Chapter V

Physico-chemical properties of aqueous α-sulfonato palmitic acid methyl ester - nonaoxyethylene monododecyl ether surfactant mixture

Abstract

The physico-chemical properties of aqueous binary α-sulfonato palmitic acid methyl ester (PES) - nonaoxyethylene monododecyl ether ($C_{12}E_9$) mixed surfactant system was studied by means of surface tension, conductivity and fluorescence measurements. The mixed critical micelle concentration values (cmcs) were intermediate between the respective surfactants' cmcs and the interaction parameter (β^m) values were negative indicating non-ideal mixing as well as attractive interaction between the constituent surfactants in the mixed micelle. The thermodynamic parameters of micellization ($\Delta G_m^0, \Delta H_m^0$ and ΔS_m^0) as well as adsorption (ΔG_{ad}^0, ΔH_{ad}^0 and ΔS_{ad}^0) and interfacial properties at the air/water interface (Γ_{max} & A_{min}) were also determined and are discussed. Steady state fluorescence measurements were employed to determine the micellar aggregation number and microenvironment/micropolarity in the mixed micelle; mixed micellar interiors are observed to be polar. The effect of various tetra alkyl ammonium bromides having different alkyl chains on the cloud point of 1% (w/v) $C_{12}E_9$ solution was also studied. Performance properties viz. foaming and viscosity of single as well as mixed surfactant system at different mole ratios were studied at different temperatures and are observed to be dependent on solution composition.

Introduction

The intrinsic duality of surfactant molecule due to the presence of both hydrophilic (water loving) and hydrophobic (water hating) moieties is responsible for aggregation of surfactants into micelles and other nanometer scale structures in aqueous solution [1] and thus for their wide spread application in modern chemistry. Surfactant systems used for practical applications mostly consist of mixtures of surfactants, either because commercial surfactants are always mixtures due to the raw materials used and method of manufacture or because mixtures of surfactants often show better performance properties than individual surfactants [2-3]. Hence study of mixing in surfactant systems has for some time now been an area of interest in academic and industrial research [4-8]. Extensive reports exist in literature on studies of different combinations of mixed surfactant systems viz. cationic-cationic [9], nonionic-nonionic [9,10], anionic-cationic [9,11], anionic-nonionic [4,12], zwitterionic-ionic [13,14]. The aggregation of surfactants in aqueous solution is controlled by the competition between the tendency of the hydrophilic head of the surfactant to deeply interact with the solvent and the tendecncy of hydophobic tail to avoid this kind of interaction. When surfactants of dissimilar charges are mixed together in water, several physicochemical properties of the mixed system compared to that of single surfactant system are changed, which may be due to the fact that there is a net interaction between the constituent amphiphiles. Also, in aqueous solution of two or more surfactants, the aggregation process is controlled by interactions of each solute with the solvent and by the interactions amongst the solutes themselves. The compromise is reached, organizing the molecules into aggregates i.e., 'micelle', where both these tendencies balance. Ionic-nonionic surfactant mixtures are commonly used in many practical applications, as the solution behavior of these surfactants can be complementary and also from fundamental viewpoint, ionic-nonionic surfactant mixtures are important as they exhibit highly non-ideal behavior. Also, the addition of nonionic surfactant to an ionic surfactant micelle can reduce the electrostatic repulsions between the charged surfactant head groups and thus facilitate mixed micelle formation [15].

In order to characterize the mixed micellization of surfactants in ionic-nonionic surfactant mixture, we have reported detailed investigation on physico-chemical and performance

properties of anionic-nonionic surfactant mixture at different temperatures. The surfactant mixture, we have chosen includes a nonionic surfactant of alkyl poly ethylene oxide type ($C_{12}E_9$) – which are widely used as detergents, emulsifiers and solubilizer [10]; whereas anionic surfactant is of α-sulfonato fatty acid methyl ester class (PES) - having superior detergency for fabrics, good tolerance against calcium ions and good biodegradability [16, 17]. Practically, the understanding of fundamentals of micellization as well as nature of interactions between these surfactants in the mixed micelle can help in formulating an eco-friendly detergent with desirable performance properties.

2. Materials and methods.

2.1 Materials.

Nonaoxyethylene monododecyl ether [$CH_3(CH_2)_{11}(OCH_2CH_2)_9OH$] i.e., $C_{12}E_9$, [MW=582.8] and α-sulfonato palmitic acid methyl ester – $C_{14}H_{29}CH(SO_3Na)COOCH_3$ i.e., PES [MW=372.5] were obtained from Lion Corporation, Tokyo, Japan as a gift. PES was recrystallized thrice from dry ethanol prior to use. Tetraethylammonium bromide, tetrapropylammonium bromide and tetrabutylammonium bromide were of Spectrochem India, whereas tetraethylammonium bromide was purchased from BDH, England. Cetyl pyridinium chloride procured from Loba Chemie, Baroda, India was recrystallized twice from benzene. Pyrene (Fluka, Germany) was recrystallized from cyclohexane. All solutions were prepared using doubly distilled water.

