

REPRINTS



Membrane electrode sensitive to a cationic surfactant in aquo-organic media

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Received 17 January 2004, received in revised form 7 May 2004, accepted 7 May 2004

Abstract

An electrode originally sensitive to dodecyltrimethylammonium ions (DTA⁺) was proven to be sensitive to tetradecyltrimethylammonium ions (TTA⁺) and was used for determination of critical micelle concentration of tetradecyltrimethylammonium bromide (TTAB) in water. Moreover the response of the electrode was tested in presence of non-aqueous polar solvents i.e. dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) in water and was observed to be Nernstian within the concentration range studied (up to 40% v/v of DMF and DMSO). The validity of this electrode, for electrochemical measurements, was checked by comparing the critical micelle concentration values of TTAB obtained by using the electrode, with those obtained by conductivity measurements in mixed polar solvents. The effect of solvent on the micellization of TTAB has been discussed.

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Keywords: Ion selective electrode, Tetradecyltrimethylammonium bromide, Critical micelle concentration, Hydrophobic effect

1. Introduction

Surfactants are important in various phenomena of interfacial science and continue to be critical in many applications in agrochemicals, emulsion polymerization, paper manufacturing, water treatment, oil recovery, fire fighting and plastic manufacturing [1]. Handling of surfactants for use, formulation or production needs simple and reliable analytical technique to determine their quantity in reaction media [2]. Hence ion selective electrodes for surfactants have been developed in the last three decades [3–6] and have been used to study biomolecule–surfactant interactions [7]. The principle of these electrodes is based on a selectively permeable membrane between two electrolyte phases across which only a single ion can penetrate. Polymeric membranes are easy to handle and also prevent rapid loss of expensive electro active material dissolved in a plasticizer. Complexing agents having selectivity towards ions of interest are dissolved in it, and they provide the mechanism for selective charge transport across the boundaries of the membrane. Different associa-

tive behavior of surfactants in water and other solvents have stimulated the interest to elucidate how solvent properties influence aggregation and many studies have been performed to gain information on the role of solvent in the aggregation process [8]. Hence, in order to understand (a) the behavior of polymeric membrane electrodes in aquo-organic medium and (b) the role of solvent on aggregation of surfactant, we determined the critical micelle concentration (CMC) of a cationic surfactant, tetradecyltrimethylammonium bromide (TTAB), in H₂O/DMF as well as in H₂O/DMSO medium using the cationic surfactant ion selective electrode (ISE). We have also compared the CMC values of TTAB obtained by electrochemical measurements using ISE with those obtained by conductivity measurements at the same temperature to determine the response nature of surfactant electrode in mixed aquo-organic medium.

2. Experimental

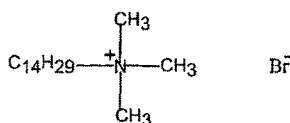
2.1. Materials

Tetradecyltrimethylammonium bromide procured from Lancaster, UK was recrystallized thrice in acetone prior to use. Dimethyl formamide (DMF), tetrahydrofuran (THF)

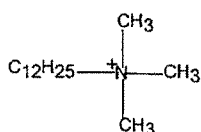
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59 (Qualigens, India) and dimethyl sulfoxide (DMSO) (E.
60 Merck, India) were purified as per standard methods re-
61 ported in the literature [9]. Dodecyltrimethylammonium
62 bromide (DTAB) obtained from Acros Organics was recryst-
63 tallized twice from methanol and then dried under vacuum
64 at room temperature. Sodium tetraphenylborate ($\text{NaB}\phi_4$)
65 was obtained from E. Merck, Germany and used as received.
66 Dioctyl phthalate (plasticizer) was purchased from Suv-
67 math Laboratories, India. Doubly distilled water, having
68 conductivity $< 6 \mu\text{S cm}^{-1}$ was used in all the experiments.
69 The structures of TTAB and DTA^+ are presented below.

(a) Tetradecyltrimethylammonium bromide ($\text{TTA}^+ \text{Br}^-$)



(b) Dodecyltrimethylammonium ion (DTA^+)



72 2.2. Methods

73 2.2.1. Electrochemical measurements

74 The cationic surfactant ion selective electrode was pre-
75 pared in our laboratory as detailed below. Membranes were
76 made from low molecular weight poly (vinyl chloride)
77 (PVC) mixed with a large quantity of plasticizer. PVC
78 (0.8 g) and dioctyl phthalate (DOP, 1.2 g) were mixed in
79 10 mL of THF until PVC was completely soluble (Solution
80 A). $\text{DTAB}\phi_4$ was used in order to have $\text{B}\phi_4^-$ ion as mobile
81 anionic site in the membrane for TTA^+ detection, which
82 was prepared by mixing equimolar aqueous solutions of
83 two salts: dodecyltrimethylammonium bromide and sodium
84 tetraphenylborate ($\text{NaB}\phi_4$). The solution obtained was ex-
85 tracted three times in dichloromethane. After evaporation
86 of solvent, the precipitate was recrystallized twice from
87 ether-methanol mixture. A 10^{-2} M solution (Solution B) of
88 $\text{DTAB}\phi_4$ in THF was made. Three milliliters of Solution A
89 was mixed with 0.2 mL of Solution B and the clear solution
90 was spread on clean and clear glass surface of a flat dish,
91 which lost THF by evaporation at room temperature form-
92 ing the membrane in the form of thin film (~ 0.1 mm thick).

