
Chapter IV

**Physicochemical properties of anionic-nonionic surfactant mixture:
 α -sulfonato myristic acid methyl ester (MES) – nonaoxyethylene
monododecyl ether (C₁₂E₉)**

We report the interfacial, thermodynamic and performance properties of the binary mixture of α -sulfonato myristic acid methyl ester (MES) and nonaoxyethylene monododecyl ether ($C_{12}E_9$). The critical micelle concentration (cmc), thermodynamics of micellization and adsorption, and minimum area occupied by the surfactant at the air/water interface, micellar aggregation number (N_{agg}) have been determined. The mixed micellar composition and interaction parameter (β^m) were also evaluated. The estimated interaction parameter indicates an overall attractive interaction in the mixed micelles. Moreover the performance properties of pure and mixed surfactant systems like foaming, and viscosity were also studied.

Surfactants find extensive applications in various fields due to their property of adsorbing on to surfaces or interfaces and thereby altering to a marked degree, the surface free energy of those surfaces or interfaces¹. In fundamental and applied fields, mixed surfactants are prevalent. The functions and properties of surfactant systems depend on their structural type, concentration and compositions in addition to other factors viz. temperature, pressure, pH, solvent and additives². Mixed surfactant systems exhibit superior performance properties compared to individual surfactants. Some combinations exhibit synergistic properties, they show a remarkable decrease in surface tension and lower critical micelle concentration (cmc) values than each of the individual surfactant. Thus fundamental studies are essential for exact and detailed understanding of self-organising behaviour of surfactant(s)³. In recent years studies on different types of combinations formed by different surfactants such as anionic-cationic⁴, nonionic-nonionic⁵, anionic-nonionic^{6,7}, nonionic-cationic⁸, anionic-zwitterionic⁹ etc. have been studied. Rationale for selection of nonionic surfactant of the alkyl polyoxyethylene ether, C_nE_m type is its wide use as detergent, solubilizer and emulsifier¹⁰ and α -sulfonato fatty acid methyl esters have superior detergency, high tolerance against calcium ions and good biodegradability^{11,12}.

The present article deals interaction of nonaoxyethylene monododecyl ether (C₁₂E₉) with α -sulfonato myristic acid methyl ester (MES) in aqueous solution, with reference to mixed micelle formation, thermodynamics of micellization and adsorption of surfactant at the air/water interface. The micellar aggregation number and the microenvironment of the mixed micelle are also been discussed. The intermicellar interactions and the composition of the mixed micelle are also studied using Rubingh's theory¹³. Viscosity and foamability of surfactant solutions are also presented.

Results and discussion

Critical micelle concentration:

The critical micelle concentrations for aqueous solution of single and mixed surfactant systems of different mole fractions at 30, 35, 40 and 45° are presented in Table 1.

Table 1. Critical micelle concentration (cmc) values of C₁₂E₉/MES mixed surfactant system in aqueous media at different temperatures.

N_{MES}	cmc (mM)			
	303	308	313	318 K
0.0	0.0812	0.0794	0.0758	0.0741
0.1	0.093	0.088	0.085	0.082
0.3	0.109	0.104	0.099	0.097
0.5	0.120	0.115	0.109	0.107
0.7	0.180	0.109	0.165	0.147
0.9	0.397	0.380	0.346	0.315
1.0	2.39	2.51	2.63	3.16
	3.16 ^a	3.24	3.32	3.48
	(0.634)*	(0.641)	(0.646)	(0.656)

^a- Conductivity data. ^bValues in parenthesis are the degree of ionization of micelle of MES.

The cmc values of MES obtained by conductivity method are in good agreement with those reported in literature¹¹, though the cmc obtained by surface tension and conductance method are different. Variations in cmc values depending on the method of determination have been reported in literature^{14,15}. The cmc values of MES increase with increase in temperature (30 – 45°) which may be due to the corresponding increase in ionic repulsive forces¹⁶. For the nonionic surfactant, C₁₂E₉ the cmc values decrease with increase in temperature which has generally been observed earlier also^{17,18}. The cmc values of C₁₂E₉/MES mixed surfactant system, were evaluated by surface tension measurements only as specific conductance-concentration did not show any break. Thus we treated

C₁₂E₉/MES surfactant mixture as a nonionic one. i.e. mixed micelles are nonionic in nature.

