
Chapter III

**α - Sulfonato Palmitic Acid Methyl Ester–Hexaoxyethylene Monododecyl
Ether Mixed Surfactant System: Interfacial, Thermodynamic, and
Performance Property Study**

ABSTRACT: Interfacial, thermodynamic and performance properties of aqueous binary mixtures of α -sulfonato palmitic acid methyl ester, $C_{14}H_{29}CH(SO_3Na)COOCH_3$ (PES), and Hexaoxyethylene monododecyl ether, $CH_3(CH_2)_{11}(OCH_2CH_2)_6OH$ ($C_{12}E_6$), were investigated with tensiometric, conductometric, fluorimetric and viscometric techniques. The critical micelle concentration (cmc), maximum surface excess, minimum area per molecule of surfactant at the air/water interface, and thermodynamics of micellization and adsorption were determined. The CMC was very low for mixed systems, indicating probable use as detergent with less effect on environment because of surfactant biodegradability and less amount in environment. The interaction parameter β^m , computed by using the theory of Rubingh and Maeda indicated an attractive interaction (synergism) between the surfactant molecules, which was also confirmed by proton nuclear magnetic resonance studies in the mixed micelle. The micellar aggregation number (N_{agg}) determined by using steady-state fluorescence quenching method at a total surfactant concentration of about ~ 10 mM at $25^\circ C$, was almost independent of surfactant mixture composition. The micropolarity and the binding constant (K_{sv}) for the $C_{12}E_6$ /PES mixed system were determined by the ratio of intensities (I_1/I_3) of the pyrene fluorescence emission spectrum and local microenvironment inside the micelle was found to be polar. The viscosity of the mixed system at all mole fractions suggested that mixed micelles are non-spherical in nature. The cloud point of oxyethylene group-containing surfactant was increased by addition of PES. Foaming was temperature dependent, and a 1:1 mixed system showed minimum foaming. All performance properties were found to be composition dependent.

KEY WORDS: Foaming, interaction parameter, micellization, mixed surfactant, viscosity.

Abbreviations:

α , degree of ionization of micelle; A_{CMC} , area per molecule at cmc; A_{min} , limiting surface area per molecule:area per molecule; $-\beta^m$, interaction parameter; γ , surface tension; Γ_{max} , maximum surface excess; $C_{12}E_6$, hexaoxyethylene monododecyl ether; CMC, critical micelle concentration; CP, cloud point; ϵ , dielectric constant; f_1 , activity coefficient of surfactant 1 (PES) in the micelle; η , intrinsic viscosity; η_r , relative viscosity; K_{sv} , Stern- Volmer binding constant; N_{agg} , micellar aggregation number; NMR, nuclear magnetic resonance; N_{PES} , stoichiometric mole fraction of PES in the mixture; PES, α -sulfonato palmitic acid methyl ester; σ , Traube's constant; X_1 , mole fraction of ionic surfactant in the mixed micelle; X_{cmc} , CMC expressed as mole fraction.

The association of surfactant molecules into finite sized molecular aggregates such as micelles in aqueous solution is significant for their use in solubilization, catalysis, dispersion, technological, biochemical and pharmaceutical formulations (1,2). In practical applications, mixed surfactants exhibit superior performance than single surfactants and composition as well as concentration can be optimized for a particular application (3). The synergistic interactions between surfactant molecules in the mixed surfactant systems may be exploited to reduce the total amount of surfactant used in a particular application and this will ultimately lead to reduction of cost and environmental impact (4). Because of their distinctive behaviour compared to single surfactants, mixed surfactant systems such as nonionic-nonionic (5,6), nonionic-anionic (7,8), nonionic-cationic (9), anionic-zwitterionic (10) combinations, have attracted attention both in theoretical studies and in practical applications (11). Determination of various physico-chemical properties of surfactant mixture can provide a means to optimize their properties.

We have studied the physicochemical properties of α -sulfonato palmitic acid methyl ester (PES), an anionic surfactant in the presence of hexaoxyethylene monododecyl ether ($C_{12}E_6$), a nonionic surfactant. Besides their ready availability from renewable vegetable material and good biodegradability, PES have superior detergency for fabrics and a high tolerance against calcium ions¹², indicating it can possibly be used in hard water. Moreover the mixed system is expected to have low CMC values; hence, the required amount for use will be low which is important from both cost and environmental point of view. We are also interested in comparing properties of the various fatty acid derivatives (eg. myristic acid, palmitic acid, stearic acid etc.) in mixed systems with $C_{12}E_6$ to determine which mixture will be a better detergent from all points of view. It will also help in optimizing the biodegradability and minimize toxicity.

Physicochemical properties of binary mixtures of PES and $C_{12}E_6$ at different temperatures are reported here, including foaming, viscosity and cloud point. Rubingh's regular solution theory (13) is used to estimate the composition of mixed aggregates, activity coefficients, and interaction parameters of the surfactants.

EXPERIMENTAL PROCEDURES

Materials. C₁₂E₆ and PES were obtained from Lion Corporation (Tokyo, Japan). PES was recrystallized from dry alcohol. Cetyl pyridinium chloride, procured from Loba Chemie, (Baroda, India), was recrystallized twice from benzene. Pyrene (Fluka, Buchs, Switzerland) was recrystallized from cyclohexane. All solutions were prepared using doubly distilled water.

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 $\pm 0.1^\circ\text{C}$ by circulating thermostated water through a jacketed vessel containing the solution.

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.

Cloud point (CP) measurement. The CP of C₁₂E₆ (1% wt/vol) in the presence of increasing amounts of PES was determined as described earlier (14). The CP are averages of temperatures at which clouding appears and disappears. These temperatures did not differ by more than 0.4°C .

Fluorescence measurements. The micellar aggregation number (N_{agg}) of surfactant solutions was determined by steady state fluorescence measurements. Pyrene was used as probe and cetyl pyridinium chloride as quencher. Excitation and emission wavelengths were 335 and 385 nm, respectively. All measurements were carried out at room temperature ($\sim 25^\circ\text{C}$) with a Hitachi F-4010 Fluorescence spectrophotometer. Excitation and emission band passes were 3 and 1.5 nm, respectively. The scan speed was 60 nm min^{-1} . Each spectrum had five vibronic peaks in the range 350-430 nm (Fig. 1). Each trace represents a different quencher concentration.