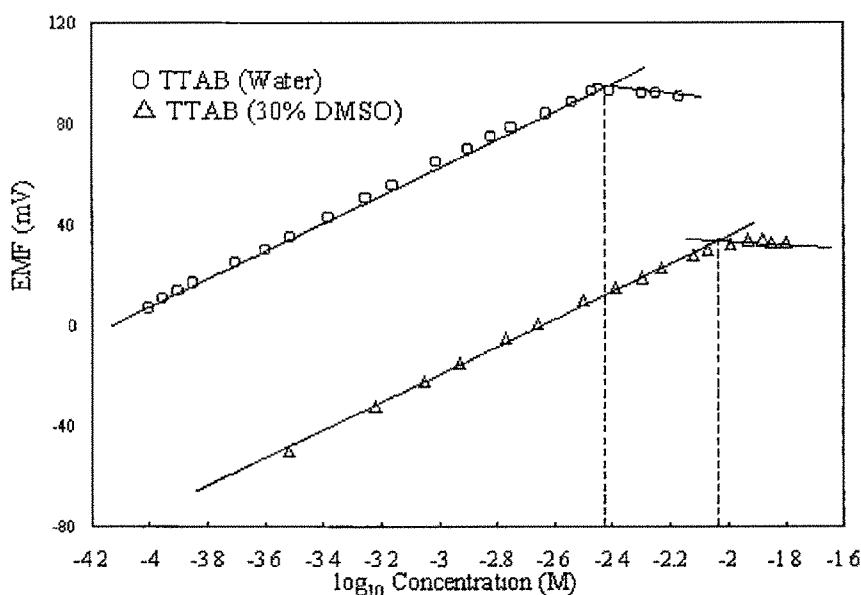
If the plasticizer (i.e. dioctyl phthalate) exceeded 1.2 g, the
resultant membrane used to be too much flexible, sticky,
having low mechanical strength and thus very difficult to
handle. Whereas, if the DOP content was lower than 1.2 g,
the resultant film was stiff, less flexible and it was difficult
to fix up on the narrow end of the glass tube. Even if such
membrane was glued at the end of the narrow glass tube,
it used to leak and thus unfit for experimental purpose.
Thus the method mentioned above at the beginning of the
paragraph incorporates the optimized contents of various
ingredients required for preparation of the membrane suit-
able for the electrochemical measurements. The membrane
was removed and cut into small pieces and fixed on the
open end of a narrow glass tube of 1 mm diameter using
PVC-THF paste as glue. The membrane was conditioned
with the reference solution (very dilute solution of TTAB)
prior to electrochemical measurements. The experimental
setup for electrochemical measurements is as shown in
Scheme 1.

The reference electrode of the KCl-saturated calomel was
protected from amphiphile diffusion by a saline agar-agar
gel made of saturated KCl. Moreover, to limit the diffusion
speed of surfactant, the gel was contained in a Teflon cap-
illary tube. Aliquot addition of known concentration of sur-
factant solution to a fixed quantity of solvent [water/DMF
or water/DMSO mixture (max. 40% v/v)] was done and the
corresponding emf values were recorded.

The aquo-DMF and aquo-DMSO solutions were neutral
to 0.001 M aquo-NaOH solution. Stable emf values (mV,
 $\pm 2\%$) were recorded at regular interval of 3 min after each
aliquot addition. The emf values thus obtained were plot-
ted as a function of logarithm of surfactant concentration
and the break in emf-log concentration of surfactant pro-
file was considered as the critical micelle concentration
(CMC) of the surfactant (Fig. 1). Total duration to com-
plete one set of experiment was ~ 3 h. The reproducibility
of the emf measurements and hence CMC determinations
was crosschecked by carrying out duplicate runs and the
CMC values were reproducible within $\pm 4\%$. The mem-
brane showed good resistance and stable electrochemical
response in aquo-organic solvent and was unaffected by
the solvent medium [water/DMF or water/DMSO mixture
(max. 40% v/v of DMF or DMSO)]. No leaching/leakage of
the polymeric membrane was observed and the polymeric
film remained intact throughout the experimental duration
(~ 3 h and more). The same electrode was used for at least
six times or more covering 3 days or more with prior rins-
ing followed by conditioning with reference solution before
each experimental run. However our attempt to work with

Cu	Calomel reference electrode	KCl saturated agar agar salt bridge	Reference solution (very dilute solution of TTAB)	Membrane electrode	Aqueous unknown solution	KCl saturated agar agar salt bridge	Calomel reference electrode	Cu
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Scheme 1

Fig. 1. Representative emf vs \log [TTAB] plots at 35 °C for various systems

141 water–ethylene glycol mixed solvent was unsuccessful at
 142 any concentration of ethylene glycol. In the DMF–water
 143 and DMSO–water medium, the lower limit of detection of
 144 cation was found to be 1×10^{-5} M, accuracy of detection
 145 of cation was $\pm 4\%$, the emf versus $\log_{10} C$ plot was linear
 146 although from lower limit of 1×10^{-5} M to desired higher
 147 concentration. The thermodynamic background of such
 148 electrode has been discussed in detail by Turmine et al. [10].

2.2.2. Conductivity measurements

149 The conductance (k) measurements were done with Well-
 150 tronix (India) conductivity bridge. A dip type cell of cell
 151 constant 1.01 cm^{-1} was used. The conductance of differ-
 152 ent solutions, which were obtained on aliquot addition of a
 153 known concentrated surfactant solution to a given volume
 154 of the thermostated solvent, was measured. Conductance (k)
 155 versus concentration of surfactant (mol/L) plots are shown

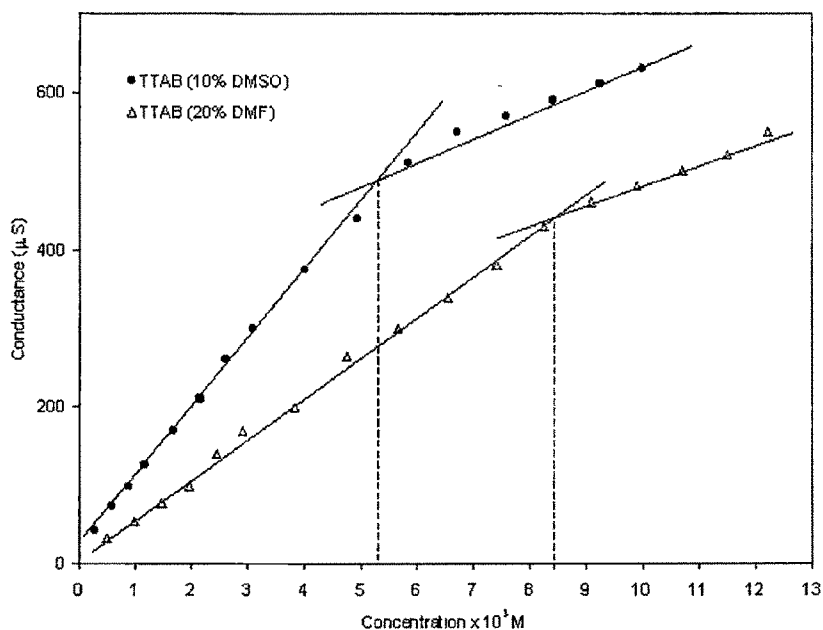


Fig. 2. Representative conductivity vs concentration plots at 35 °C for various systems