Thermodynamics of Micellization:

The standard free energy of micellization for a nonionic surfactant is given by the relation¹⁷,

$$\Delta G_m^0 = RT \ln X_{cmc}$$

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

whereas for an ionic surfactant,

$$\Delta G_m^0 = (2 - \alpha)RT \ln X_{cmc}$$

where α is the degree of ionization of micelle.

Table 2. The thermodynamic parameters of micellization of C₁₂E₉/MES mixed surfactant system.

N_{MES}	- ΔG_m^0 (kJmol ⁻¹) at				ΔH_m^0 kJmol ⁻¹	ΔS_m^0 Jmol ⁻¹ K ⁻¹
	303	308	313	318 K		
0.0	33.8	34.5	35.1	35.8	6.2	132
0.1	33.5	34.2	34.8	35.5	6.5	132
0.3	33.1	33.8	34.4	35	5.0	126
0.5	32.9	33.5	34.2	34.8	5.9	128
0.7	31.8	32.5	33.1	33.9	10.0	138
0.9	29.8	30.5	31.2	31.9	12.6	140
1.0	33.6	33.9	34.3	34.4	-16.7	56

The degree of ionization of micelle (α) was computed from the ratio between slopes of the post micellar and premicellar regions of the Conductance – Concentration profile of MES¹⁹. The ΔG_m^0 values are presented in Table 2. It is evident from Table 2 that, ΔG_m^0 values become more negative with increase in temperature. That is the formation micelles becomes relatively more spontaneous. The standard enthalpy, ΔH_m^0 and standard entropy, ΔS_m^0 of micellization were evaluated from ΔG_m^0 - T plot. 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. The entropy of micellization, ΔS_m^0 values are positive indicating that micellization is entropy dominated. High entropy changes are associated with a phase change. Thus it can be assumed that the micelles are separate phases in this system²⁰.

The maximum surface excess (Γ_{\max}) and minimum area per molecule of the surfactant at the air/water interface calculated using Gibb's adsorption equation²⁴ are presented in Table 3.

Table 3. Maximum Surface Excess (Γ_{\max}) and limiting surface area per molecule (A_{\min}) of C₁₂E₉/MES mixed surfactant system.

N_{MES}	$\Gamma_{\max} \times 10^{10} \text{ mol cm}^{-2} \text{ at}$				$A_{\min} (\text{nm}^2)$			
	303	308	313	318 K	303	308	313	318 K
0.0	3.35	3.21	2.45	3.36	0.49	0.52	0.67	0.50
0.1	2.46	1.8	2.10	2.41	0.67	0.75	0.79	0.69
0.3	2.01	2.0	2.05	1.64	0.67	0.76	0.80	0.97
0.5	2.47	2.82	2.10	1.64	0.61	0.52	0.77	1.01
0.7	1.62	2.0	1.67	1.47	1.02	0.83	0.99	1.12
0.9	2.27	2.11	2.27	2.24	0.73	0.78	0.73	0.74
1.0	1.25	1.16	1.08	1.06	1.33	1.43	1.53	1.57

The lower values (A_{\min}) in the mixed systems may be due to closer packing at the air water interface owing to the decreased repulsion between the oriented headgroups of surfactants. The thermodynamic parameters of adsorption of surfactants at the air/water interface, evaluated using the relation²²,

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

are presented in Table 4 and N , Π_{cmc} and A_{cmc} are Avogadro number, surface pressure at cmc ($\gamma_0 - \gamma_{cmc}$) and area per molecule at cmc respectively. The standard state for the adsorbed surfactant here is a hypothetical monolayer at its minimum surface area per molecule but at zero surface pressure.