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. N_{agg} was deduced from the following equation (15),

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

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 (17),

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

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

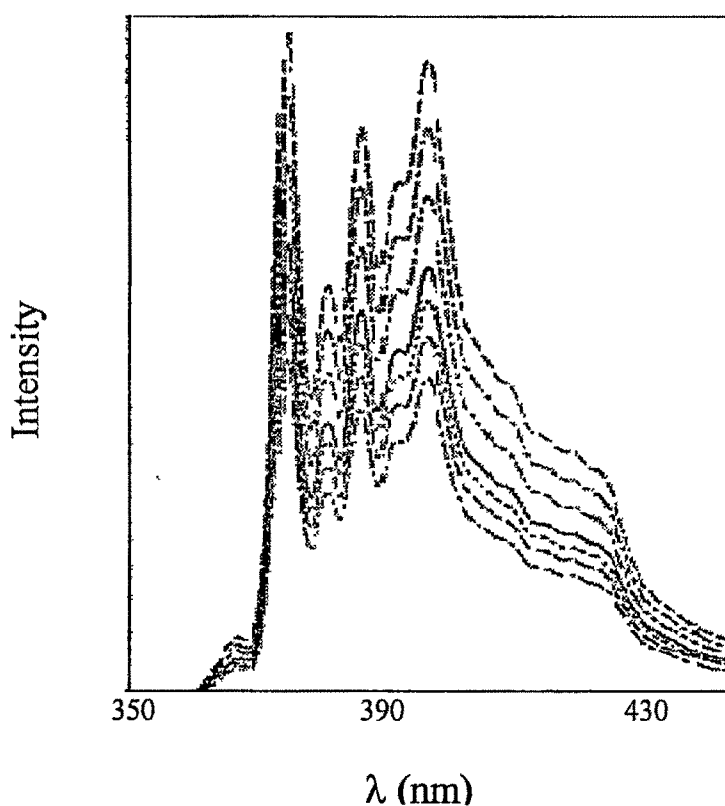


Fig. 1. Representative emission fluorescence spectra of 10^{-6} M pyrene in aqueous micellar solution of $C_{12}E_6/PES$ (5:5), at various quencher concentration. From top to bottom: (A) zero; (B) 1.8×10^{-5} M; (C) 4.0×10^{-5} M (D) 6.6×10^{-5} M; (E) $(8.6 \times 10^{-5}$ M); (F) 10×10^{-5} M; (G) 12×10^{-5} M.

the result of bimolecular collision and not a first-order decay. The ratio of intensity of first and third vibronic peaks (I_1/I_3) of the pyrene fluorescence emission spectrum in the presence of surfactants is an index of micropolarity of the system and provides an idea of microenvironment in the micelle (18).

NMR Measurement. Proton NMR measurements were carried out in deuterium oxide (D_2O , 99.9 atom % D; Aldrich, Milwaukee, WI) at room temperature ($\sim 25^\circ C$). The mixed solutions of PES and $C_{12}E_6$ with concentrations of 0.05M each were prepared for PES mole fractions of 0.0, 0.1, 0.3, 0.7, 0.9, and 1.0. Proton NMR spectra were recorded with Bruker Avance 300 spectrophotometer operating at 300 MHz. 1H NMR chemical shifts were referred to internal tetramethylsilane.

Viscosity. The interaction of water with both the hydrophobic core and the hydrophilic outer shell of the micelles contributes to the viscosity of a surfactant solution (18). Viscosity is a measure of solute-solvent interaction as well as shape and size of the micelle. The latter are affected by temperature changes. Thus, we determined the relative viscosity values of 5% (wt/vol) $C_{12}E_6$ /PES mixed surfactant solutions by using a Ubbelohde suspended level viscometer at 30, 35, 40 and $45^\circ C$, in order to understand the effect of temperature on geometry of micelles and the interactions within micellar core. The intrinsic viscosity $[\eta]$ can be calculated using the relation,

$$[\eta] = \lim (\eta_r - 1)/C \quad [3]$$

where limit $C \rightarrow 0$ suggests that intermolecular interactions are absent and η_r indicates the relative viscosity of the surfactant solution. Some researchers (19,20) 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 $4 \text{ cm}^3 \text{ g}^{-1}$ for globular particles; it becomes very large for elongated particles (21). In this article we calculated $[\eta]$ without taking the zero concentration limit as we did earlier (14).

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 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 $\pm 2\%$. Normal statistical procedures were used in the data treatment.

RESULTS AND DISCUSSION

Surface tension. Representative illustrations of surface tension (γ) vs surfactant concentration ($\log_{10}C$) are shown in Figure 2. Reproducibility of surface tension measurements was ± 0.1 dyn/cm. The plot of surface tension vs. concentration did not show any minimum.

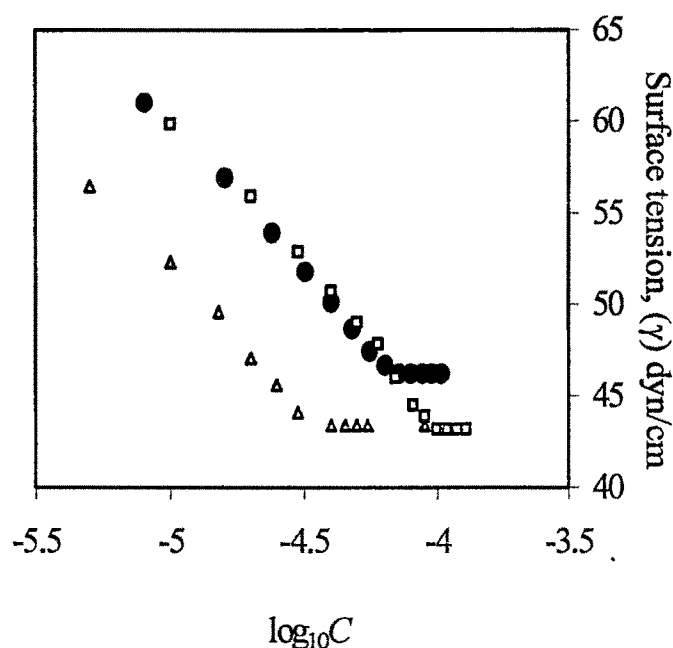


FIG. 1. Representative plots of surface tension (γ) vs. log concentration ($\log C$) of surfactant. (\square) - 3 : 7, $C_{12}E_6$: PES at 40 °C; (Δ)- 9 : 1; $C_{12}E_6$: PES at 45 °C, (\bullet) - 1 : 9 , $C_{12}E_6$ /PES at 45 °C.

Conductance. 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) 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.

CMC. Intramicellar interactions in surfactant mixtures are studied at their CMC, where their effect on mixed micelle formation can be measured (23). The CMC of pure and mixed surfactant systems were determined at different temperatures (Table 1).