Table 1
Critical micelle concentration (mM) values of tetradecyltrimethylammonium bromide at 35 °C using different methods

Organic solvent (% v/v)	Critical micelle concentration (mM)			
	DMF		DMSO	
	Conductance	Potentiometry	Conductance	Potentiometry
0	3.80 ± 0.04	3.70 ± 0.03	3.80 ± 0.04	3.70 ± 0.03
10	6.65 ± 0.13	6.45 ± 0.13	5.20 ± 0.10	5.01 ± 0.07
20	8.50 ± 0.22	8.32 ± 0.24	6.10 ± 0.16	6.02 ± 0.14
30	11.10 ± 0.27	10.96 ± 0.26	8.80 ± 0.19	8.91 ± 0.22
40	14.30 ± 0.31	14.40 ± 0.36	12.50 ± 0.29	12.58 ± 0.26

156 in Fig. 2, for TTAB. The break in conductance-concentration
157 profile was considered as the critical micelle concentration
158 [11].

159 3. Results and discussion

160 The critical micelle concentration is probably the simplest
161 means of characterizing the colloid and surface behavior
162 of a surfactant, which in turn determines its industrial use-
163 fulness and biological activity and also gives a measure of
164 solute–solute interactions [12]. Electrochemical measure-
165 ments were carried out to study the micellization of the
166 cationic surfactant in aquo-organic medium using ISE selec-
167 tive to a surfactant ion, as this will be then an additional tool
168 of characterization of micellar aggregates in aquo-organic
169 medium, besides the existing conventional techniques (sur-
170 face tension, conductivity, etc.). Potentiometric measure-
171 ments were carried out with ISE sensitive to TTA⁺ ions
172 using a Systronics, India, multimeter. The EMF values were
173 reproducible and had ±0.5 mV stability. Fig. 1. shows the
174 representative potentiometric curve obtained for TTAB in
175 aqueous as well as aquo-organic medium at 35 °C. Initially
176 the potential response was linear, however as the concentra-
177 tion of surfactant increased, a break corresponding to critical
178 micelle concentration of TTAB was observed. The potential
179 response of this membrane was equal to (59 ± 3 mV) per
180 decade indicating a reasonably good Nernstian slope.

181 The CMC values of TTAB obtained in aquo-organic
182 medium (containing varying amount (% v/v) of DMF and
183 DMSO by electrochemical as well as conductivity measure-
184 ments are reported in Table 1. It is evident from Table 1,
185 that the critical micelle concentration value of TTAB in
186 aqueous medium is lower than that in presence of DMF
187 and DMSO. The micelle formation is dependent on the
188 hydrophobic effect and London dispersion forces [13,14].
189 The increase in CMC values of TTAB in presence of DMF
190 and DMSO, can be attributed to the increase in solva-
191 tion of the hydrocarbon chains of the surfactant by DMF
192 ($\epsilon = 36.7$) and DMSO ($\epsilon = 46.6$). Thus lowering of hy-
193 drophobic effect—the driving force for micellization leads
194 to higher values of CMC in presence of DMF and DMSO
195 and in aquo-DMF medium more than in aquo-DMSO. We
196 observed that the electrode potential (mV) plotted against

197 the $\log_{10} C$ of the ion (i.e. [TTA⁺]) gave a straight line of
198 gradient $2.3RT/z_iF$, where z_i and F are the charge of ions
199 (i.e. TTA⁺) and Faraday constant, respectively. This means
200 that the response of the electrode for the studied system in
201 aquo-organic medium is Nernstian. Though the electrode
202 showed Nernstian response, it lost its sensitivity at higher
203 concentrations of DMF and DMSO in the solvent [$>40\%$
204 v/v], and could not be used for CMC determination using
205 electrochemical measurements. Also the membrane made
206 of DTAB ϕ_4 could be successfully used for the detection of
207 TTA⁺ ions in water, suggesting the possibility of their use
208 as cation selective electrode irrespective of the chain length
209 of the cation as well as in aquo-organic medium.

210 4. Conclusions

211 A surfactant ion selective electrode originally sensitive
212 to dodecyltrimethylammonium ions (DTA⁺) was proved
213 to be sensitive towards tetradecyltrimethylammonium ions
214 (TTA⁺) and successfully employed for evaluation of criti-
215 cal micelle concentration of tetradecyltrimethylammonium
216 bromide. The electrode was also used for determination of
217 critical micelle concentration of tetradecyltrimethylammo-
218 nium bromide in aquo-organic medium i.e. water/dimethyl
219 formamide and water/dimethyl sulfoxide mixture, up to
220 40% v/v of the organic liquid. The validity of this ISE,
221 for electrochemical measurements, was substantiated by
222 comparable values of critical micelle concentration of
223 tetradecyltrimethylammonium bromide obtained by using
224 this electrode, with those obtained by conductivity mea-
225 surements in aquo-organic media. The ISE showed good
226 resistance towards the mixed solvent system (within the
227 concentration range studied) and hence it can prove to be an
228 important tool for studying the self-aggregation of cationic
229 surfactants in aquo-organic medium.

