Fig. 4) as well as ΔS_{ad}^0 & ΔH_{ad}^0 are observed for this system and the compensation temperature is 298 and 299 K, respectively. Such behaviour has been suggested by Lumry et al. and was observed earlier.^[32,41,42] This implies that at 298 K, the micellization process is independent of structural changes in the system and is dependent of enthalpic factors^[29,43] and for the adsorption process, the corresponding temperature is 299 K.

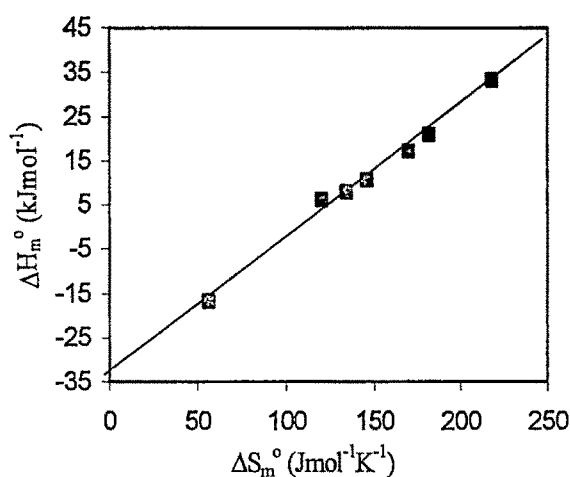


Figure 4. Plot of Entropy (ΔS_m^0) vs. Enthalpy (ΔH_m^0).

The values of interaction between the surfactant molecules in the mixed micelle (β^m) evaluated using Rubingh's equation^[44] are presented in Table 5. The interaction parameter (β^m) values are all negative at all mole fractions of C₁₂E₆/MES system indicating an attractive interaction between the MES and C₁₂E₆ headgroups in the mixed micelle, leading to electrostatic stabilization. As can be seen from Table 1, the cmc of MES seems to differ when surface tension or conductance methods are used. Hence, to calculate β^m , the micellar interaction parameter, we used both types of cmc data of MES. It can be seen from Table 5, that the calculated β^m values do not differ much (maximum about 10%) and the interaction is always attractive in nature. The composition of the micelle seems to remain exactly the same. The maximum difference in X_1 values by using

different cmc values (i.e., either conductance or surface tension) was ~7% though, in most cases it was less than 2%. This indicates that the composition of mixed micelle is without much error.

Table 5. Interaction parameter (β^m) values of C₁₂E₆/MES mixed surfactant system in aqueous media at different temperatures.

N_{MES}	Temperature (K)			
	303	308	313	318
0.1	-5.17/-4.85 ^a (0.116)	-4.33/-4.05 (0.0768)	-3.93/-3.68 (0.0540)	-4.38/-4.28 (0.064)
0.3	-2.43/-2.13 (0.0717)	-1.3/-1.07 (0.028)	—	—
0.5	-2.43/-2.11 (0.123)	-3.34/-3.04 (0.158)	-3.60/-3.32 (0.155)	-4.86/-4.73 (0.199)
0.7	-4.16/-3.77 (0.267)	-3.96/-3.61 (0.247)	-3.47/-3.17 (0.210)	-3.40/-3.28 (0.197)
0.9	-2.53/-2.10 (0.326)	-2.49/-2.12 (0.308)	-2.08/-1.76 (0.267)	-1.95/-1.81 (0.246)

Note: - , - Iteration did not coalesce. Values in parenthesis are X_1 i.e mole fraction of MES.

^a The data after '/' was calculated using cmc of MES by ST Measurement.

It is suggested that nonionic surfactants of poly (ethylene oxide) class have a weak cationic character resulting either from oxonium ion formation with protons from water or sharing of H of water by hydrogen bond formation. Thus the attractive interaction is probably due to this weak cation with anionic surfactant, MES.^[45] The activity coefficient values were also evaluated using the relations:^[1]

$$\ln f_1 = \beta^m (1 - X_1^2) \quad (5)$$

$$\ln f_2 = \beta^m (X_1^2) \quad (6)$$

where X_1 is mole fraction of surfactant 1 in the micelle and f_1 and f_2 are the activity coefficients of surfactants 1 & 2 respectively, in the mixed micelle. The f_1 & f_2 values are tabulated in Table 6. The much lower mole fraction (X_1) of MES is reflected in its small activity coefficient (f_1) values, which suggests that MES in the mixed micelle is far away

from the standard state. The (f_2) values of $C_{12}E_6$ are obviously higher (close to unity) which increase with increasing temperature, indicating that $C_{12}E_6$ in the mixed micelle is near its standard state.^[46,37]

Table 6. Activity coefficient (f_1 & f_2) values of $C_{12}E_6$ / MES mixed surfactant system in aqueous media at different temperatures.