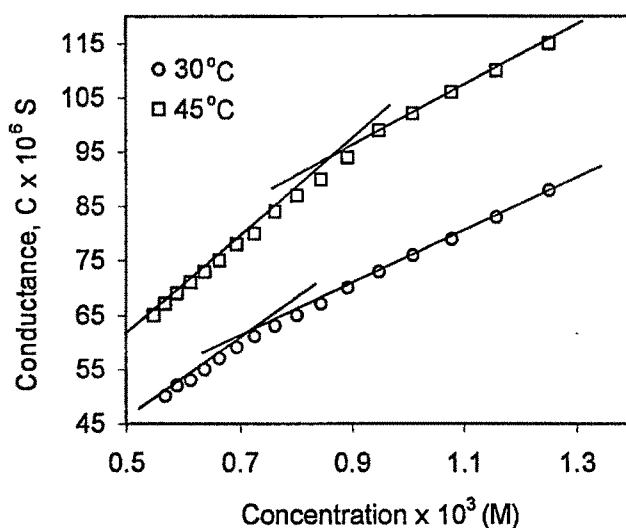


FIG. 2. Representative plots of Conductance (κ) vs. Concentration of PES.

(O) - PES at 30 °C; (□) - PES at 45 °C.

The CMC values of $C_{12}E_6$ decreased with increasing temperature. The CMC values at 30 and 35°C (71 and 62 μM , respectively) are reasonably close to 67 and 72 μM , respectively, obtained by two different earlier workers (see citations in Ref.24). Moreover, at 20°C, there are variations in CMC values of $C_{12}E_6$ in the literature. However, for a given batch of $C_{12}E_6$, which we are using, the CMC decreases with increasing temperature. This is because the literature data vary from 60 to 100 μM and at 25°C from 69.9 to 90 μM (24,25). Rosen (22) noted a CMC of 87 μM for $C_{12}E_6$ at 20°C. With an increase in temperature, the hydration of hydrophilic group in $C_{12}E_6$ decreases, which results in an increase in hydrophobic interaction and consequently the CMC decreases. However, CMC values of PES increased with increasing temperature. This may be due to the disruption of

structured water around the hydrophobic group with an increase in temperature, which opposes micellization (26). For the C₁₂E₆/PES mixed system, CMC values were evaluated by surface tension measurements only, because conductance vs. concentration plots did not show break points. CMC values of PES obtained by surface tension were different from those by conductance measurements (Table 1). Variations in CMC values as a function of the method of determination have been reported before (27-29). We have no explanation for the discrepancy observed here. The reproducibilities of CMC by conductance and surface tension measurements are less than 1%. This was determined by at least two measurements.

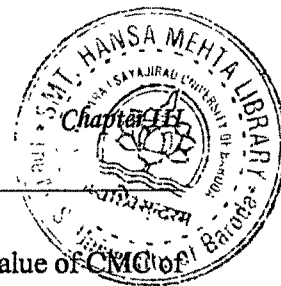
TABLE 1

**Critical Micelle Concentration, (CMC) (mM) Values of C₁₂E₆ / PES
Mixed Surfactant Systems In Aqueous Media at Selected Temperatures**

| N_{PES} | Temperature | | | |
|-----------|---------------------|---------------------|---------------------|---------------------|
| | 303 K | 308 K | 313 K | 318 K |
| 0.0 | 0.071 | 0.062 | 0.051 | 0.047 |
| 0.1 | 0.040 | 0.038 | 0.035 | 0.034 |
| 0.3 | 0.060 | 0.057 | 0.060 | 0.060 |
| 0.5 | 0.069 | 0.065 | 0.072 | 0.072 |
| 0.7 | 0.087 | 0.077 | 0.095 | 0.097 |
| 0.9 | 0.131 | 0.151 | 0.158 | 0.165 |
| 1.0 | 0.588 | 0.616 | 0.691 | 0.724 |
| | 0.74 ^b | 0.76 | 0.83 | 0.88 |
| | (0.66) ^a | (0.64) ^a | (0.66) ^a | (0.70) ^a |

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

^bCMC values were determined from Conductivity measurements



Thermodynamics of micellization and interfacial adsorption. The value of CMC of surfactant in aqueous medium has been widely used to determine the free energy of micellization of the surfactant. The standard free energy of micellization for a nonionic surfactant is given by the relation (26),

$$\Delta G_m^0 = RT \ln X_{cmc} \quad [4]$$

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

$$\Delta G_m^0 = (2 - \alpha)RT \ln X_{cmc} \quad [5]$$

The degree of micelle ionization (α) was computed from the ratio between slopes of the post micellar and premicellar regions of the conductance vs. concentration profile of PES (30). We did not observe a break point in the conductance vs. concentration profile for the $C_{12}E_6$ /PES mixed surfactant system and hence treated the mixed systems as nonionic one.

TABLE 2

The Thermodynamic Parameters of Micellization of $C_{12}E_6$ /PES Mixed Surfactant Systems at Four Temperatures^a

| N_{PES} | $-\Delta G_m^0$ (kJmol ⁻¹) at | | | | ΔH_m^0 (kJ.mol ⁻¹) | ΔS_m^0 (J.mol ⁻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 | 35.6 | 36.3 | 37.1 | 37.8 | 9.2 | 148 |
| 0.3 | 34.6 | 35.3 | 35.7 | 36.3 | -1.3 | 110 |
| 0.5 | 34.3 | 35.0 | 35.3 | 35.8 | -5.3 | 96 |
| 0.7 | 33.7 | 34.5 | 34.6 | 35.0 | -9.6 | 80 |
| 0.9 | 32.6 | 32.8 | 33.2 | 33.6 | -11.9 | 68 |
| 1.0 ^b | 37.9 | 39 | 38.7 | 38 | -69.9 | -100 |

^aThe correlation coefficient was ~0.99 for all plots.

^b In this ΔG_m^0 -T plot, the point at temperature 303 K was dropped.