230 Acknowledgements

231 Thanks are due to Prof. P. Letellier and his colleagues
232 at Pierre et Marie Curie University, Paris for help in the
233 making of the ISE of surfactants and relevant discussion on
234 surfactant sensitive ISE.

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

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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 the thermodynamics of micellization and adsorption were determined. The CMC was very low for mixed systems, indicating probable use as a detergent with less effect on the environment because of surfactant biodegradability and less amount in the 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 a steady-state fluorescence quenching method at a total surfactant concentration of about ~ 10 mM at 25°C , was almost independent of the 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 the intensities (I_1/I_3) of the pyrene fluorescence emission spectrum, and the 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 nonspherical in nature. The cloud point of oxyethylene group-containing surfactants was increased by the addition of PES. Foaming was temperature dependent, and a 1:1 mixed system showed minimum foaming. All performance properties were composition dependent.

Paper no. S1349 in *JSD* 7, 87–96 (January 2004)

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

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Abbreviations: α , degree of micelle ionization, A_{CMC} , area per molecule at CMC, A_{lim} , limiting surface area per molecule, β^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 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 a 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, and technological, biochemical, and pharmaceutical formulations (1,2). Mixed surfactants exhibit performance superior to that of single surfactants, and composition as well as concentration can be optimized for a particular application (3). Synergistic interactions between surfactant molecules in mixed surfactant systems may be exploited to reduce the total amount of surfactant used in a particular application, which ultimately can lead to a reduction in cost and environmental impact (4). Because of their distinctive behavior compared to single surfactants, mixed surfactant systems, such as nonionic–nonionic (5,6), nonionic–anionic (7,8), nonionic–cationic (9), and anionic–zwitterionic (10) combinations, have attracted attention in both theoretical studies and practical applications (11). Determination of various physicochemical properties of surfactant mixtures 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 plant material and good biodegradability, PES have superior detergency for fabrics and a high tolerance against calcium ions (12), indicating it can possibly be used in hard water. Moreover, the mixed system is expected to have low CMC values; hence, the amount required for use will be low. We are also interested in comparing properties of derivatives of various fatty acids (e.g., myristic, palmitic, and stearic acids) in mixed systems with $C_{12}E_6$ to determine which mixture will be a better detergent and to optimize 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. $C_{12}E_6$ 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 duNoüy 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 a 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 C_{12}E_6 (1% wt/vol) in the presence of increasing amounts of PES was determined as described earlier (14). The CP are averages of the temperatures at which clouding appears and then 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 bandpasses were 3 and 1.5 nm, respectively. The scan speed was 60 nm min^{-1} . Each spectrum

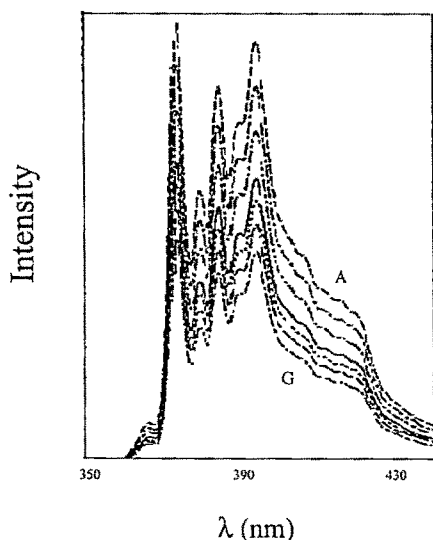


FIG. 1. Representative emission fluorescence spectra of 10^{-6} M pyrene in aqueous micellar solutions of $\text{C}_{12}\text{E}_6/\text{PES}$ (5:5) at various quencher concentrations. From top to bottom (A) zero, (B) $1.8 \times 10^{-5}\text{ M}$, (C) $4.0 \times 10^{-5}\text{ M}$, (D) $6.6 \times 10^{-5}\text{ M}$, (E) $8.6 \times 10^{-5}\text{ M}$, (F) $1.0 \times 10^{-4}\text{ M}$, (G) $1.2 \times 10^{-4}\text{ M}$ C_{12}E_6 , hexaoxyethylene monododecyl ether, PES, α -sulfonato palmitic acid methyl ester

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 $12 \times 10^{-5}\text{ M}$. N_{agg} was deduced from the following equation (15):

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

where $[Q]$ and $[S]$ are the concentrations of quencher and total surfactant, respectively. I_0 and I are the fluorescence intensities in the absence and presence of quencher. I_0 and I values also can be used to calculate the Stern–Volmer binding constant K_{SV} by using the following relation (16):

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

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

The ratio of the intensity of the first and third vibronic peaks (I_1/I_3) of the pyrene fluorescence emission spectrum in the presence of surfactants is an index of the micropolarity of the system and provides an idea of the microenvironment in the micelle (17).

NMR measurement. Proton NMR measurements were carried out in deuterium oxide (D_2O , 99.9 atom% D; Aldrich, Milwaukee, WI) at room temperature ($\sim 25^\circ\text{C}$). The mixed solutions of PES and C_{12}E_6 with concentrations of 0.05 M 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 the shape and size of the micelle. The latter are affected by temperature changes. Thus, we determined the relative viscosity values of 5% (wt/vol) $\text{C}_{12}\text{E}_6/\text{PES}$ 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 on the geometry of micelles and the interactions within the micellar core. The intrinsic viscosity $[\eta]$ can be calculated with the relation

$$[\eta] = \lim_{C \rightarrow 0} (\eta_r - 1) / C \quad [3]$$

where $\lim_{C \rightarrow 0}$ 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 with a variation of the Ross-Miles method (22). Two hundred milliliters of surfactant solution (5.8 mM) was allowed to fall freely into 50 mL of the same solution through a 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 values for surface tension (γ) vs. surfactant concentration ($\log_{10} C$) are shown in Figure 2. Reproducibility of surface tension measurements was $\pm 0.1 \text{ dyn/cm}$. The plot of surface tension vs. concentration did not show any minimum.