N_{MES}	Temperature (K)			
	303	308	313	318
0.1	0.018 (0.933)	0.025 (0.975)	0.0297 (0.989)	0.0224 (0.982)
0.3	0.123 (0.988)	0.280 (0.99)	—	—
0.5	0.154 (0.96)	0.094 (0.92)	0.076 (0.917)	0.044 (0.82)
0.7	0.107 (0.743)	0.105(0.79)	0.115 (0.858)	0.112 (0.876)
0.9	0.317 (0.764)	0.303 (0.79)	0.327 (0.862)	0.330 (0.889)

Note: Values in parenthesis are (f_2) i.e, activity coefficient of nonionic surfactant.

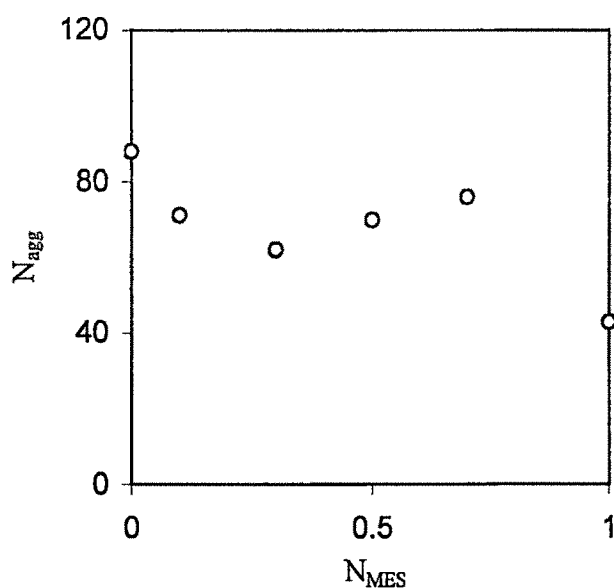


Figure 5. Plot of Micellar Aggregation Number (N_{agg}) vs Mole fraction of MES.

The micellar aggregation numbers (N_{agg}) determined by steady state fluorescence quenching method are represented in Fig. 5. It is evident from Fig. 5 that (N_{agg}) values of mixed surfactant at all the mole ratios are different than those of single surfactants, though a regularity is difficult to visualize. This may be attributed to two competing factors: a) decrease in steric interactions of $C_{12}E_6$ because of incorporation of MES in to $C_{12}E_6$ micelle, b) decrease in repulsive headgroup interactions in MES due to the presence of $C_{12}E_6$, and thus a larger mixed micelle is formed compared to $C_{12}E_6$ or MES.^[29,47]

The K_{SV} values calculated from Eq. (3) and given in Table 7 are the ratio of bimolecular quenching constant to unimolecular decay constant, and hence, we can say from the magnitudes of K_{SV} that the quenching is very efficient in these micelles. It should also be noted that K_{SV} is equal to the product of k_q , the rate constant of quenching process and τ , the actual lifetime of fluorescing molecule in absence of bimolecular quenching.⁴⁸ We have not been able to determine the exact magnitude of τ . However, we can assume that τ for all mixed systems, presented in this paper and in pure MES are almost same since k_q can be assumed to be similar. For $C_{12}E_6$ the fluorescence lifetime is much higher.

Table 7. Micropolarity (I_1/I_3) and Binding Constant (K_{SV}) for $C_{12}E_6$ /MES mixed surfactant systems.

N_{MES}	0	0.1	0.3	0.5	0.7	0.9	1.0
(I_1/I_3)	1.17	1.17	1.16	1.15	1.13	1.12	1.10
$K_{SV} \times 10^{-5} (\text{L mol}^{-1})$	0.16	0.11	0.10	0.11	0.13	—	0.11

The effect of electrolytes like NaCl, NaBr and nonelectrolytes like polyethylene glycols (MW 200, 300 & 400) on CP of $C_{12}E_6$ (1%, w/v) solution are represented in Figs. 6 & 7, respectively. The PEGs have negligible effect on CP, though electrolytes have large but different type of effects within the concentration range studied. The CP of $C_{12}E_6$ (1% w/v) is 46.5°C. NaBr does not affect the CP significantly.