The ΔG_m^0 values are presented in Table 2. It is evident from Table 2, where all ΔG_m^0 values negative and become increasingly negative with an increase in temperature. The standard enthalpy ΔH_m^0 and ΔS_m^0 of micellization were evaluated from a ΔG_m^0 vs. T plot. The slope and intercept gave ΔS_m^0 and ΔH_m^0 , respectively. The maximum errors in ΔG_m^0 , ΔH_m^0 and ΔS_m^0 were $0.034 \text{ kJ.mol}^{-1}$, 2.4 kJ.mol^{-1} and $7.7 \text{ J.mol}^{-1}.\text{K}^{-1}$, respectively. The micellization process was exothermic for PES and for most of the mole ratios of the two surfactants, whereas it was endothermic for C_{12}E_6 and when the mole fraction of PES in the mixture N_{PES} was 0.1. For almost all nonionic surfactants, CMC decreases as temperature increases, i.e., thermodynamically the system is endothermic (26). For ionic surfactants, both exothermic and endothermic properties are temperature dependent. A plot of CMC vs. temperature generally shows a minimum around 30°C . In the present case, as more and more PES was added, the micellization process changed from endothermic to exothermic. Moreover ΔH_m^0 vs. composition plot was reasonably linear, particularly when the two pure surfactants were not considered. This linear variation means a regular change in the mixed micellization process from endothermic to exothermic.

The surfactant molecule– water and water–water interactions both change continuously as the composition of mixed micelle changes. The ΔH_m^0 values declined as the mole fraction of PES in the mixed system increased (Table 2). This implies a change in the environment surrounding the hydrocarbon chain of the surfactant molecules (5). The exothermic and endothermic characteristics of micellization are specific to a surfactant and the temperature of micellization (31,32), particularly for ionic surfactants. For mixed surfactant systems this also seems to be true. In practical applications, the use of mixed surfactants is preferred over pure surfactants because less is needed to accomplish the same task, the cost is not high. The biodegradability of PES, and the nontoxicity of C_{12}E_6 are therefore very useful as a combination that will provide the required condition for use. All values of entropy of micellization are positive suggesting micellization is entropy dominated except in the pure PES system, where a ΔG_m^0 vs. T plot shows a minimum.

The maximum surface excess (Γ_{\max}) is an effective measure of adsorption at the air/liquid interface. The Γ_{\max} and limiting surface area per molecule (A_{\min}) values calculated using Gibbs adsorption equation (33) are presented in Table 3. The slope of the tangent at the given concentration of the γ vs. $\log_{10}C$ plot, i.e., $d\gamma/d\log C$, was used to calculate Γ_{\max} by fitting a curve to a polynomial of the form $y = ax^2 + bx + c$ in Microsoft excel. The regression coefficient (R^2) value for the fit was between 0.9922 and 0.9999. The lower values of A_{\min} in a mixed system can be related to closer packing at the interface owing to decreased repulsion between the oriented headgroups in a binary combination.

TABLE 3
Maximum Surface Excess (Γ_{\max}) And Limiting Surface Area per Molecule (A_{\min}) of C₁₂E₆/PES Mixed Surfactant Systems at Selected Temperatures.

| N_{PES} | $\Gamma_{\max} \times 10^{10} \text{ mol cm}^{-2} \text{ at}$ | | | | $A_{\min} \text{ (nm}^2\text{)}$ | | | |
|------------------|---|-------|-------|-------|----------------------------------|-------|-------|-------|
| | 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 | 3.46 | 3.18 | 3.42 | 3.22 | 0.48 | 0.52 | 0.48 | 0.51 |
| 0.3 | 2.40 | 2.40 | 2.80 | 2.84 | 0.69 | 0.69 | 0.59 | 0.58 |
| 0.5 | 2.96 | 3.12 | 3.44 | 3.42 | 0.56 | 0.53 | 0.48 | 0.48 |
| 0.7 | 3.04 | 2.90 | 3.34 | 3.01 | 0.55 | 0.57 | 0.50 | 0.55 |
| 0.9 | 2.90 | 2.82 | 3.46 | 3.14 | 0.57 | 0.59 | 0.48 | 0.53 |
| 1.0 | 1.23 | 1.18 | 1.13 | 1.03 | 1.35 | 1.4 | 1.47 | 1.61 |

The thermodynamic parameters of adsorption of surfactants at the air/water interface were evaluated using the relation (34,35)

$$\Delta G_{ad}^0 = \Delta G_m^0 - N\pi_{CMC} A_{CMC} \quad [6]$$

where N , π_{CMC} and A_{CMC} are Avogadro's number, the surface pressure at the CMC ($\gamma_0 - \gamma_{CMC}$) and area per molecule at the CMC respectively. The second term in Equation 6 represents surface work involved in changing from zero surface pressure to surface pressure at CMC (π_{CMC}) at a constant minimum surface area per molecule. ΔG_{ad}^0 values are presented in Table 4.

TABLE 4.
The Free Energy of Adsorption^a and Traube's Constant of C₁₂E₆ / PES Mixed Surfactant System.

| N_{PES} | - $\Delta G_{\text{ad}}^{\circ}$ (kJmol ⁻¹) at | | | |
|------------------|--|-----------------------------------|----------------------------------|----------------------------------|
| | 303 K | 308 K | 313 K | 318 K |
| 0.0 | 44.5 (4.7 x 10 ⁷) | 44.7 (3.8 x 10 ⁷) | 45.3 (3.6 x 10 ⁷) | 45.5 (3.0 x 10 ⁷) |
| 0.1 | 43.9 (3.4 x 10 ⁷) | 44.1 (3.0 x 10 ⁷) | 44.3 (2.5x 10 ⁷) | 45.3 (3.6 x 10 ⁷) |
| 0.3 | 45.5 (7.0 x 10 ⁷) | 45 (4.3 x 10 ⁷) | 46.6 (6.0 x 10 ⁷) | 46.1 (4.9 x 10 ⁷) |
| 0.5 | 42.7 (2.3 x 10 ⁷) | 42 (1.3 x 10 ⁷) | 42.9 (1.4 x 10 ⁷) | 43 (1.5 x 10 ⁷) |
| 0.7 | 43.3 (2.9 x 10 ⁷) | 43.7 (2.6 x 10 ⁷) | 43.1 (1.5 x 10 ⁷) | 44 (2.2 x 10 ⁷) |
| 0.9 | 39.9 (0.7 x 10 ⁷) | 42.4 (1.5 x 10 ⁷) | 40.7 (0.6 x 10 ⁷) | 42.2 (1.1 x 10 ⁷) |
| 1.0 | 58.3 (1.1 x 10 ¹⁰) | 55.8 (2.9 x 10 ¹⁰) | 58.7 (6.2 x 10 ⁹) | 60.3 (8.0 x 10 ⁹) |

^a The error is less than 1%.

^b Values in parentheses are Traube's Constant (σ), which is defined as $(\partial\pi/\partial C)_{C \rightarrow 0} = -(\partial\gamma/\partial C)_{C \rightarrow 0}$, i.e., change in surface pressure (or surface tension at infinite dilution).