2.2 Surface tension measurements.

Surface tension (γ) was measured by the ring method using a duNouy tensiometer (S. C. Dey & Co.) at 30, 35, 40 and 45°C. Temperatures were maintained within ± 0.1°C by circulating thermostated water through a jacketed vessel containing the solution. Representative illustrations of surface tension (γ) vs. surfactant concentration ($\log_{10}C$) are shown in Figure 1. Reproducibility of surface tension measurements was ± 0.1 dyne cm^{-1}. The plot of surface tension vs. concentration did not show any minimum.
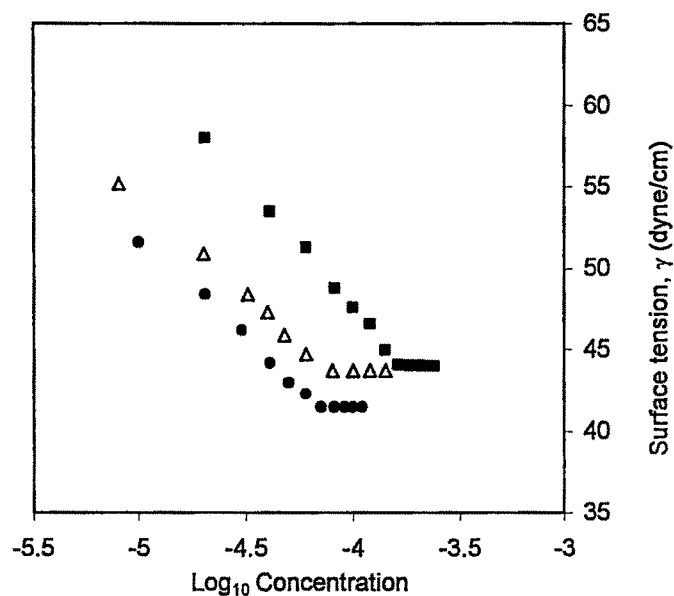
Figure 1: Representative plots of Surface tension (γ) vs $\log_{10}C$ of surfactant. • - 9 : 1, $C_{12}E_9$: PES at 308 K, ■ - 1 : 9 , $C_{12}E_9$: PES at 318 K, △ - 7 : 3 , $C_{12}E_9$: PES at 318 K.
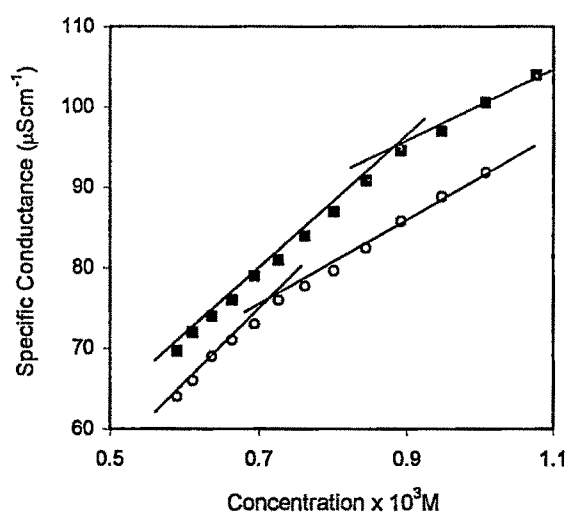

Figure 2: Representative plots of Specific conductance (κ) vs. Concentration of PES.

O - PES at 308 K, ■ - PES at 318 K.

2.3 Conductance measurements.

Conductance measurements were made with Welltronix (India), conductivity bridge. A dip-type cell of cell constant 1.01 cm^{-1} was used. Aliquot additions of stock surfactant solutions to given volumes of thermostated solvent, were made to prepare solutions for measurement.. 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, was measured. Conductance (k) vs concentration of surfactant (mole $litre^{-1}$) plots are shown in Figure 2 for pure PES only, as no break in the conductance vs concentration plots was observed in any of the mixed surfactant systems.

2.4 Cloud Point measurement.

Cloud Point (CP) of $C_{12}E_9$ (1% w/v) solution in presence of different tetraalkylammonium bromides was determined. The method for cloud point determination was same as described earlier [18]. The cloud points are the averages of temperatures at which clouding appears and then disappears. These temperatures did not differ by more than $0.4°C$.