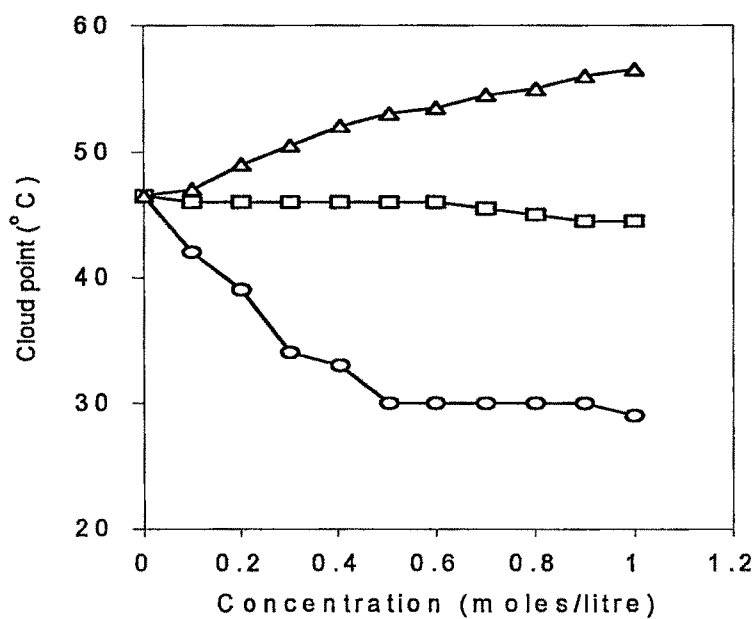


Figure 6. Plot of CP of C₁₂E₆ (1% w/v) vs Concentration (moles/litre) of electrolytes.
Key: O, NaCl; Δ, NaI; □, NaBr.

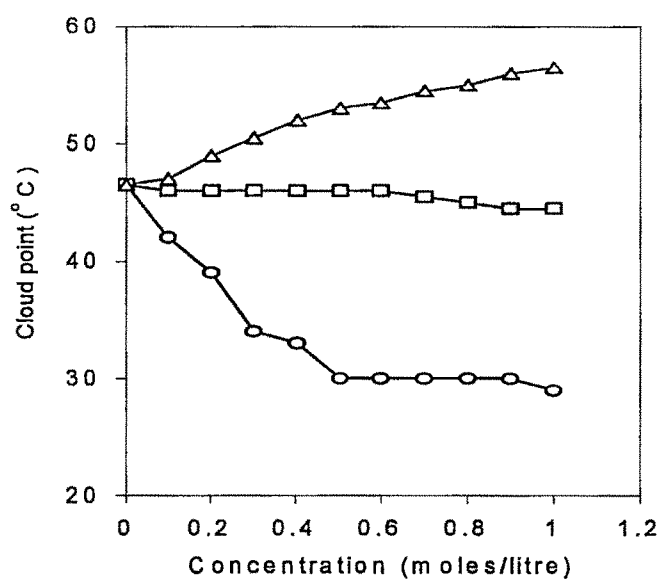


Figure 7. Plot of CP of C₁₂E₆ (1% w/v) vs Concentration (mole %) of PEGs.
Key: Δ, PEG 200; □, PEG 300; O, PEG 400.

NaI increases the CP of C₁₂E₆ because of less hydrophobicity of I⁻ ions, which decreases the possibility of two molecules coming together due to the presence of water, whereas CP decreases in presence of NaCl, which may be due to high solvation of Cl⁻ ions and which leads to disruption of water around the micelles and hence easy approach to each other.

The relative viscosity values of surfactant solution of C₁₂E₆ (5%, w/v) in presence of NaCl at different temperatures were determined (Table 8). The relative viscosity of C₁₂E₆ increased on addition of NaCl and was double than that of C₁₂E₆ in absence of NaCl. The relative viscosity values of C₁₂E₆ in the presence of 0.2 M NaCl could be determined at 30°C, 35°C, and 40°C only, whereas the η_{rel} were evaluated at 30°C and 35°C only for C₁₂E₆ + 0.5 M NaCl, as the solution became turbid because the CP was reached. The $|\eta|$ values of C₁₂E₆ in the presence of NaCl are higher (~200 cm³g⁻¹), which is expected as the viscosity of concentrated surfactant solution increases in the presence of inorganic salt.^[49] Such a large change in viscosity may be due to changes in the micelle, because of the salting out effect of NaCl. The presence of NaCl leads to salting out of surfactant, which favours micellization.^[1] Also, the steric interactions in C₁₂E₆ may be reduced due to the presence of NaCl, resulting in the increase in micelle size and relative viscosity of C₁₂E₆ (5%, w/v).