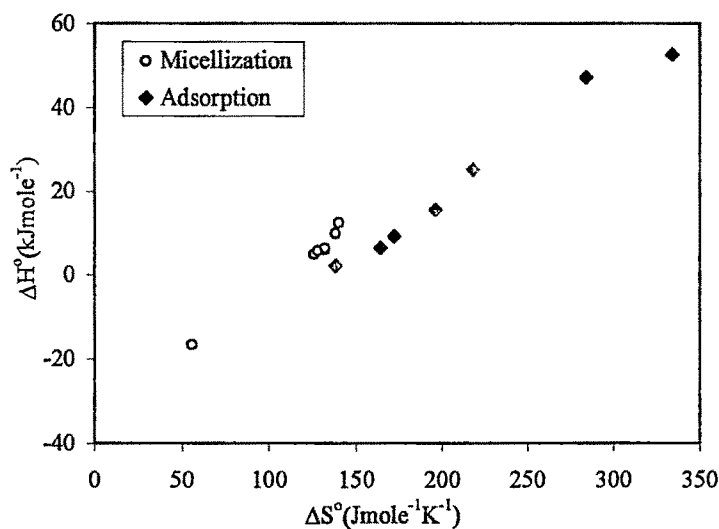
Table 4. The thermodynamic parameters of adsorption of C₁₂E₉ / MES mixed surfactant system.

N_{MES}	- ΔG_{ad}° (kJmol ⁻¹) at				ΔH_{ad}° kJmol ⁻¹	ΔS_{ad}° Jmol ⁻¹ K ⁻¹
	303	308	313	318 K		
0.0	40.6	41.6	44.1	43.4	25.2	218
0.1	42.9	45.2	46.9	45.6	15.7	196
0.3	43.0	43.6	44.1	45.7	9.3	172
0.5	39.0	40.0	41.6	43.2	47.2	284
0.7	44.6	41.7	44.8	46.3	6.6	164
0.9	39.3	40.4	40.7	41.5	2.4	138
1.0	48.4	50.3	52.3	53.3	52.6	334

The standard enthalpy, ΔH_{ad}^0 and standard entropy, ΔS_{ad}^0 values were evaluated from $\Delta G_{ad}^0 - T$ plot. The ΔG_{ad}^0 values are negative throughout indicating that adsorption at the air/water interface takes place spontaneously in pure as well as mixed surfactants. The ΔH_{ad}^0 values suggest that adsorption process is endothermic and entropy of adsorption values are high reflecting that there is more freedom for motion of hydrocarbon chains at the interface.

A linear correlation between ΔS_m^0 & ΔH_m^0 as well as ΔS_{ad}^0 & ΔH_{ad}^0 (Fig. 1) was observed for this system which has been suggested by Lumry and Rajender²³. The compensation temperature for micellization and adsorption process are 314 and 281 K respectively. Such behaviour has been observed earlier also²⁴ and it implies that at 314 K the micellization process is independent of structural changes in the system and is dependent on enthalpic factors²⁵.

Fig. 1. Enthalpy-entropy compensation plot.



The (β^m) values, a measure of interaction between the surfactant molecules in the mixed micelle (μ) are presented in Table 5. The interaction parameter (β^m) values are all

negative at all mole fractions of C₁₂E₉/MES system except $N_{MES} = 0.1$, indicating an attractive interaction between the MES and C₁₂E₉ headgroups in the mixed micelle leading to electrostatic stabilization.

Table 5. Interaction parameter (β^m) values of C₁₂E₉ / MES mixed surfactant system in aqueous media at different temperatures.

N_{MES}	$(\beta^m)^a$			
	303	308	313	318
0.1	—	—	—	—
0.3	-1.87/-1.57 [†] (0.0551)	-2.33/-2.06 (0.072)	-2.30/-2.20 (0.067)	-2.50/-2.39 (0.072)
0.5	-3.32/-2.98 (0.178)	-3.57/-3.20 (0.186)	-3.65/-3.36 (0.185)	-3.70/-3.58 (0.182)
0.7	-2.91/-2.55 (0.227)	-3.51/-2.86 (0.236)	-3.64/-3.05 (0.185)	-3.77/-3.64 (0.189)
0.9	-2.55/-2.12 (0.341)	-2.72/-2.32 (0.343)	-3.03/-2.67 (0.344)	-3.46/-3.30 (0.350)

* Values in parenthesis are X_1 i.e mole fraction of MES.