2.5 Fluorescence measurements.

The micellar aggregation number (N_{agg}) of surfactant solutions was determined by steady state fluorescence measurements. Pyrene was used as a probe and cetyl pyridinium chloride as quencher. Excitation and emission wavelengths were 335 and 385 nm, respectively. All the measurements were carried out at room temperature (~ $25°C$) with a Hitachi F-4010 Fluorescence spectrophotometer. Excitation and emission band passes were 3 and 1.5 nm, respectively. The scan speed was $60nm\ min^{-1}$. Each spectrum had five vibronic peaks in the range 350-430 nm (Fig. 3). Each trace in Fig. 3 represents a different quencher concentration. The lowest quencher concentration being 'a' (zero) and the highest being 'g' (12×10^{-5}).
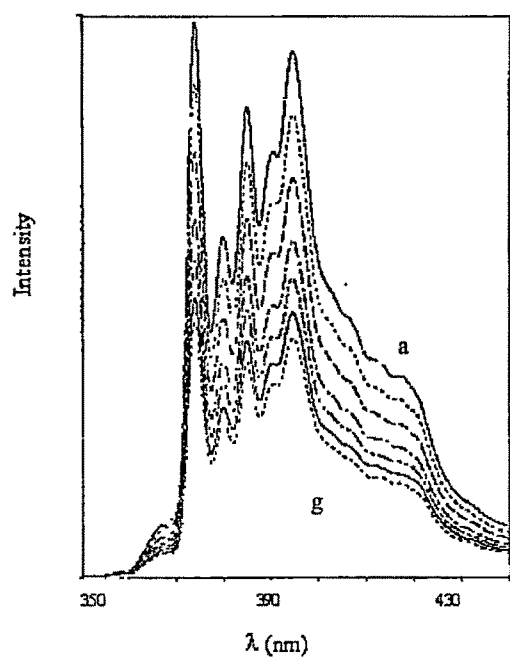
Figure 3: Representative emission fluorescence spectra of 10^{-6} M pyrene in aqueous micellar solution of $C_{12}E_9$: PES (7 : 3).
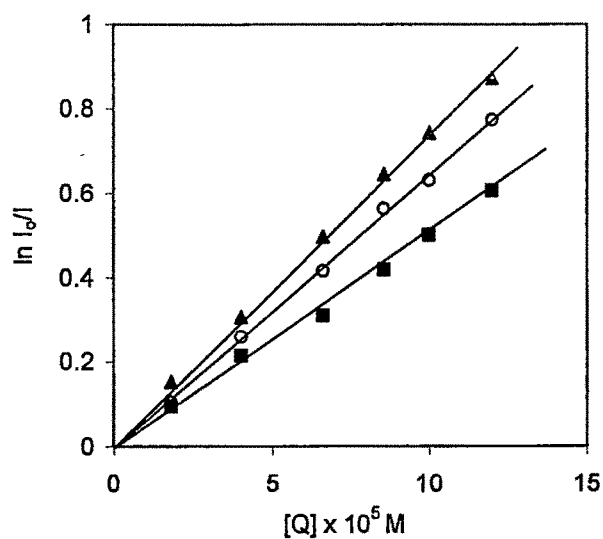

Figure 4: Representative plots of ln Io/I vs Cetyl Pyridinium Chloride Concentration [Q] for $C_{12}E_9$/PES mixed surfactant system. ▲ - $C_{12}E_9$, o – 9:1 $C_{12}E_9$: PES, ■ – PES.

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 the concentration of pyrene was kept constant at 10^{-6} M. The quencher concentration was varied from 0 to 12×10^{-5}M (Fig. 4). N_{agg} was deduced from the following equation [19],

$$\ln I = \ln I_0 - N_{agg}. [Q]/([S] - CMC) \qquad [1]$$

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. I_0 & I values also can be used to calculate the Stern-Volmer binding constant K_{SV} by using the following relation [20],

$$I_0/I = 1 + K_{SV} [Q] \qquad [2]$$

where K_{SV} is a product of k_q, the bimolecular quenching reaction constant and τ, the life time of the fluorescence molecule. High K_{SV} values indicate that the quenching process is the result of bimolecular collision and not a first-order decay.

2.6 Viscosity.

The interaction of water with both the hydrophobic core and the hydrophilic outer shell of the micelles contribute to the viscosity of a surfactant solution [21]. Moreover, viscosity is a measure of solute-solvent interaction as well as shape and size of the micelle. The latter are affected by temperature changes. Hence, we determined the relative viscosity values of 5% (w/v) $C_{12}E_9$/PES mixed surfactant solutions by using a Ubbelohde suspended level viscometer at 30, 35, 40 and 45°C, in order to understand the effect of temperature as well as mixed micelle composition on the geometry of micelles as well as interactions within the micellar core. The intrinsic viscosity $|\eta|$ can be calculated using the relation,

$$|\eta| = \lim_{C \to 0} \frac{(\eta_r - 1)}{C} \qquad [3]$$

where limit $C \to 0$ suggests that intermolecular interactions are absent and η_r indicates the relative viscosity of the surfactant solution. Some researchers [22,23] have taken $|\eta|$

to be equal to $(\eta_r - 1)/C$ without the condition of limiting concentration. $|\eta|$ has been defined as the shape factor and is expected to have a value between 2.5 and 4 cm^3g^{-1} for globular particles; it becomes very large for elongated particles [24]. In this article, we calculated $|\eta|$ without taking the zero concentration limit as we did earlier [25,26].

2.7 Foaming.

Foam height was measured using a variation of the Ross-Miles method [22]. Two hundred millilitres of surfactant solution (5.8 mM) was allowed to fall freely into 50 mL of the same solution through a tube 90-cm long tube (1.5 cm internal diameter). The reproducibility of initial foam height values was ± 2%. Normal statistical procedures were used in the data treatment.

3. Results and discussion

3.1 Critical micelle concentration. The critical micelle concentration (cmc) values of single as well as binary surfactant mixture ($C_{12}E_9$/PES) were evaluated at different temperatures (Table 1). The cmcs of binary combinations fall between the cmc values of the constituent surfactants. The cmc values for nonionic surfactant ($C_{12}E_9$) as well as for $C_{12}E_9$/PES mixture decrease with increase in temperature. The decrease in cmc of $C_{12}E_9$ with increase in temperature results due to subsequent dehydration of ethylene oxide moiety of $C_{12}E_9$ molecule, resulting in increase of hydrophobic interaction; which facilitates micelle formation. Whereas, the cmc values for anionic surfactant (PES), increase with increase in temperature due to subsequent increase in hydrophilicity, hence interplay between increased solubility as well as repulsions between the charged surfactant head groups, which oppose micelle formation [28, 29]. The magnitude of cmc values of PES obtained by surface tension and conductivity measurements are different. Such variations in cmc values depending on the method of determination have been observed earlier too [30-32]. The reproducibility of cmc values evaluated by surface tension and conductivity measurements are less than 2%. This was determined by at least two measurements. The cmc values for $C_{12}E_9$/PES mixture at different temperatures were

evaluated by surface tension measurements only as specific conductance vs. concentration of surfactant profile for mixed surfactant system did not show any break and hence we treated $C_{12}E_9$/PES mixed micelles as nonionic.