Conductance. Conductance vs. surfactant concentration (mol/L) plots are shown in Figure 3 for pure PES only. No break in 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). 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

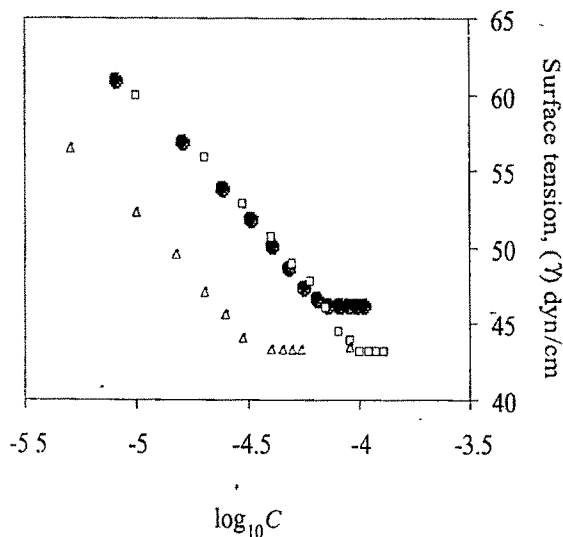


FIG. 2. Representative plots of surface tension (γ) vs. log concentration ($\log C$) of surfactant (\square) 3.7, $C_{12}E_6$ /PES at 40°C, (Δ) 9.1, $C_{12}E_6$ /PES at 45°C, (\bullet) 1.9, $C_{12}E_6$ /PES at 45°C

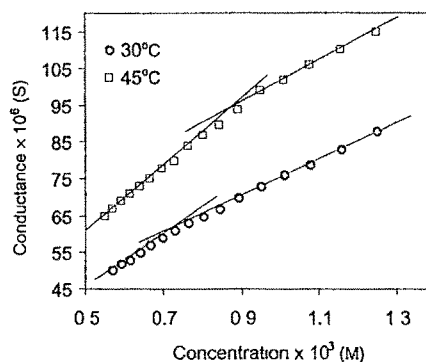


FIG. 3. Representative plots of conductance vs. PES concentration. For abbreviation see Figure 1

(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 the 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 $C_{12}E_6$ /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

TABLE 1
Critical Micelle Concentration (CMC) (mM) Values of $C_{12}E_6$ /PES Mixed Surfactant Systems in Aqueous Media at Selected Temperatures^a

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) ^c	(0.64) ^c	(0.66) ^c	(0.70) ^c

^a $C_{12}E_6$, hexaoxyethylene monododecyl ether, PES, α -sulfonato palmitic acid methyl ester, N_{PES} , mole fraction of PES in mixture

^bValues in parentheses are the degree of ionization of micelle (α) of PES or values can range between 0 and 1

^cCMC values were determined from conductivity measurements

by conductance and surface tension measurements are less than 1%. This was determined by at least two measurements.

Thermodynamics of micellization and interfacial adsorption. The value of the CMC of a surfactant in an 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)

$$\Delta G_m^\circ = RT \ln X_{\text{CMC}} \quad [4]$$

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

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

The degree of micelle ionization (α) was computed from the ratio between the slopes of the postmicellar 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 system as nonionic. The ΔG_m° values are presented in Table 2, where all ΔG_m° values are negative and become increasingly negative with an increase in temperature. The standard enthalpy ΔH_m° and ΔS_m° of micellization were evaluated from a ΔG_m° vs. T plot. The slope and intercept gave ΔS_m° and ΔH_m° , respectively. The maximum errors in ΔG_m° , ΔH_m° , and ΔS_m° were $0.034 \text{ kJ}\cdot\text{mol}^{-1}$, $2.4 \text{ kJ}\cdot\text{mol}^{-1}$, and $7.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively. The micelliza-

tion 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, the ΔH_m° 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 the mixed micelle changes. The ΔH_m° 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 the CMC values are very low and, because less is needed to accomplish the same task, the cost is not

TABLE 2
Thermodynamic Parameters of Micellization of $C_{12}E_6$ /PES Mixed Surfactant Systems at Four Temperatures^a

N_{PES}	$-\Delta G_m^\circ$ (kJ·mol ⁻¹) at				ΔH_m° (kJ·mol ⁻¹)	ΔS_m° (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. For abbreviations see Table 1

^bIn the plot of ΔG_m° vs. T , the point at temperature 303 K was dropped

TABLE 3
Maximum Surface Excess (Γ_{max}) and Limiting Surface Area per Molecule (A_{min}) of $C_{12}E_6$ /PES Mixed Surfactant Systems^a at Selected Temperatures

N_{PES}	$\Gamma_{\text{max}} \times 10^{10}$ mol cm ⁻² at				A_{min} (nm ²)			
	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K
0.0	2.48	2.71	2.86	2.98	0.67	0.61	0.58	0.55
0.1	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

^aFor abbreviations see Table 1

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° 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 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) 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.

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

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

where N , π_{CMC} , and A_{CMC} are Avogadro's number, the surface pressure at the CMC ($\gamma_0 - \gamma_{\text{CMC}}$), 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 the surface pressure at CMC (π_{CMC}) at a constant minimum surface area per molecule. $\Delta G_{\text{ad}}^\circ$ values are presented in Table 4. 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 the micellization process and that micellization occurs only after the interface becomes saturated

TABLE 4
Free Energy of Adsorption^a and Traube's Constant^b for $C_{12}E_6$ /PES Mixed Surfactant Systems^a at Selected Temperatures