A straight-line relation with temperature was not obtained. The $\Delta G_{\text{ad}}^{\circ}$ values in Table 4 suggest that 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. It has been suggested (36) that

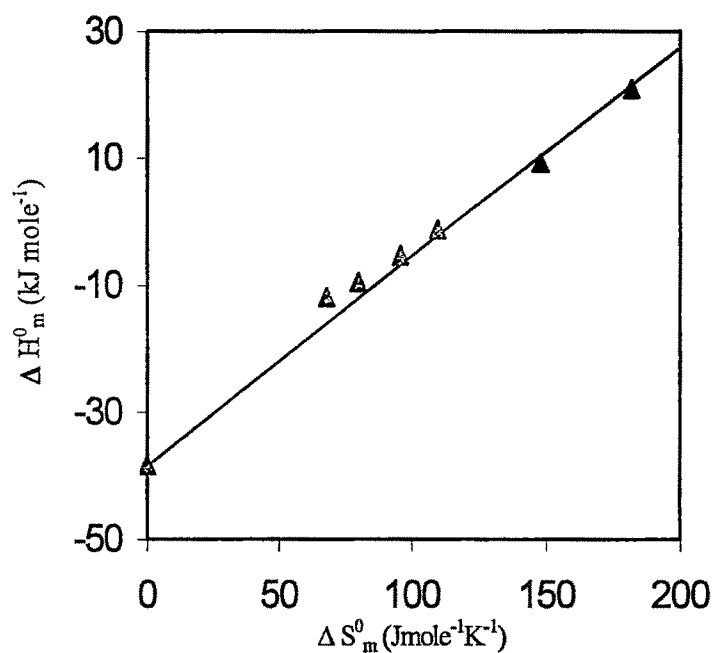
$$\Delta G_{ad}^0 = -RT \ln \sigma \quad [7]$$

where σ is $\sigma = (\partial\pi/\partial C)_{C \rightarrow 0} = -(\partial\gamma/\partial C)_{C \rightarrow 0}$ Traube's constant (37) and is defined by the relation

$$\sigma = (\partial\pi/\partial C)_{C \rightarrow 0} = -(\partial\gamma/\partial C)_{C \rightarrow 0} \quad [8]$$

This means σ is the rate of change of surface pressure per unit concentration change at infinite dilution. The σ values are given in parentheses in Table 4. The calculated values for $C_{12}E_6$ compare favourably with literature values (38). A plot of σ vs. T plot for pure $C_{12}E_6$ gives a reasonably good straight line with a negative slope, although for the other systems a minimum is observed near 310 K.

FIG. 4. Enthalpy-entropy compensation plot of micellization of a $C_{12}E_6$ /PES mixed surfactant system.



A linear correlation between ΔS_m^0 and ΔH_m^0 (Fig. 4), as suggested by Lumry and Rajendar (39), is observed for this system. The compensation temperature was 316 K for micellization. This implies that at 316 K, the micellization process is independent of structural changes in the system and dependent only on enthalpic factors (40) as previously reported (41).

Composition of mixed micelle and intermicellar interaction. The interaction parameter (β^m), a measure of interaction between the surfactant molecules in the mixed micelle, was evaluated using Rubingh's equation and method (13); data are presented in Table 5. The anionic surfactant PES mixed with $C_{12}E_6$ shows a stronger interaction in the mixed micelle as indicated by negative (β^m) values. Nonionic surfactants of poly (ethylene oxide) class has a weak cationic character resulting either from oxonium ion formation with protons from water or sharing of the hydrogen in water by hydrogen bond formation. Thus, the attractive interaction is probably between this weak cation with the anionic surfactant (PES) (42). It is clear from Table 1 that the CMC values of PES differ depending on whether surface tension or conductance methods are used for the determination. We used both methods of deriving CMC data of PES to calculate β^m . The calculated β^m values do not differ much (maximum about 10%), and the interaction is always attractive. The composition of the micelles remains unperturbed. The maximum difference in X_1 (mole fraction of ionic surfactant in the mixed micelle) values obtained by using different CMC values (conductance or surface tension) was ~5%, although in most cases it was less than 3%. This suggests the composition of mixed micelles is without much error.

The activity coefficient values were also evaluated using the relations (22)

$$\ln f_1 = \beta^m (1 - X_1^2) \quad [9]$$

$$\ln f_2 = \beta^m (X_1^2) \quad [10]$$

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 and 2, respectively, in the mixed micelle.

TABLE 5
Interaction Parameter (β^m) Values of C₁₂E₆/PES Mixed Surfactant Systems in Aqueous Media at Different Temperatures.

| N_{PES} | Temperature | | | |
|-----------|-------------------------------------|------------------------|------------------------|------------------------|
| | 303 K | 308 K | 313 K | 318 K |
| 0.1 | -6.68/-6.37 (0.244) ^b | -6.42/-6.15 (0.228) | -6.11/-5.88 (0.204) | -5.96/-5.72 (0.191) |
| 0.3 | -4.05/-3.75 (0.245) | -3.79/-3.47 (0.223) | -2.48/-2.26 (0.137) | -1.83/-1.61 (0.092) |
| 0.5 | -3.87/-3.54 (0.304) | -3.74/-3.44 (0.286) | -2.53/-2.3 (0.210) | -2.18/-1.95 (0.178) |
| 0.7 | -3.85/-3.47 (0.385) | -4.04/-3.7 (0.364) | -2.63/-2.37 (0.296) | -2.32/-2.05 (0.268) |
| 0.9 | -4.28/-3.82 (0.488) | -3.48/-3.07 (0.472) | -3.03/-2.7 (0.441) | -2.76/-2.42 (0.423) |

^aData following the slash (/) were calculated by using the CMC of PES by surface tension measurement.

^bValues in parentheses are X_1 , i.e., the mole fraction of PES.

The f_1 & f_2 values are tabulated in Table 6. The mole fraction of PES (X_{PES}) in the micelle is rather low compared to the stoichiometric mole fraction (N_{PES}) in the case of most mixed surfactant systems in Table 5. The activity coefficient values of PES are low, and although activity coefficient values of C₁₂E₆ (f_2) are higher, they are not close to unity, indicating that C₁₂E₆ and PES in the mixed micelle are not in the standard state. β^m determined by regular solution theory explains the long-range electrical interaction in the mixed micelle.