Table 1. Critical Micelle Concentration, cmc (mM) Values of $C_{12}E_9$ / PES mixed Surfactant System In Aqueous Media.

N_{PES}	Critical micelle concentration, (mM)			
	303	308	313	318 K
0.0	0.0812	0.0794	0.0758	0.0741
0.1	0.0770	0.0692	0.063	0.0602
0.3	0.0831	0.0794	0.0776	0.0741
0.5	0.128	0.117	0.114	0.107
0.7	0.174	0.166	0.158	0.145
0.9	0.214	0.195	0.182	0.166
1.0	0.588 0.74* *(0.66)*	0.616 0.76 *(0.64)*	0.691 0.83 *(0.66)*	0.724 0.88 *(0.70)*

Values in parenthesis are the degree of ionization of micelle (α) of PES.

* cmc from Conductivity measurements

3.2 *Surfactant-Surfactant Interaction*. The cmc values for the mixed surfactant system can be calculated theoretically using the Clint's equation [33], if the cmc values for constituent surfactants of the mixed micelle are known. Clint's equation is

$$\frac{1}{cmc_{mix}} = \frac{\alpha_1}{cmc_1} + \frac{1 - \alpha_1}{cmc_2} \qquad [4]$$

where cmc_{mix}, cmc_1 and cmc_2 are the cmc values of the mixture, surfactant 1 i.e., PES and surfactant 2 i.e., $C_{12}E_9$ respectively. α_1 is the mole fraction of surfactant 1 and α_2 (i.e $1-\alpha_1$) is the mole fraction of surfactant 2 respectively.
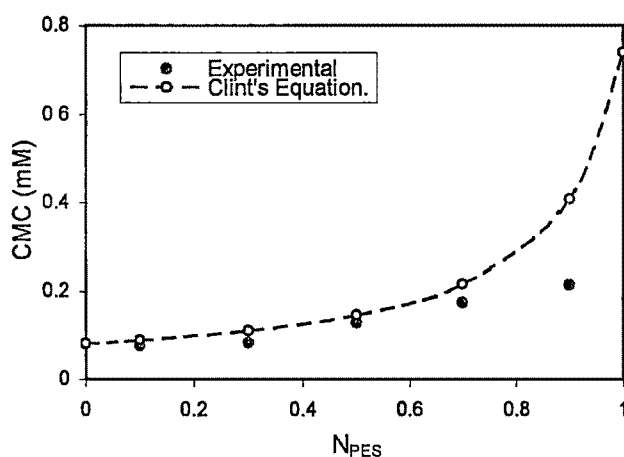

Figure 5: Representative plot of variation of cmc as a function of molefraction of PES for

$C_{12}E_9$/PES mixed surfactant system at 303 K

The cmc values for $C_{12}E_9$/PES mixed surfactant system obtained experimentally are lower than the cmc values calculated from Eq. 3 (Fig. 5). This indicates that there are interactions between the constituent surfactants in the mixed micelle, resulting in non-ideal behaviour. Hence, interaction parameter (β^m)– a measure of interaction between two different surfactants relative to the self interaction of two surfactants under the same conditions before mixing; was evaluated from the critical micelle concentration data using Rubingh's method and equations [34],

$$\frac{(X_1)^2 \ln\left(\alpha_1 C_{12} \Big/ X_1 C_1\right)}{(1-X_1)^2 \ln\left[(1-\alpha_1)C_{12} \Big/ (1-X_1)C_2\right]} = 1 \qquad [5]$$

$$\beta^m = \frac{\ln\left(\alpha_1 C_{12} \Big/ X_1 C_1\right)}{(1-X_1)^2} \qquad [6]$$

where X_1 is the mole fraction of surfactant 1 in the mixed surfactant micelle, C_1, C_2 and C_{12} are the critical micelle concentrations of surfactant 1, surfactant 2, and their mixture, respectively at the mole fraction α_1.

Table 2. Interaction Parameter (β) Values of $C_{12}E_9$/PES Mixed Surfactant System In Aqueous Media At Different Temperatures.

N_{PES}	Interaction Parameter (β^m)			
	Temperature (K)			
	303	308	313	318
0.1	-2.77/-3.0[†] (0.115)	-3.58/-3.83 (0.149)	-4.13/-4.35 (0.164)	-4.38/-4.61 (0.170)
0.3	-2.49/-2.78 (0.204)	-2.72/-2.98 (0.210)	-2.77/-3.00 (0.199)	-3.01/-3.25 (0.205)
0.5	-0.83/-1.11 (0.188)	-1.33/-1.60 (0.215)	-1.41/-1.64 (0.201)	-1.749/-1.99 (0.216)
0.7	-0.81/-1.14 (0.306)	-1.03/-1.33 (0.308)	-1.27/-1.53 (0.299)	-1.67/-1.95 (0.31)
0.9	-2.11/-2.58 (0.526)	-2.54/-3.05 (0.516)	-2.96/-3.31 (0.498)	-3.37/-3.75 (0.492)

* Values in parentheses are X_1 i.e mole fraction of PES.