N_{PES}	$-\Delta G_{\text{ad}}^\circ$ (kJ mol ⁻¹) at			
	303 K	308 K	313 K	318 K
0.0	44.5 (4.7×10^7)	44.7 (3.8×10^7)	45.3 (3.6×10^7)	45.5 (3.0×10^7)
0.1	43.9 (3.4×10^7)	44.1 (3.0×10^7)	44.3 (2.5×10^7)	45.3 (3.6×10^7)
0.3	45.5 (7.0×10^7)	45 (4.3×10^7)	46.6 (6.0×10^7)	46.1 (4.9×10^7)
0.5	42.7 (2.0×10^7)	42 (1.3×10^7)	42.9 (1.4×10^7)	43 (1.5×10^7)
0.7	43.3 (2.9×10^7)	43.7 (2.6×10^7)	43.1 (1.5×10^7)	44 (2.2×10^7)
0.9	39.9 (0.7×10^7)	42.4 (1.5×10^7)	40.7 (0.6×10^7)	42.2 (1.1×10^7)
1.0	58.3 (1.1×10^{10})	55.8 (2.9×10^{10})	58.7 (6.2×10^9)	60.3 (8.0×10^9)

^aError is less than 1%

^bValues 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

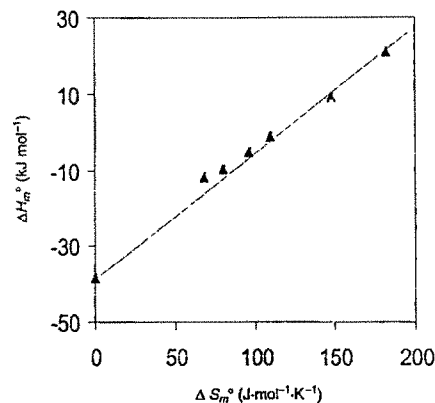


FIG. 4. Enthalpy-entropy compensation plot of micellization of a $C_{12}E_6$ /PES mixed surfactant system. For abbreviations see Figure 1

with the monomeric surfactant. It has been suggested (36) that

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

where σ is Traube's constant (37) as 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 favorably with literature values (38). A plot of σ vs. T for pure $C_{12}E_6$ gives a reasonably straight line with a negative slope, although for the other systems a minimum is observed near 310 K. A linear correlation between ΔS_m° and ΔH_m° (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

TABLE 5
Interaction Parameter (β^m) Values of $C_{12}E_6$ /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. For abbreviations see Table 1

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 the poly(ethylene oxide) class have a weak cationic character resulting either from oxonium ion formation with protons from water or the sharing of the hydrogen in water by hydrogen bond formation. Thus, the attractive interaction is probably between this weak cation and 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 for 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 the X_1 (mole fraction of ionic surfactant in the mixed micelle) values obtained 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 determined without much error. The activity coefficient values also were 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 and f_2 are the activity coefficients of surfactants 1 and 2, respectively, in the mixed micelle. The f_1 and 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 the mixed surfactant sys-

TABLE 6
Activity Coefficient (f_1 and f_2) Values of $C_{12}E_6$ /PES Mixed Surfactant Systems in Aqueous Media at Different Temperatures

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

^aValues in parentheses are f_2 , i.e., the activity coefficient of the nonionic surfactant ($C_{12}E_6$). For abbreviations see Table 1

tems in Table 5. The activity coefficient values of PES are low, and although activity coefficient values of $C_{12}E_6$ (f_2) are higher, they are not close to unity, indicating that $C_{12}E_6$ 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. 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)

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

where $B_0 = \ln C_1$ (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 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 the nonionic surfactant has 12 carbon atoms. 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 also may be the reason for attractive interaction in the present system. The free energies of micellization calculated from Equations 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.

TABLE 7
 B_0 , B_1 , and B_2 Values for $C_{12}E_6$ /PES Mixed Surfactant Systems^a

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. For other abbreviations see Table 1

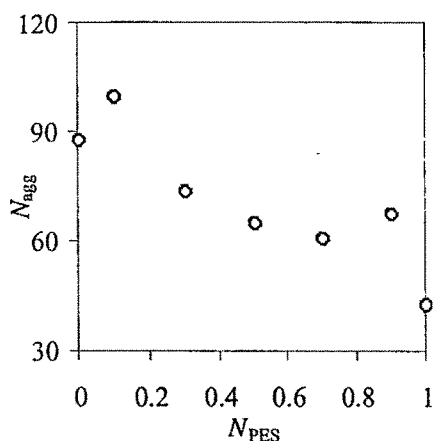


FIG. 5. Plot of micellar aggregation number (N_{agg}) vs mole fraction of PES (N_{PES}) at room temperature (-25°C).

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

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

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 $C_{12}E_6$ /PES mixture are presented in Figure 5. The N_{agg} values of mixtures are larger than those of pure PES but are in general lower than that of $C_{12}E_6$. Such behavior may be due to the presence of $C_{12}E_6$ in the mixed micelle, resulting in screening of headgroup interactions, compared to pure PES.

Microenvironment. The ratio of the first and 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 of surfactants 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_{SV} values calculated from Equation 2 are presented in Table 8. K_{SV} is the ratio of the bimolecular quenching constant to the unimolecular decay constant. Also, K_{SV} is the product of k_q , the rate constant of the quenching process, and τ is the actual lifetime of the probe in the absence of bimolecular quenching (18). Thus, from the values of K_{SV} , we can assume that quenching is efficient and also that the lifetime of the pyrene in $C_{12}E_6$ and most of the mole ratios in the mixed micelle are higher if we assume that k_q for all systems are of similar magnitude.

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

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

We evaluated the apparent ϵ of the pure and mixed micelles

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^a

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

^aFor other abbreviations see Table 1

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 differed from the calculated values. We believe this difference results from attractive interaction between the surfactants inside the micelle.

NMR measurement. Proton NMR spectroscopy also was used to study $C_{12}E_6$ /PES mixed surfactant behavior. 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 to methylene protons [$(\text{CH}_2)_9$]. The changes in chemical shifts were monitored with the change in surfactant proportions, and the shift due to oxyethylene showed a significant change compared to other peaks.