TABLE 6

Activity Coefficient (f_1 & f_2) Values of $C_{12}E_6$ /PES Mixed Surfactant Systems in Aqueous Media at Different Temperatures.

| N_{PES} | Activity coefficient (f_1) of anionic surfactant (PES) ^a | | | |
|-----------|---|---------|---------|---------|
| | 303 | 308 | 313 | 318 |
| 0.1 | 0.022 | 0.021 | 0.021 | 0.020 |
| | (0.671) | (0.716) | (0.775) | (0.804) |
| 0.3 | 0.099 | 0.101 | 0.157 | 0.220 |
| | (0.784) | (0.828) | (0.955) | (0.984) |
| 0.5 | 0.153 | 0.148 | 0.206 | 0.229 |
| | (0.699) | (0.92) | (0.894) | (0.933) |
| 0.7 | 0.220 | 0.195 | 0.271 | 0.288 |
| | (0.586) | (0.585) | (0.794) | (0.846) |
| 0.9 | 0.325 | 0.379 | 0.387 | 0.398 |
| | (0.360) | (0.460) | (0.554) | (0.610) |

^aValues in parentheses are f_2 , i.e., activity coefficient of the nonionic surfactant ($C_{12}E_6$).

However, Maeda (43) and Ruiz and Aguiar (44) have indicated there are chain-chain interactions present in a mixed system in addition to headgroup-headgroup interactions. Therefore, another interaction parameter (B_1), encompassing the hydrocarbon chain-chain interactions, also could be responsible for the stability of the mixed micelle. The free energy of micellization is given by the relation (43)

$$\Delta G_{mic} / RT = B_0 + B_1 X_1 + B_2 X_2^2 \quad [11]$$

where $B_0 = \ln C_2$ (C_1 is the cmc of the nonionic surfactant),

$$B_1 + B_2 = \ln C_2 / C_1 \quad [12]$$

where C_2 and X_1 are the CMC and mole fraction of the ionic surfactant respectively, in the micelle and B_2 is equal to $-\beta^m$.

Calculated B_1 and B_2 values thus calculated are presented in Table 7. The B_1 values are all negative, indicating that chain-chain interaction contributes to the stability of

the mixed micelle. The ionic surfactant has a hydrophobic chain of 14 carbons, whereas nonionic surfactant has 12 carbon atoms.

TABLE 7

 B_0 , B_1 , and B_2 Values For $C_{12}E_6$ / PES Mixed Surfactant System

| N_{PES} | B_0 (avg.) | $-B_1$ (avg.) | B_2 (avg.) |
|-----------|--------------|---------------|--------------|
| 0.1 | | 3.62 | 6.29 |
| 0.3 | | 0.59 | 2.82 |
| 0.5 | -13.78 | 0.44 | 3.08 |
| 0.7 | | 0.57 | 3.21 |
| 0.9 | | 0.63 | 3.38 |

^a $B_0 = \ln C_1$, the CMC of the nonionic surfactant; $B_1 + B_2 = \ln C_2/C_1$, where C_2 is the CMC of the ionic surfactant in the micelle.

Therefore, chain-chain interactions should improve the stability of the micelle. However, the headgroups are hydrated, and if the water molecules of one hydration shell are also the part of another hydration shell, i.e., the water molecules act as a bridge between surfactant molecules just below the water-micelle interface, then the attractive interaction will also ensue. Mukerjee (45) also suggested the existence of an attractive interaction between hydrocarbon and fluorocarbon surfactants in the mixed micelle by what is termed as "contact hydrophobic interaction". Such contact hydrophobic interaction may also be the reason for attractive interaction in the present system. The free energies of micellization calculated from equation 4 and 11 are almost equal, suggesting the counterion bindings are very high in the system and that is why no break point was obtained in the conductance-concentration plot.

The excess free energy of mixing (ΔG_e) can be calculated using the activity coefficient data as follows

$$\Delta G_e = RT[X_1 \ln(f_1) + (1 - X_1) \ln(f_2)] \quad [13]$$

The calculated ΔG_e values are all negative, indicating relatively more stable mixed micelles.

N_{agg} . N_{agg} . determined by steady-state fluorescence measurements at different mole ratios of the binary C₁₂E₆/PES mixture are presented in Figure 5. The N_{agg} values of mixtures are larger than that of PES but are in general lower than that of C₁₂E₆. Such behaviour may be due to the presence of C₁₂E₆ in the mixed micelle, resulting in screening of headgroup interactions, compared to pure PES.

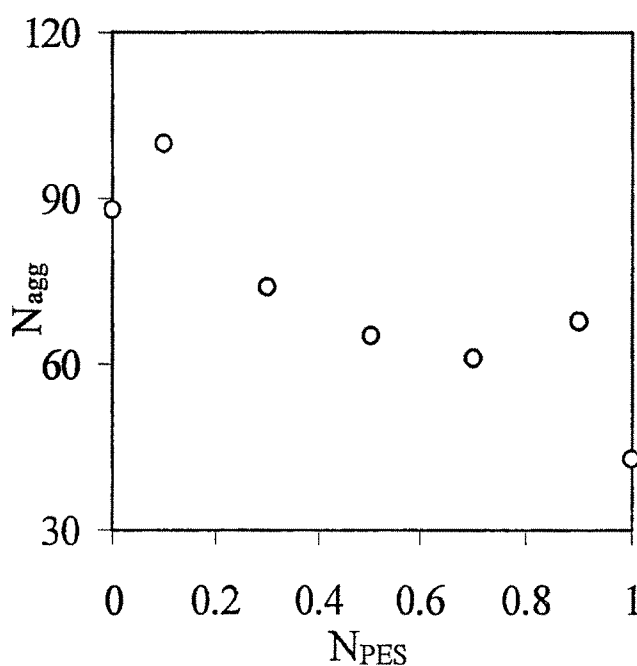


FIG. 5. Plot of micellar aggregation number (N_{agg}) vs. mole fraction of PES (N_{PES}) at room temperature ($\sim 25^\circ\text{C}$).

Microenvironment. The ratio of the first and the third vibronic peaks, I_1/I_3 , in a monomeric pyrene fluorescence emission spectrum is sensitive to local polarity around the probe (17). Figure 1 represents seven plots of intensity against wavelength (emission) of the binary combination to yield I_1/I_3 values. I_1/I_3 values that are >1 suggest a polar environment in the micelle interior. The K_{SY} values calculated from Equation 2 are

presented in Table 8. K_{SV} is the ratio of bimolecular quenching constant to the unimolecular decay constant. Also, K_{SV} is the product of κ_q , the rate constant of the quenching process, and τ is the actual lifetime of probe in absence of bimolecular quenching (18). Thus, from the values of K_{SV} , we can assume that quenching is efficient and also that the life time of the pyrene in $C_{12}E_6$ and most of the mole ratios in the mixed micelle are higher and most of the mole ratios in the mixed micelle are higher, if we assume that κ_q for all systems are of similar magnitude.