[†] The data after '/' was calculated using cmc of PES by ST Measurement

In case of micellar interaction these are cmc values. Equation 5 is solved iteratively for X_1, which is then substituted in Eq. 6 to calculate β^m. Table 2 lists the β^m values for $C_{12}E_9$/PES mixed surfactant system at different mole fractions. The β^m values are negative at all mole fractions of the mixed surfactant system suggesting stronger attractive interaction between $C_{12}E_9$ and PES in the mixed micelle. Nonionic surfactant of alkyl polyethylene oxide class ($C_{12}E_9$) has a weak cationic character resulting either from oxonium ion formation with protons from water or by sharing of hydrogen of water though hydrogen bond formation [35]. The negative values of β^m are a result of attraction between this weak cation and anionic surfactant PES. Although the cmc values of PES obtained by surface tension and conductance measurements differ, the β^m values computed using both the cmc data do not differ much and the interaction is always attractive. The composition of the micelles remains unperturbed. The maximum difference in X_1 values by using different cmc values (i.e either conductance or surface tension) was ~5% though in most cases it was less than 3%. This indicates that the composition of mixed micelles is without much error. The calculated values of mole fraction of PES (X_1) in the mixed micellar compositions are found to be low compared to the stoichiometric values suggesting less transfer of PES from the solution to the micellar phase [36]. The activity coefficient values were also evaluated using the relations [27],

$$\ln f_1 = \beta^m (1 - X_1)^2 \tag{7}$$

$$\ln f_2 = \beta^m (X_1^2) \tag{8}$$

where X_1 is mole fraction of surfactant 1(i.e PES) in the micelle and f_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 3. The activity coefficient values of PES are low and though activity coefficient values of $C_{12}E_9$ (f_2) are higher, they are not close to unity indicating that $C_{12}E_9$ and PES in the mixed micelle are away from the standard state.

Table 3. Activity Coefficient (f_1 & f_2) Values of $C_{12}E_9$/PES Mixed Surfactant System In Aqueous Media At Different Temperatures.

N_{PES}	Activity coefficient (f_1) of anionic surfactant			
	Temperature (K)			
	303	308	313	318
0.1	0.115 (0.964)	0.070 (0.923)	0.055 (0.895)	0.049 (0.881)
0.3	0.206 (0.901)	0.183 (0.887)	0.169 (0.896)	0.149 (0.88)
0.5	0.578 (0.97)	0.440 (0.94)	0.400 (0.94)	0.340 (0.92)
0.7	0.676 (0.92)	0.490 (0.906)	0.530 (0.892)	0.450 (0.851)
0.9	0.622 (0.56)	0.550 (0.47)	0.474 (0.48)	0.419 (0.442)

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

3.3 Thermodynamics of micellization and interfacial adsorption. The standard free energy of micellization of nonionic surfactant is given by the relation [28],

$$\Delta G_m^0 = RT \ln X_{cmc} \qquad [9]$$

where X_{cmc} is the cmc in mole fraction scale, whereas for an ionic surfactant

$$\Delta G_m^0 = (2 - \alpha)RT \ln X_{cmc} \qquad [10]$$

The degree of ionization of micelle (α) was computed from the ratio between the slopes of the post micellar and premicellar regions of the specific conductance vs. concentration profile of PES [37]. We did not observe a break point in the specific conductance vs. concentration of surfactant profile for $C_{12}E_9$/PES mixed surfactant system and hence treated the mixed systems as nonionic and calculated ΔG_m^0 using Eq. 9.

Table 4. The Thermodynamic Parameters of Micellization of $C_{12}E_9$/PES
Mixed Surfactant System.

N_{PES}	$-\Delta G_m^0$ (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	6.1	132
0.1	33.9	34.8	35.6	36.3	14.5	160
0.3	33.8	34.4	35.0	35.7	4.4	126
0.5	32.7	33.4	34.0	34.8	9.1	138
0.7	31.9	32.5	33.2	34.0	10.6	140
0.9	31.4	32.1	32.8	33.6	12.8	146
1.0*	37.9	39	38.7	38	-69.9	-100

* In this ΔG_m^0-T plot, the point at temperature 303 K was dropped.
The correlation coefficient was ~0.99, for all plots.

The ΔG_m^0 values are presented in Table 4, where all ΔG_m^0 values are negative and become increasingly negative with an increase in temperature suggesting spontaneous micelle formation. The standard enthalpy (ΔH_m^0) and standard entropy (ΔS_m^0) of micellization were evaluated from a ΔG_m^0 vs. temperature plot. The slope and intercept gave ΔS_m^0 and ΔH_m^0 respectively. The micellization process is found to be endothermic for $C_{12}E_9$ as well as mixed surfactant system at all mole fraction. This is quite obvious as the cmc values for $C_{12}E_9$ as well as $C_{12}E_9$/PES mixed surfactant system decreases with increase in temperature, which indicates that thermodynamically the system is endothermic. The micellization process for PES is found to be exothermic. All values of

entropy of micellization ΔS_m^0 are positive suggesting that micellization process is entropy dominanted except in the pure PES system, where ΔG_m^0 vs. temperature plot shows a minimum. The standard free energy of interfacial adsorption (ΔG_{ad}^0) per mole of monomer unit with reference to the standard state of unit mole fraction has been obtained from the relation [38,39],

$$\Delta G_{ad}^{\circ} = RT \ln cmc - N\Pi_{cmc}A_{cmc} \qquad [11]$$

where N, Π_{cmc} and A_{cmc} are Avogadro number, surface pressure at cmc (γ_0-γ_{cmc}) and area per molecule at cmc respectively. The second term in Eq. 11 represents surface work involved in going from zero surface pressure to the surface pressure at cmc (Π_{cmc}) at a constant minimum surface area per molecule. The ΔG_{ad}^0, ΔH_{ad}^0 and ΔS_{ad}^0 values are presented in Table 5.