Table 8. Viscosity study of C₁₂E₆ (5% w/v) at different temperatures and in the presence of different amount of NaCl.

Concentration of NaCl (M)	η_{rel}				$ \eta $ cm ³ /g			
	30	35	40	45°C	30	35	40	45°C
0.0	3.05	4.24	5.86	7.72	41	64.8	97.2	134.4
0.2	4.476	6.556	9.016	—	69.6	111.1	160.3	—
0.5	7.547	10.929	—	—	131	198.6	—	—

The viscosity of 5% (w/v) $C_{12}E_6$ /MES mixed surfactant solution (Fig. 8) shows negative deviation from linearity. The $\eta_{rel.}$ values of $C_{12}E_6$ are much higher than those of MES. That $|\eta| = 2.5 - 4.0 \text{ cm}^3 \text{ g}^{-1}$ indicates globular particles.^[22] The intrinsic viscosity values of $C_{12}E_6$, MES, and $C_{12}E_6$ /MES mixed surfactant solution at all mole fractions are high. The lowest $|\eta|$ is $6.2 \text{ cm}^3 \text{ g}^{-1}$.

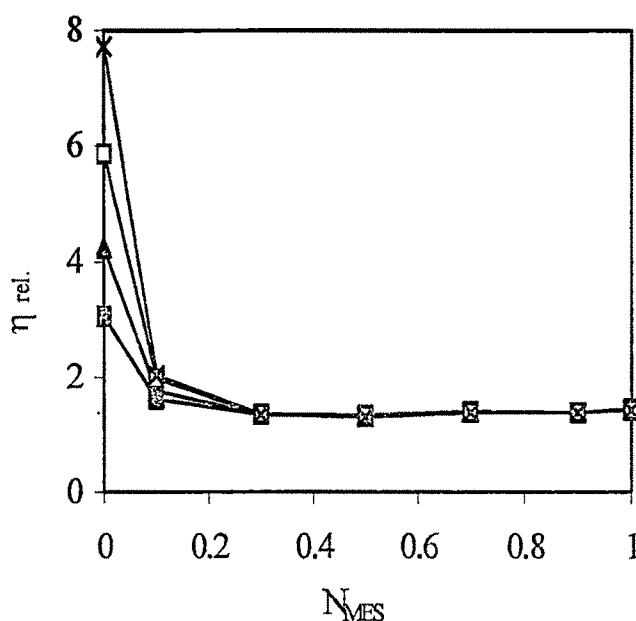


Figure 8. Plot of relative viscosity (η_{rel}) vs. mole fraction of MES (N_{MES}).

The η_{rel} values of $C_{12}E_6$ show a minimum at about 35°C with increasing temperature at low surfactant solution (0.25% w/v), (Table 9). However at high concentration (i.e. 5%w/v) η_{rel} increases with temperature. In presence of NaCl, $\eta_{rel.}$ and $|\eta|$ both increase with temperature indicating formation of elongated micellar species.^[22] Temperature has no significant effect on the viscosity of MES and $C_{12}E_6$ /MES mixed surfactant system at higher MES ratio (Fig.8).

Table 9. Viscosity study of $C_{12}E_6$ (0.25 % w/v) at different temperatures.

Temperature ($^{\circ}C$)	$\eta_{rel.}$	η_{abs} (poise)
30	0.986	0.00785
35	0.975	0.0070
40	0.997	0.0065
45	1.056	0.0063