^a(-) Iteration did not coalesce.

^bThe data after '/' was calculated using cmc of MES by ST Measurement

As can be seen from Table 1, the cmc of MES seems to differ when surface tension or conductance methods are used. β^m values calculated by surface tension and conductance data are different but the interaction is always attractive.

The activity coefficient values were also evaluated using the relations¹,

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

and

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

where X_1 is mole fraction of surfactant 1 in the micelle and γ_1 & 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.

Table 6. Activity coefficient (f_1 & f_2) values of C₁₂E₉/MES mixed surfactant system in aqueous media at different temperatures.

N_{MES}	f_1 of anionic surfactant			
	303	308	313	318 K
0.1	—	—	—	—
0.3	0.188 (0.994)	0.134 (0.987)	0.135 (0.989)	0.116 (0.987)
0.5	0.106 (0.900)	0.094 (0.883)	0.089 (0.882)	0.084 (0.884)
0.7	0.175 (0.86)	0.154 (0.836)	0.133 (0.816)	0.118 (0.793)
0.9	0.330 (0.743)	0.309 (0.726)	0.271 (0.698)	0.232 (0.654)

* Values in parentheses are activity coefficient (f_2) of nonionic surfactant.

The activity coefficient (f_1) values of MES are lower, suggesting that MES in the mixed micelle is away from the standard state. The (f_2) values of C₁₂E₉ are higher which increase with increase in temperature indicating that C₁₂E₉ in the mixed micelle is near its standard state.

Micellar aggregation number and microenvironment:

The micellar aggregation numbers (N_{agg}) determined by steady state fluorescence measurements at different mole ratios of binary C₁₂E₉/MES mixture are presented in Fig. 2. The aggregation number values of mixtures are larger than that of MES but more or less comparable with C₁₂E₉. Such behaviour may be due to the presence of C₁₂E₉ in the mixed

micelle, resulting in screening of interionic interactions in comparison with pure MES micelle. Consequently, the head group repulsive interactions are much reduced, leading to an increase in aggregation number in the mixed micelles.

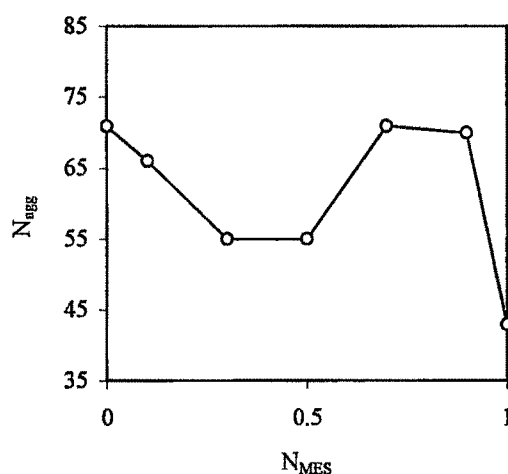


Fig. 2. Plot of Micellar Aggregation Number (N_{agg}) vs Mole fraction of MES (N_{MES}) at room temperature ($\sim 25^\circ\text{C}$).

The ratio of the first (375nm) and third (385nm) peaks, I_1/I_3 in pyrene fluorescence emission spectrum is known to be sensitive to local polarity around the probe. The I_1/I_3 values obtained for this system are all greater than 1, suggesting a polar environment around pyrene. K_{SV} , the Stern-Volmer binding constant which is the ratio of bimolecular quenching constant to unimolecular decay constant was also calculated using the equation²⁶,

$$\ln \frac{I_0}{I} = 1 + K_{SV}[Q] \quad [8]$$

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 fluorescence molecule in absence of

bimolecular quenching. From the values of K_{SV} it can be inferred that quenching is efficient in this system and also the lifetime of pyrene is higher, if we assume that k_q s for all systems are of similar magnitude.