Table 5. The Thermodynamic Parameters of Adsorption of $C_{12}E_9$ / PES Mixed Surfactant System.

N_{PES}	$-\Delta G_{ad}^0$ (kJmol^{-1}) at				ΔH_{ad}^0 (kJmol^{-1})	ΔS_{ad}^0 (Jmol^{-1}K^{-1})
	303	308	313	318 K		
0.0*	40.6	41.6	44.1	43.4	44.4	280
0.1	45.6	46.3	47.0	47.5	-6.8	128
0.3	43.0	43.9	44.4	45.1	-1.9	136
0.5	43.6	44.6	45.6	46.4	13.3	188
0.7	40.6	42.7	43.2	44.1	25.6	220
0.9	38.9	40.0	41.3	42.0	25.2	212
1.0	58.3	55.8	58.7	60.3	-	-

*In this ΔG_{ad}^0-T plot, the point at temperature 303 K was dropped.

The ΔG_{ad}^{0} values in Table 5 suggest that, the adsorption of surfactants at the air/water interface is more spontaneous than micellization process and that micellization occurs only after the interface becomes saturated with the monomeric surfactant. All the values of entropy of adsorption of surfactant (ΔS_{ad}^{0}) are positive reflecting greater freedom of motion of hydrocarbon chains of surfactant monomers at the planar air/water interface compared to that in the cramped interior beneath the convex surface of the micelle [39].

The maximum surface excess ($\Gamma_{max.}$) is an effective measure of adsorption of surfactants at the air/water interface. The $\Gamma_{max.}$ and limiting surface area per moelcule $A_{min.}$ values calculated using Gibbs adsorption equation [38] are presented in Table 6. The slope of the tangent at the given concentration of the surface tension (γ) vs. $\log_{10}C$ plot i.e., ($d\gamma/d\log C$) was used to calculate Γ_{max}

Table 6. Maximum Surface Excess (Γ_{max}) And Limiting Surface Area Per Molecule ($A_{min.}$) of $C_{12}E_9$/ PES Mixed Surfactant Systems.

N_{PES}	$\Gamma_{max.} \times 10^{10}$ mol cm^{-2} at				A_{min} (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	2.27	2.44	2.55	2.55	0.73	0.68	0.65	0.65
0.3	2.96	2.51	2.76	2.55	0.56	0.66	0.60	0.65
0.5	2.76	2.76	2.37	2.51	0.60	0.60	0.70	0.66
0.7	2.86	3.13	2.40	2.37	0.58	0.53	0.69	0.70
0.9	3.13	3.19	2.96	2.96	0.53	0.52	0.56	0.56
1.0	1.23	1.18	1.13	1.03	1.35	1.4	1.47	1.61

This was obtained by fitting a curve to a polynomial of the form $y = ax^2 + bx + c$ in Microsoft Excel. The R^2 (Regression coefficient) value for the fit lies between 0.9945 and 0.9999. The lower values of $A_{min.}$ in mixed system can be related to closer packing at the interface owing to the decreased repulsion between the oriented headgroups in a binary combination.

3.4 Micellar Aggregation and Micropolarity. Figure 6 illustrates the variation of micellar aggregation number ($N_{agg.}$) as a function of mole fraction of PES for $C_{12}E_9$/PES mixed surfactant system. The micellar aggregation number (N_{agg}) values of mixtures are higher than those of pure PES, but are in general lower than that of $C_{12}E_9$. The decrease in $N_{agg.}$ with increasing concentration of PES in the mixed micelle is due to the corresponding increase in the repulsive interactions between the charged PES headgroups as $C_{12}E_9$ molecules are progressively replaced by PES. Thus the smallest aggregation number corresponds to the surfactant with highest charge density i.e pure anionic surfactant PES [40].
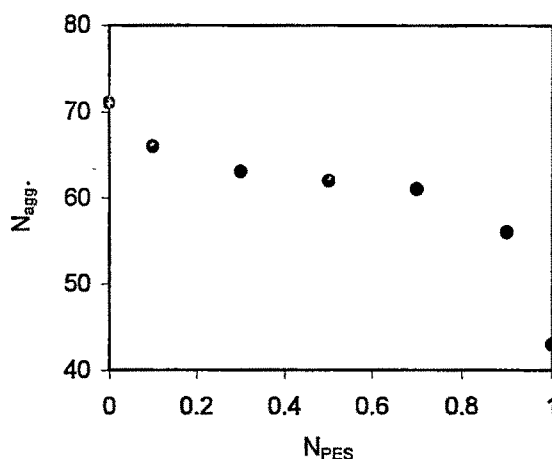

Figure 6: Plot of Micellar Aggregation Number (N_{agg}) vs Mole fraction of PES (N_{PES}) $C_{12}E_9$/PES mixed surfactant system at room temperature (~25°C).