Foaming is an inherent property of surfactant solutions. Nonionic surfactants containing the poly(oxyethylene) groups produce both less foam and less stable foam than ionic surfactants. However the foaming efficiency and stability of surfactants can be altered by addition of certain additives.^[1,50] We studied the foaming efficiency and foam stability of $C_{12}E_6$ in presence of different mole fractions of MES at 30 $^{\circ}C$, 35 $^{\circ}C$, and 40 $^{\circ}C$. The foam heights indicative of foamability $C_{12}E_6$ /MES mixed surfactant system were evaluated at different temperatures and are presented in Table 10. It is evident from Table 10 that these values are higher in most of mole fractions of mixed surfactant solutions than individual surfactants. Also, the foam heights increased with increase in temperature for pure as well as mixed surfactants, indicating better foaming efficiency at higher temperatures. In the case of mixed surfactants, there is a possibility of rapid variation of concentration at air/water interface, which is one of the main requirements for good foam-forming qualities,^[51] which is enhanced with rise in temperature. Thus, higher foam heights for mixed surfactants indicate higher interfacial activity. Foams are very complex and it seems that a clear relation between foam height and variables does not exist. Moreover drainage, evaporation, interaction with environment etc. also affect the foam stability.^[52]

Table 10. Foam stability of C₁₂E₆/MES mixed surfactant system as a function of temperature. Total Surfactant Concentration (5.8 mM) (Average of atleast two runs).

N_{MES}	Foam height (cms \pm 1.1)		
	30 °C	35 °C	40 °C
0.0	12.6	14.3	17.1
0.1	14.3	15.7	17.5
0.3	15.5	19.6	23.2
0.5	22.5	27.1	31.5
0.7	20.8	24.0	28.8
0.9	18.9	22.4	26.5
1.0	16.8	20.5	25.0

Detergency of surfactant solutions was also studied using dye removal method and is represented in Figs. 9-12. The temperatures were maintained at 35°C and 50°C. For cotton fabric at 35°C, MES was found to be most effective detergent at the initial point and the mixture the least effective. However, with time the mixture was a better detergent than the pure ones. However, at 50°C, MES was more efficient at the starting point, with time the mixture as well as pure had the same efficiency. For terry cotton C₁₂E₆ was an efficient detergent both at 35°C and 50°C. The detergency efficiency of C₁₂E₆ was higher than MES, as nonionic surfactants, because of low critical micelle concentration are better solubilizing agents than ionics.^[53] The results did not show any synergistic behaviour in this property in the mixed systems.

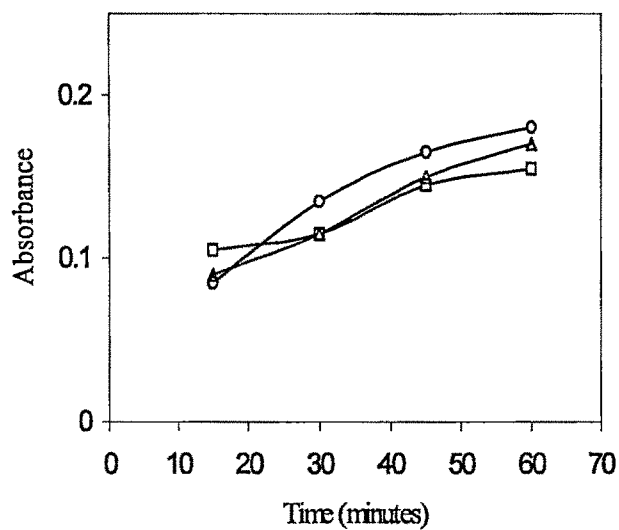


Figure 9. Plot of absorbance vs. time (minutes) at 35 °C. Key: □, MES; Δ, C₁₂E₆; ○, 5:5 C₁₂E₆:MES.

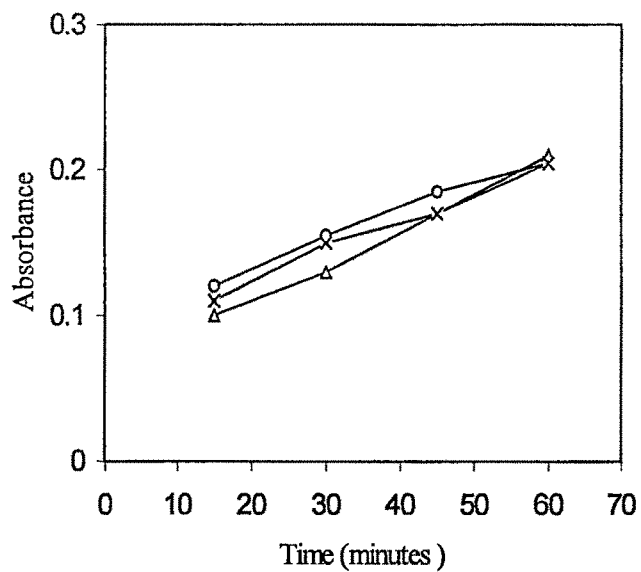


Figure 10. Plot of absorbance vs. time (minutes) at 50 °C. Key: ○, MES; Δ, C₁₂E₆; x, 5:5 C₁₂E₆:MES.