Table 7. Micropolarity (I_1/I_3) and Binding Constant (K_{SV}) for $C_{12}E_9$ / MES

mixed surfactant System.

N_{MES}	0	0.1	0.3	0.5	0.7	0.9	1.0
I_1/I_3	1.22	1.20	1.19	1.17	1.16	1.11	1.10
$K_{SV} \times 10^{-4}$ ($l \text{ mol}^{-1}$)	1.2	1.03	0.85	0.82	0.74	1.22	1.10

In Fig. 3, the relative viscosity (η_{rel}) values for 5% (w/v) $C_{12}E_9$ /MES mixed surfactant solutions as a function of mole fraction is plotted.

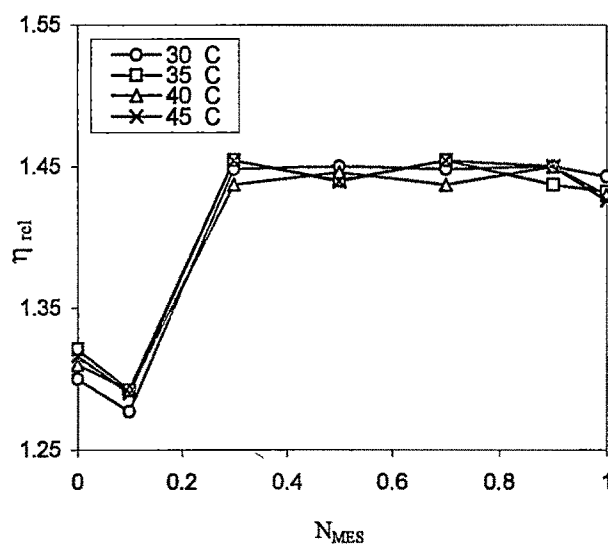


Fig. 3. Plot of relative viscosity vs. N_{MES} for $C_{12}E_9$ /MES system.

The ($\eta_{rel.}$) for C₁₂E₉ is low, initially ($\eta_{rel.}$) decreases and then suddenly increases and shows a maximum at $N_{MES} = 0.3$. The maximum in viscosity arises due to formation of mixed micelle. In general the relative viscosity i.e($\eta_{rel.}$) shows positive deviation from linearity. Increase in temperature has no significant effect on the viscosity of surfactant solution.

The intrinsic viscosity $|\eta|$ was calculated using the relation,

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

where limit to zero concentration indicates that intermolecular interactions are absent. In this study we have calculated $|\eta|$ without taking the zero concentration limit.

Table 8. Intrinsic Viscosity data for C₁₂E₉/MES mixed surfactant system.

N_{MES}	$ \eta \text{ cm}^3\text{g}^{-1} \text{ at}$			
	303	308	313	318 K
0.0	6.0	6.4	6.2	6.3
0.1	5.5	5.8	5.8	5.8
0.3	9.0	9.1	8.7	9.1
0.5	8.8	8.7	8.7	8.5
0.7	8.8	8.8	9.2	9.2
0.9	9.0	8.7	9.0	9.0
1.0	8.8	5.6	8.6	8.4

The intrinsic viscosity values (Table 8) of C₁₂E₉/MES mixed surfactant system at all mole fractions indicate that micelles are non-spherical as $|\eta|$ should be between 2.5-4 cm³ g⁻¹ for spherical systems²⁷ and the lowest $|\eta|$ for C₁₂E₉/MES system is 5.5 cm³ g⁻¹. Such results on the geometry of micelles on the basis of shape factor have been reported earlier by us²⁸, and recently Soni *et al.*²⁹ reported observations pertaining to geometry of micelles.

Foaming: Foam heights, a measure of foamability of surfactant, were determined at 30, 35 and 40° for pure as well as mixed surfactant system and are presented in Table 9.