The ratio of intensity of first (I_1) and third (I_3) vibronic peaks (I_1/I_3) of the pyrene fluorescence emission spectrum is sensitive to local polarity around the probe [41]. Figure 3 represents seven representative plots of intensity against wave length (emission) of the binary combination of surfactant to yield (I_1/I_3) value. Low values of (I_1/I_3) indicate that microenvironment of solubilized probe (pyrene) to be non-polar as in hydrocarbon solvents such as 0.6 for cyclohexane and hexane [42,43]. The higher (I_1/I_3) value is an indication of polar environment around pyrene. Table 6 contains the values of (I_1/I_3) ratio for pure and mixed micellar aggregates. It is observed that microenvironment around pyrene is more polar in $C_{12}E_9$ as compared to PES, the polarity of the mixed micellar aggregates lies in the intermediate range.

Table 7. Micropolarity (I_1/I_3), Binding Constant (K_{SV}) And Apparent Dielectric

Constant For (ε) $C_{12}E_9$/ PES Mixed Surfactant System.

N_{PES}	(I_1/I_3),	(K_{SV}) x 10^{-4} (l mol^{-1})	ε_{exp}	ε_{cal}
0	1.22	1.2	17.4	17.4
0.1	1.19	1.04	14.8	15.9
0.3	1.18	1.02	14	14.4
0.5	1.16	0.96	12.2	14.6
0.7	1.14	0.93	10.5	12.9
0.9	1.09	0.78	6.7	9.7
1.0	1.05	0.07	2.76	2.76

The K_{SV} values calculated from Eq. 2, are presented in Table 6. K_{SV} is the ratio of bimolecular quenching constant to unimolecular decay constant. Also K_{SV} is the product of k_q, the rate constant of quenching process and τ, the actual lifetime of fluorescent probe in absence of bimolecular quenching [19]. Thus from the values of K_{SV}, we can conclude that quenching is efficient and also the life time of the pyrene in $C_{12}E_9$ and most of the mole ratios in the mixed micelle is higher, if we assume that k_qs for all systems are

of similar magnitude. The dielectric constant (ε) of the medium (i.e pyrene environment inside the micelle) was evaluated by using the relation [44].

$$\frac{I_1}{I_3} = 0.0116\varepsilon + 1.01798 \qquad [12]$$

from the experimental I_1/I_3 data. The dielectric constant (ε) inside the mixed micelle can be computed from the following equation

$$\varepsilon = \sum X_i \varepsilon_i \qquad [13]$$

In Table 6, the experimentally determined and calculated dielectric constants are presented. The experimental values differed from the calculated values. Such difference is expected as the surfactants are having attractive interaction inside the micelle.

3.5 Viscosity. Viscosity is an important physico-chemical property of surfactant solution. Inspite of its importance, very few studies on the viscosity of mixed surfactant systems in aqueous medium have been carried out. Figure 7 represents the effect of mole fraction of PES in the $C_{12}E_9$/PES mixed surfactant solutions. The relative viscosities of aqueous solutions of the surfactant systems were measured at different temperatures (30, 35, 40 and 45°C).
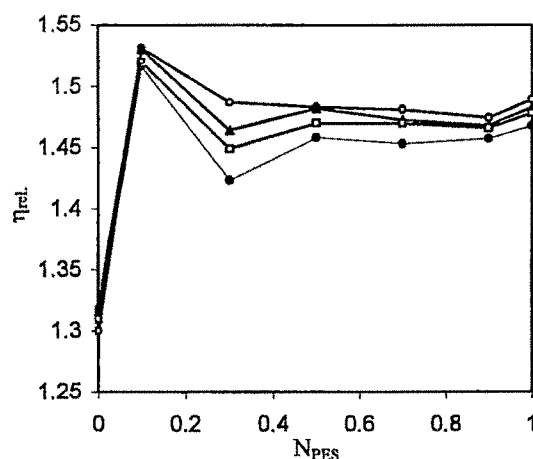

Figure 7: Plot of relative viscosity (η_{rel}) vs. mole fraction of PES (N_{PES}). O - 303 K, ▲ - 308 K,

□ - 313 K, 318 K.

It is clear from Fig. 7 that the relative viscosity $(\eta_{rel.})$ of mixed surfactant systems show a slight maximum at a mixture of mole fraction ~0.1 and above this mole fraction it becomes almost equal to η_r of PES. The positive deviation in relative viscosity has also been previously observed for $SDS/C_{16}POE_{40}$ [44] and SDBS/Triton X-100 mixed surfactant systems [25]. The cmc values for $C_{12}E_9/PES$ mixed surfactant system are listed in Table 1. It is evident that, the cmc values at $N_{PES} = 0.1$ are lower than the cmc values of both the constituent surfactants, indicating more easy mixed micelle formation at this mole ratio as compared to other mole ratios of the surfactant mixture. A colloidal particle has a hydrated layer around it and has an electrical surface charge (electroviscous effect). Both these factors can affect the viscosity of micelles. The electroviscous effect is more in the systems, where the mixed micelle forms readily and hence both these factors (mixed micelle formation and electroviscous effect) are responsible for slight maxima and hence deviation of relative viscosity from the ideal line [25, 45].