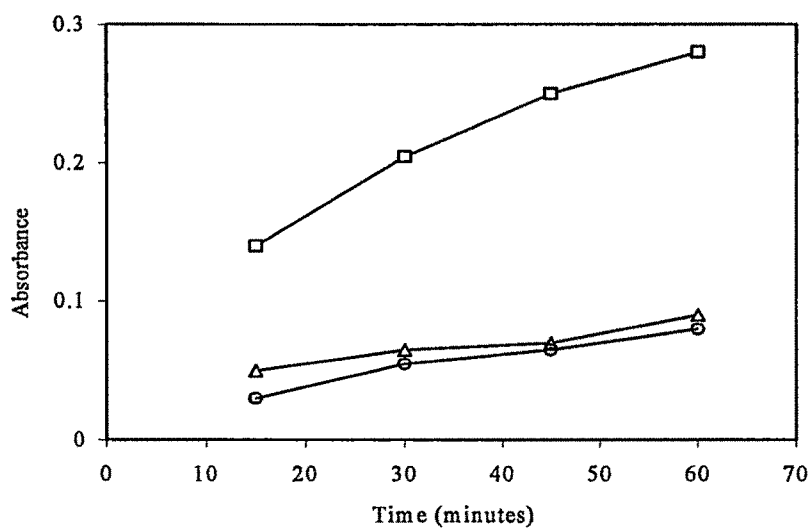


Figure 11. Plot of absorbance vs. time (minutes) at 35 °C, Key: Δ , MES; \square , C₁₂E₆; O, 5:5 C₁₂E₆ : MES.

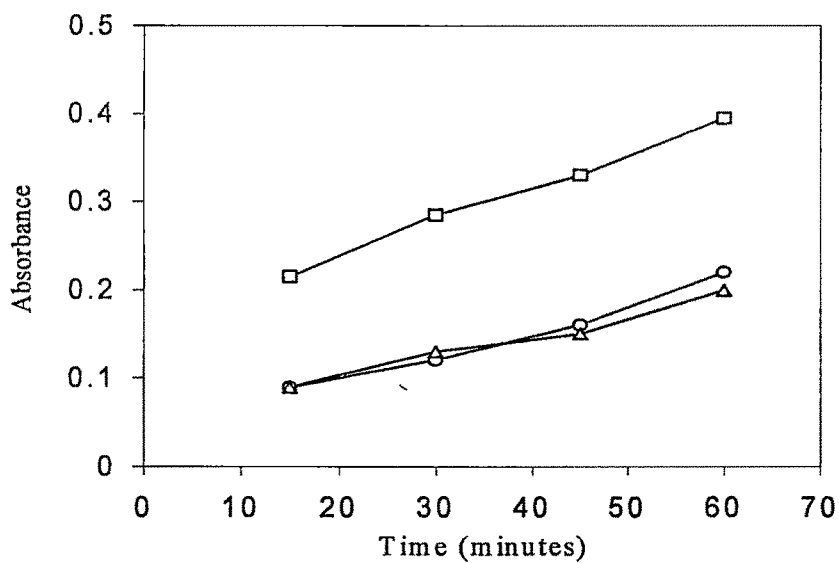


Figure 12. Plot of absorbance vs. time (minutes) at 50 °C. Key: O, MES; \square , C₁₂E₆; Δ , 5:5 C₁₂E₆ : MES.

CONCLUSIONS

The surface, thermodynamic and performance properties of α - sulfonato myristic acid methyl ester (MES) – hexaoxyethylene monododecyl ether ($C_{12}E_6$) mixed surfactant system were determined. The micellization process is very much entropy dominated. The micellar aggregation number N_{agg} values for mixed surfactant were different than those of single surfactants. The interaction parameter values were negative indicating an attractive interaction between the surfactant molecules in the mixed micelle. The detergency, viscosity and foaming properties were also studied. Although the detergency did not show synergistic character, the foaming efficiency for mixed surfactant was superior than those of single surfactants. From the intrinsic viscosity values, the mixed micelles at all mole fractions were suggested to be elongated species.

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