The polyoxyethylene signal showed 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

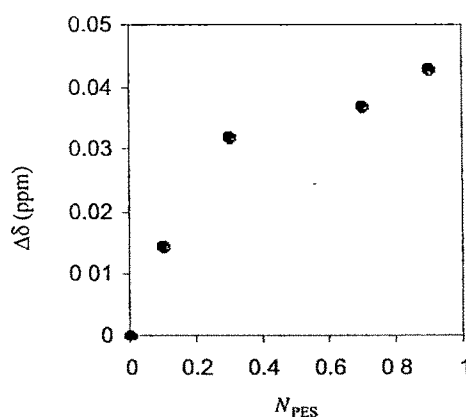


FIG. 6. Change in downfield shift of oxyethylene proton signal ($\Delta\delta$) vs mole fraction of PES (N_{PES}). For abbreviation see Figure 1

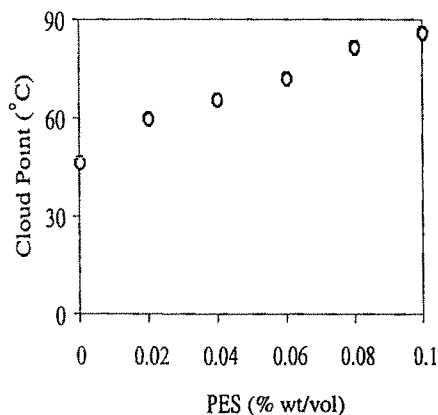


FIG. 7. Cloud point ($^{\circ}\text{C}$) of C_{12}E_6 (1% wt/vol) in the presence of PES. For abbreviations see Figure 1

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 (14,49,50). 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 behavior 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.

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

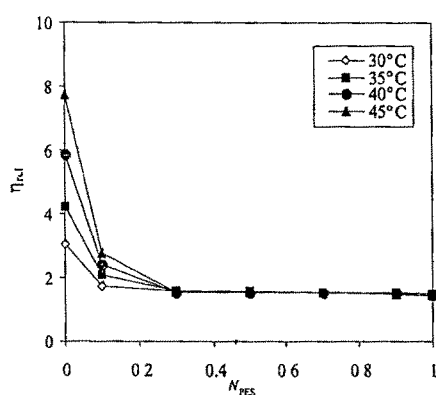


FIG. 8. Plot of relative viscosity (η_r) vs mole fraction of PES (N_{PES}). For abbreviations see Figure 1

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

^aFor abbreviations see Table 1

cated that mixed micelles were nonspherical, i.e., for spherical systems, $|\eta|$ should be between 2.5 and $4.0 \text{ cm}^3 \cdot \text{g}^{-1}$ (21). The lowest $|\eta|$ in this system was $9.4 \text{ cm}^3 \cdot \text{g}^{-1}$ (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 PES or of the mixed surfactant system at a higher PES ratio. For C_{12}E_6 (1% wt/vol) and $N_{\text{PES}} = 0.1$, 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 nonspherical. This behavior was also reported for Triton X-100 (14).

Foaming. Nonionic surfactants are known to have lower foaming, whereas ionic surfactants have higher foam-forming capability. 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 the Ross-Miles method. The concentration of the surfactant was kept at 5.8 mM, since the Ross-Miles test is usually performed at 0.25% surfactant concentration ($\sim 5.8 \text{ mM}$) (22). The CMC for both surfactants are $\leq 5.8 \text{ mM}$, so both surfactants attained their maximal foam height value. Foaminess of pure and mixed surfactant systems increased with increasing temperature (Table 10). The foam

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 ± 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 at least two runs. For abbreviations see Table 1

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. The foam heights for PES are higher and increase with increasing temperature, which is obvious because α -sulfoesters containing 16–17 carbon atoms show maximal 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 a requirement for good foam-forming qualities (53). This phenomenon is enhanced with increasing temperature, resulting in higher foam heights.

ACKNOWLEDGMENTS

Financial support from Lion Corporation, Tokyo, Japan, is gratefully acknowledged. Dr. T. Mukherjee of BARC, Mumbai, India, deserves our grateful thanks for fluorescence measurements.

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[Received January 6, 2003; accepted September 9, 2003]

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

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ABSTRACT

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

Key Words Micellization, Mixed surfactant, Interaction parameter; Foaming, Detergency

INTRODUCTION

Surfactants are versatile compounds widely used in a variety of industrial and commercial applications.^[1] The

application potential of surfactants is closely related to their surface wetting capability, detergency, and solubilization in areas like mining, petroleum, chemical, and pharmaceutical industries as well as in chemical and

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biochemical research^[2] Mixtures of surfactant solutions form mixed micellar aggregates that exhibit characteristic properties, which are superior to those of the individual components^[3,4] Synergistic behaviors of mixed surfactant systems may be exploited to reduce the total amount of surfactant used in particular applications resulting in reduction of cost and environmental impact^[5] Consequently much attention has been directed towards the experimental as well as theoretical investigation of mixed surfactant system. The studies on different varieties of combinations formed by different surfactants such as nonionic–nonionic,^[6,7] nonionic–anionic,^[8–14] nonionic–cationic,^[15] etc. are reported in the literature The α -sulfonato myristic acid methyl ester (MES) mixed with $C_{12}E_6$ was studied because of the good biodegradability and relatively quick availability of MES from renewable vegetable material.^[16] Fatty acid methyl ester based surfactants are readily degradable under aerobic conditions. Thus fatty acid ester based surfactants are the subject of recent investigation and review^[17,18] Gode et al.^[19] observed 99% primary degradation and 76% ultimate degradation of fatty acid ester based surfactants in two different tests.