TABLE 8.

Micropolarity (I_1/I_3), Binding Constant (K_{SV}) And Apparent Dielectric Constant (ϵ) For $C_{12}E_6$ / PES Mixed Surfactant Systems.

| N_{PES} | I_1/I_3 | $K_{SV} \times 10^{-4}$ (L mol ⁻¹) | ϵ_{exp} | ϵ_{cal} |
|-----------|-----------|---|------------------|------------------|
| 0 | 1.17 | 1.6 | 13.1 | 13.1 |
| 0.1 | 1.16 | 1.8 | 12.24 | 10.86 |
| 0.3 | 1.13 | 1.08 | 9.65 | 10.85 |
| 0.5 | 1.12 | 0.80 | 8.79 | 10.58 |
| 0.7 | 1.10 | 0.79 | 7.07 | 9.51 |
| 0.9 | 1.08 | 1.14 | 5.34 | 8.52 |
| 1.0 | 1.05 | 0.07 | 2.76 | 2.76 |

The dielectric constant (ϵ) of the medium (in this case, the pyrene environment inside the micelle) was evaluated by using the relation (46)

$$I_1/I_3 = 0.0116\epsilon + 1.01798 \quad [14]$$

We evaluated the apparent ϵ of the pure and mixed micelles from the experimental I_1/I_3 data. The ϵ inside the mixed micelle can be computed from the following equation

$$\epsilon = \sum X_i \epsilon_i \quad [15]$$

In Table 8, the experimentally determined and the calculated apparent dielectric constants are presented. The experimental values are differed from the calculated values. We believe this difference results from attractive interaction between the surfactants inside the micelle.

NMR measurement. Proton NMR spectroscopy was also used to study $C_{12}E_6$ /PES mixed surfactant behaviour. The peak assignments were made for $C_{12}E_6$ (47,48) with the 3.577 ppm peak corresponding to the oxyethylene moiety, 0.787 ppm to CH_3 , and 1.19 ppm peak to methylene protons $[(CH_2)_9]$. The changes in chemical shifts were monitored with the change in surfactant proportions, and the shift due to oxyethylene group showed a significant change compared to other peaks.

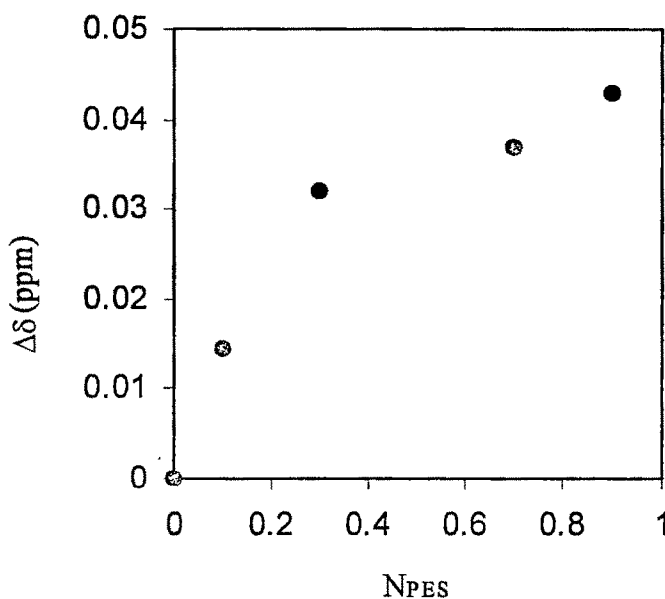


FIG. 6. Change in downfield shift of oxyethylene proton signal ($\Delta\delta$) vs. mole fraction of PES (N_{PES}).

The polyoxyethylene signal shows a downfield shift in the presence of PES, and the extent of the downfield shift increased as the mole fraction of PES in the mixed system increased (Fig. 6). This downfield shift indicates an attractive interaction between $C_{12}E_6$ and PES. This observation is in agreement with the negative values of the interaction parameter (β^m) obtained by the regular solution theory of Rubingh (13).

CP. In a number of earlier studies, the CP of the nonionic surfactant was found to increase with addition of ionic surfactant (15,49,50). The CP of 1% $C_{12}E_6$ is 47°C [literature value 52°C (51)]. The CP of $C_{12}E_6$ (1%wt/vol) solution increased on addition of PES (Fig. 7), even though the concentration of PES was very low. Such behaviour may be due to the formation of charged mixed micelles. This would result in repulsion between micelles and hinder their aggregation, thereby raising the CP. It is unclear why conductance showed no break point as a function of concentration of surfactant, although as we mentioned earlier, there may be less ionization of the mixed surfactant.

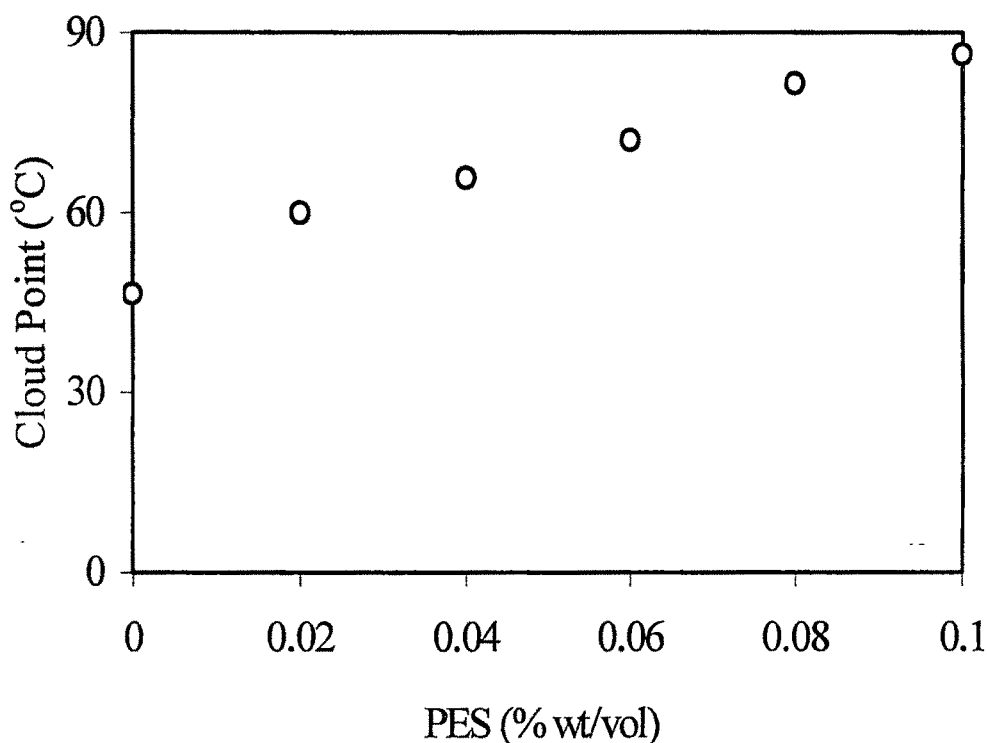


FIG. 7. Cloud point ($^\circ\text{C}$) of $C_{12}E_6$ (1% wt/vol) in the presence of PES.