Table 9. Foam stability of C₁₂E₉ / MES mixed surfactant system as a function of temperature (average of atleast two runs).

Total Surfactant Concentration = 5.8 mM

N_{MES}	Foam height (cms \pm 0.4) at		
	30	35	40°
0.0	6.9	9.5	11.0
0.1	13.9	14.8	16.0
0.3	6.7	8.1	9.9
0.5	21.4	23.2	24.5
0.7	10.3	10.8	12.6
0.9	9.6	10.4	11.7
1.0	16.8	20.5	25.0

It is clear that foaminess of pure as well as mixed surfactant increases with increase in temperature. C₁₂E₉ is less foaming compared to MES and most of the molefractions of mixed system. of MES. This is obvious as polyoxyethylene group in C₁₂E₉ has large surface area and also there is absence of surface films resulting in low foam heights¹. The foam heights in most molefractions are higher compared to C₁₂E₉, as there is possibility of rapid variation of concentration of surfactant at the air/water interface in mixed surfactant system, which is one of the main requirements of good foam forming qualities³⁰. Though

the higher foam height of MES compared to mixed surfactant system is difficult to explain. Foams are very complex and it seems that a clear correlation between foam heights and variables cannot be made. Moreover drainage, evaporation, interaction with environment etc. also affect the foam stability³¹.

Experimental

Nonaoxyethylene monododecyl ether [$\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_9 \text{OH}$] i.e C_{12}E_9 and α -sulfonato myristic acid methyl ester – $\text{C}_{12}\text{H}_{25}\text{CH}(\text{SO}_3\text{Na})\text{COOCH}_3$ i.e (MES), of Lion Corporation, Tokyo, Japan were obtained as gift and used without further purification. Cetyl pyridinium chloride procured from Loba Chemie, Baroda, India was recrystallized twice from benzene prior to use. Pyrene (Fluka, Germany) was recrystallized from cyclohexane. All solutions were prepared using doubly distilled water.

The critical micelle concentration were determined using surface tension measurements. The details of the method are same as described earlier⁵. Error in cmc values is less than 1%. Representative plots of surface tension (γ) vs logarithm of surfactant concentration ($\log C$) are shown in Fig. 1.

Conductance measurements were done with 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. No break in the specific conductance vs concentration plots was observed in any of the mixed surfactant systems.

The micellar aggregation number was 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 ($\sim 25^\circ \text{C}$) using a Hitachi F-4010 Fluorescence spectrophotometer.