It is expected that intrinsic viscosity $|\eta|$ value should be between 2.5 and 4 cm^3g^{-1} for globular particles. The lowest $|\eta|$ for this system is 6.2 cm^3g^{-1}, suggesting the micellar shape to be non-spherical in pure as well as mixed surfactant systems. The higher $|\eta|$ values in mixed system suggest rod like cylindrical micelles. The intermicellar interactions as well as chain/chain interactions of constituent surfactant molecules in the mixed micelle will be more for such micelles, resulting in a slight increase in relative viscosity of mixed micelle as compared to $C_{12}E_9$ and PES.

3.6 Cloud Point. The effect of various tetra alkyl ammonium ions having varying alkyl chain length [tetra methyl ammonium bromide (TMAB), tetra ethyl ammonium bromide (TEAB), tetra propyl ammonium bromide (TPAB) and tetra butyl ammonium bromide] on the cloud point of 1% solution of $C_{12}E_9$ was studied. Figure 8 illustrates the change in cloud point of $C_{12}E_9$ as a function of concentration of tetraalkyl ammonium bromides except TBAB (TMAB, TEAB and TPAB).
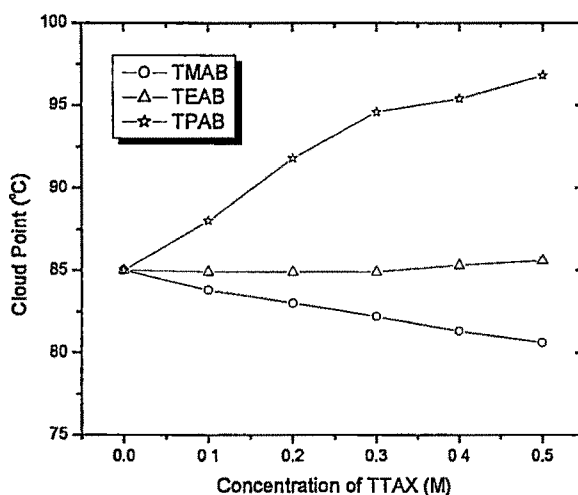
Figure 8: Change in cloud point of 1% (w/v) $C_{12}E_9$ solution as a function of different tetra alkyl ammonium bromides.

It is evident from Fig. 8 that, TMAB decreases the cloud point of $C_{12}E_9$), TEAB does not affect the CP much, whereas TPAB and TBAB increase the cloud point. The variation of CP as a function of [TBAB] is not illustrated in the figure, because the increase in cloud point is so high that we did not observe clouding of surfactant solution till 99°C. The decrease of cloud point of $C_{12}E_9$ in presence of TMAB is due to its water structure forming property, which ultimately decreases the availability of non-associated water molecules to hydrate the ether oxygens of the POE chain. The cloud point increase in case of TPAB and TBAB is ascribed to dominance of mixed micelle formation of these ions with nonionic surfactant over water structure formation. The mixed micelles thus formed with their cationic counter parts will have higher inter-micellar repulsions and stronger interaction with water and consequently clouding occurs at higher temperatures than the pure POE nonionic micelle [27,46].

3.7 Foaming. Nonionic surfactants of poly oxyethylene class are known to be less foaming, whereas ionic surfactants have good foam forming property. A anionic-nonionic surfactant mixture would be important and useful to optimize and tune the foaminess to users requirement. The initial foam heights indicative of foamability of surfactant were

determined at 30, 35 and 40 °C for pure as well as mixed surfactant system using the method described earlier. Concentration of surfactant was kept 5.8 mM, since foaminess is usually studied at 0.25% surfactant concentration (~5.8mM). It is evident from Fig. 9 that, foaminess of pure as well as mixed surfactant system increases with increase in temperature. The initial foam heights for $C_{12}E_9$ are low compared to PES as well as mixed surfactant system. This is obvious as poly oxyethylene group in $C_{12}E_9$ has large surface area and also there is absence of highly charges surface films [38]. The foam heights for PES are highest and they increase with temperature, because α-sulfo esters containing 16-17 carbon atoms show maximum foaming at higher temperatures. The higher foam heights for mixed surfactant system at different mole fractions are due to the possibility of rapid variation of concentration of surfactant at air/water interface in mixed surfactant system, which is an important prerequisite for good foam forming qualities.
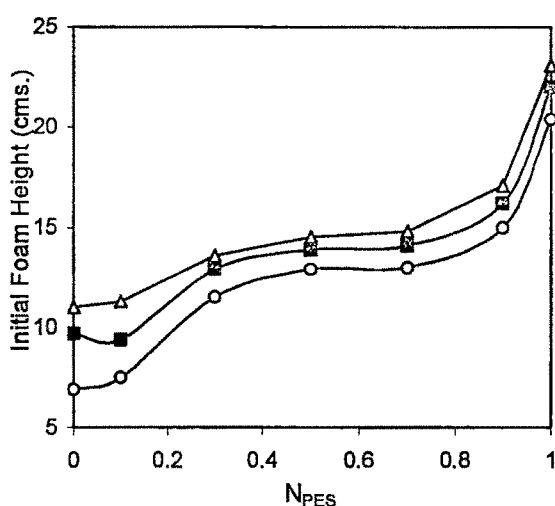

Figure 9: Plot of Initial foam height (cms) vs. mole fraction of PES (N_{PES}).O - 303 K,

■ - 308 K, △ - 313 K.

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