Viscosity. The relative viscosity (η_r) values of $C_{12}E_6$ /PES (5% wt/vol) mixed surfactant system (Fig. 8) showed a negative deviation from linearity.

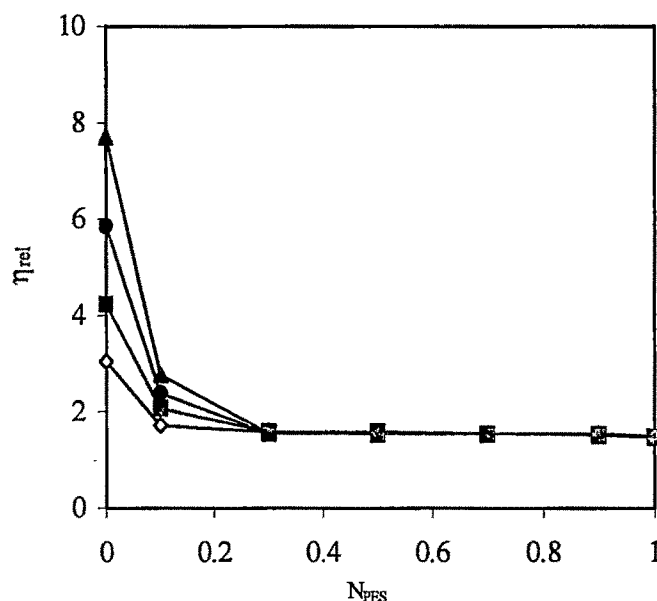


FIG. 8. Plot of relative viscosity (η_{rel}) vs. mole fraction of PES (N_{PES}). \diamond -30 °C, \square - 35 °C, \bullet - 40 °C, \blacktriangle - 45 °C.

The η_r values of $C_{12}E_6$ were much higher than those of PES. The $|\eta|$ values of the $C_{12}E_6$ /PES mixed surfactant system at all mole fractions indicated that mixed micelles were nonspherical, i.e., for spherical systems $|\eta|$ should be between 2.5 and 4.0 $cm^3 \cdot g^{-1}$ (21). The lowest $|\eta|$ in this system was 9.4 $cm^3 \cdot g^{-1}$ (Table 9). The viscosity of $C_{12}E_6$ (1%wt/vol) in the presence of PES decreased, but not to such an extent that micelles became spherical. Temperature had no significant effect on the viscosity of the mixed surfactant system at a higher PES ratio. For $C_{12}E_6$ (1%wt/vol) and $N_{PES} = 0.1$, the η_r values increased with increase in temperature. For $C_{12}E_6$, at higher temperatures dehydration took place, which led to a decrease of the effective area per polar group, which in turn led to an increased tendency for aggregates to grow in size (52). Thus, the micelle

size increased with increase in temperature, and micelles were non-spherical. This behaviour has also reported for Triton X-100 (14).

TABLE 9
Intrinsic Viscosity Data(cm^3/g) for C_{12}E_6 / PES Mixed Surfactant Systems

| N_{PES} | 303 K | 308 K | 313 K | 318 K |
|------------------|-------|-------|-------|-------|
| 0.0 | 41 | 64.8 | 97.2 | 134.4 |
| 0.1 | 14.6 | 21.7 | 27.9 | 35.3 |
| 0.3 | 11.9 | 11.8 | 11.2 | 11.2 |
| 0.5 | 11.9 | 11.7 | 11.2 | 11.1 |
| 0.7 | 11.1 | 11 | 10.9 | 10.9 |
| 0.9 | 11.1 | 10.7 | 10.6 | 10.4 |
| 1.0 | 9.8 | 9.7 | 9.6 | 9.4 |

Foaming. Nonionic surfactants are known to have lower foaming, whereas ionic surfactants have higher foam-forming property. A mixture of ionic and nonionic surfactants could be used to adjust a surfactant mixture to the users' requirements. Foaming efficiency of a surfactant also depends on temperature. Foam heights, indicative of surfactant foamability were determined at 30, 35, 40 and 45°C for both pure and mixed surfactant systems using Ross-Miles method. The concentration of surfactant was kept at 5.8 mM, since the Ross-Miles test is usually performed at 0.25% surfactant concentration (~5.8mM) (22). The CMC for both surfactants are ≤ 5.8 mM, so both surfactants attained their maximum foam height value. Foaminess of pure and mixed surfactant systems increased with increasing temperature (Table 10). The foam heights for C_{12}E_6 are low compared with those of PES and the mixed surfactant system because the polyoxyethylene

group in $C_{12}E_6$ has a large surface area and also because highly charged surface films are absent.

TABLE 10.

Foam Stability of $C_{12}E_6$ /PES Mixed Surfactant Systems as a Function of Temperature^a

| N_{PES} | Foam height (cm; SD \pm 0.4) at | | |
|-----------|-----------------------------------|-------|-------|
| | 303 K | 308 K | 313 K |
| 0.0 | 12.6 | 14.3 | 17.1 |
| 0.1 | 12.5 | 14.0 | 15.2 |
| 0.3 | 14.5 | 15.7 | 17.8 |
| 0.5 | 11.2 | 12.0 | 12.7 |
| 0.7 | 16.8 | 18.0 | 20.2 |
| 0.9 | 17.7 | 18.7 | 20.1 |
| 1.0 | 20.4 | 22.0 | 23.1 |

^aTotal surfactant concentration, 5.8 mM; average of atleast two runs.

The foam heights for PES are higher and increase with increasing temperature, which is obvious because α -sulfoesters containing 16-17 carbon atoms show maximum foaming at higher temperatures (22). The foam heights at most of the mole ratios were higher because of the rapid variation of concentration at the air/water interface in mixed surfactant systems, which is a requirement for good foam-forming qualities (53). This phenomenon is enhanced with increasing temperature, resulting in higher foam heights.

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