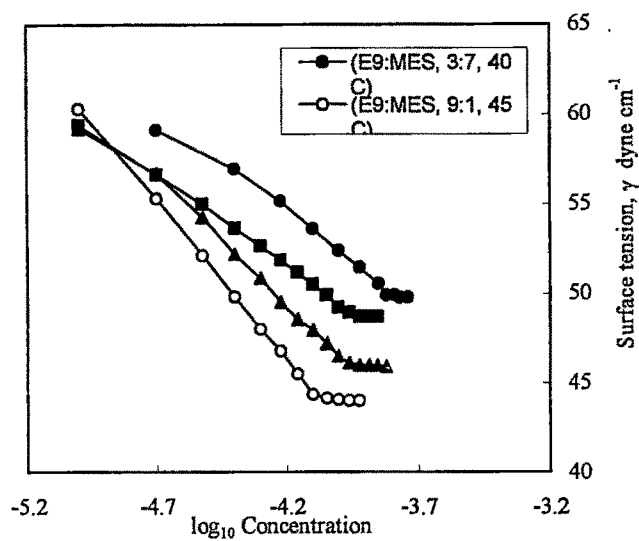


Fig. 4. Representative plots of surface tension vs. log concentration

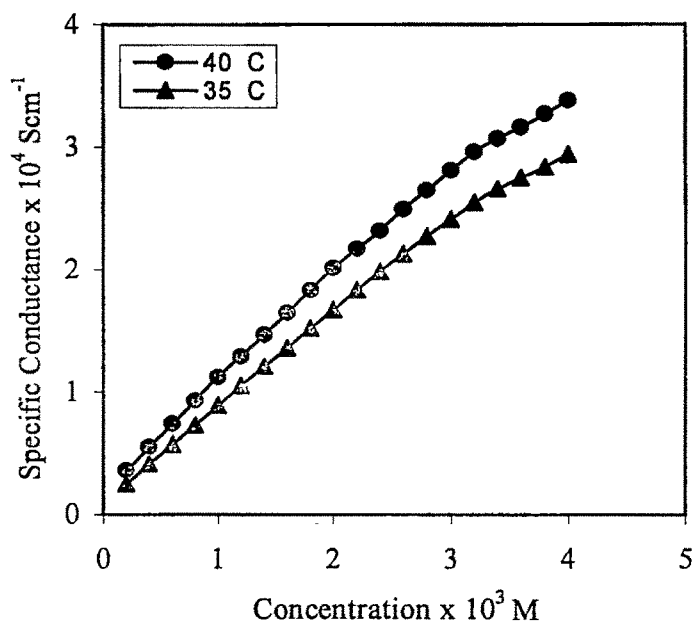


Fig. 5. Representative plots of specific conductance (κ) vs. concentration of MES.

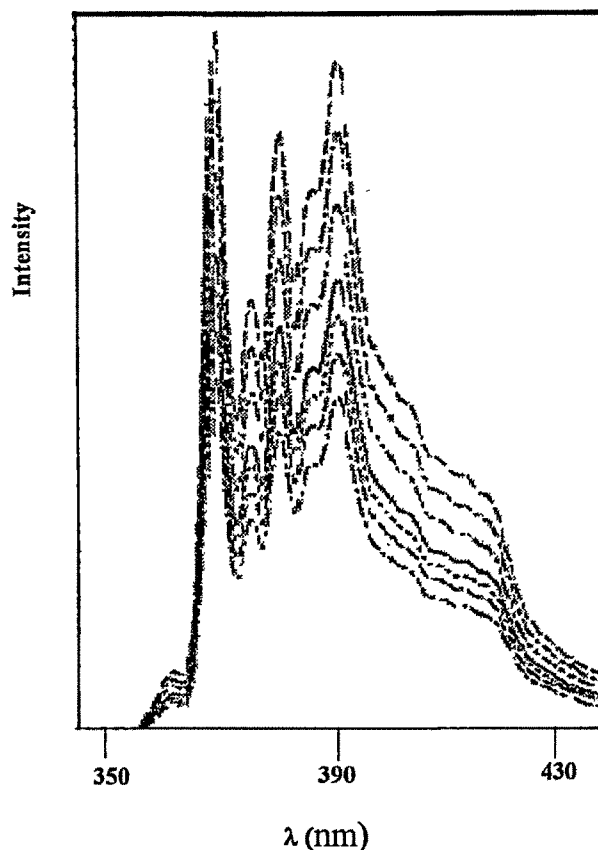


Fig. 6. Representative fluorescence (emission) spectra of 10^{-6} M pyrene in aqueous micellar solution of $C_{12}E_9$: MES (5:5).

Each spectrum had one to five vibronic peaks from shorter to longer wavelengths (Fig. 2). 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 equation³²

$$\ln I = \ln I_0 - N_{agg} \frac{[Q]}{[S] - cmc}$$

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

The ratio of intensity of first (375 nm) and third (385 nm) vibronic peaks i.e. I_1/I_3 of the pyrene fluorescence emission 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 site³³.

The viscosity of 5 % (w/v) C₁₂E₉/MES mixed surfactant solution was studied using Ubbelohde suspended level viscometer. The temperatures were 30, 35, 40 and 45° and were maintained within ($\pm 1^\circ$) in a thermostated bath.

Foam height was measured using a variation of Ross-Miles method³⁴. 200 ml. of surfactant solution of known concentration (5.8 mM) was allowed a free fall into 50 ml. of the same solution through a tube 90 cm long (1.5 cm internal diameter). The reproducibility of initial foam height values was within $\pm 2\%$.

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