This article deals with the physicochemical investigation of surfactants, which involves the cmc determination by surface tension and conductivity measurements and computation of standard thermodynamic parameters of micellization (ΔG_m° , ΔH_m° , and ΔS_m°). Interfacial parameters such as maximum surface excess (Γ_{max}), minimum area per molecule (A_{min}) and the standard thermodynamic parameters of adsorption at the air–water interface (ΔG_{ad}° , ΔH_{ad}° , and ΔS_{ad}°) were also computed from surface tension data. The micellar aggregation numbers (N_{agg}) were determined by fluorescence measurements. Performance properties, viz detergency, foaming, and viscosity were also studied. Cloud points (CP) of the nonionic $C_{12}E_6$ in the presence and absence of electrolytes (NaCl, NaBr, and NaI) and nonelectrolytes like polyethylene glycols (MW 200, 300, and 400) were also evaluated

EXPERIMENTAL SECTION

Materials

Hexaoxyethylene monododecylether [$CH_3(CH_2)_{11}(OCH_2CH_2)_6OH$], i.e., $C_{12}E_6$, and α -sulfonato myristic acid methyl ester, $C_{12}H_{25}CH(SO_3Na)COOCH_3$ (MES), of Lion Corporation, Tokyo, Japan were used without further purification NaBr, NaI, (Loba Chemie, Baroda, India) and NaCl (Qualigens, India) were used as received Polyethylene glycols (MW 200, 300 and 400)

were obtained from Merck, India Cetyl pyridinium chloride (Loba Chemie, Baroda, India) was recrystallized twice from benzene. Pyrene (Fluka, Germany) was recrystallized from cyclohexane All solutions were prepared using doubly distilled water

Surface Tension Measurements

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

Conductivity Measurements

The conductance (k) measurements were done with an Equiptronics (India) conductivity bridge A dip type cell of cell constant 1.01 cm^{-1} was used The conductance of different solutions, which were obtained on aliquot addition of a known concentrated surfactant solution to a given volume of the thermostated solvent, were measured. Specific conductance (k) vs concentration of surfactant (mol L^{-1}) plots are shown in Fig 2 for pure MES only, as no break in the specific conductance vs concentration plots was observed in any of the mixed surfactant systems.

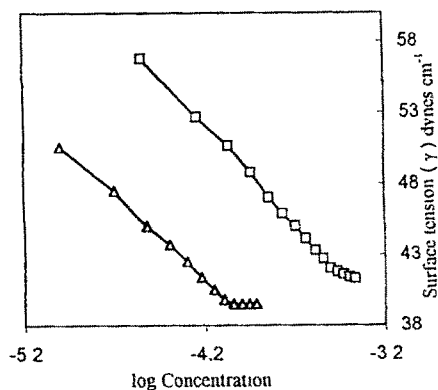


Figure 1. Representative plots of surface tension (γ) vs log concentration ($\log C$) of surfactant K_{e1} Δ , 7.3, $C_{12}E_6$, MES at 40°C, \square , 1.9, $C_{12}E_6$, MES at 45°C

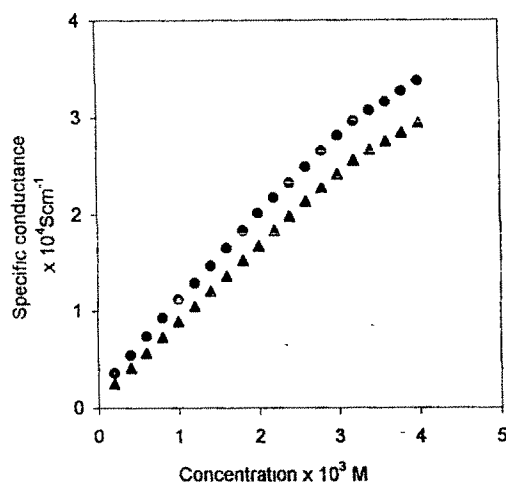


Figure 2. Representative plots of specific conductance (κ) vs. concentration of MES. Key: ●, MES at 40°C; ▲, MES at 35°C.

Viscosity

The viscosity of 0.25% (w/v) $C_{12}E_6$, 5% (w/v) $C_{12}E_6$ /MES mixed surfactant solution was studied using an Ubbelohde suspended level viscometer. The effect of NaCl of different concentration on viscosity of 5% (w/v) $C_{12}E_6$ was also studied. The temperatures were 30°C, 35°C, 40°C, and 45°C and were maintained within ($\pm 1^\circ\text{C}$) in a thermostated bath. The intrinsic viscosity $[\eta]$ can be calculated using the relation,

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

where zero concentration limit indicates that intermolecular interactions are absent. Some researchers^[20,21] have taken $[\eta]$ to be equal to $(\eta_r - 1)/C$ without the condition of limiting concentration. It has been defined as the shape factor and is expected to have a value between 2.5 and $4 \text{ cm}^3 \text{ g}^{-1}$ for globular particles.^[22] In this article we have calculated $[\eta]$ without taking the zero concentration limit.

Foaming

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

Fluorescence Measurements

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

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

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

where $[Q]$, $[M]$, and $[S]$ are the concentrations of quencher, micelle, and total surfactant, respectively.

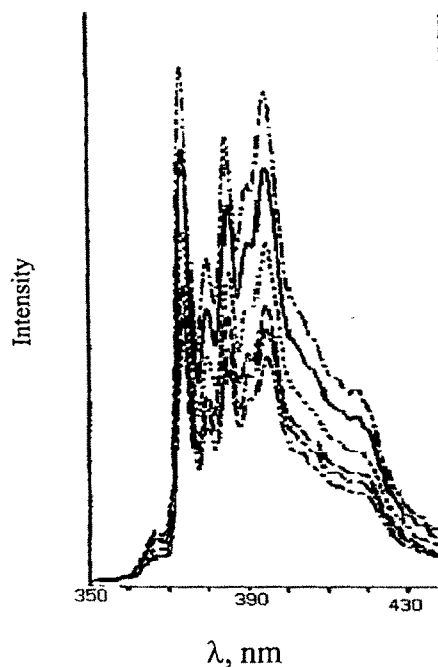


Figure 3. Representative emission fluorescence spectra of 10^{-6} M pyrene in aqueous micellar solution of $C_{12}E_6 \cdot \text{MES}$ (5.5)

The I_0 and I are the fluorescence intensities in the absence and presence of quencher, respectively. I_0 and I values can also be used to calculate the Stern-Volmer binding constant K_{SV} by using the following relation.

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

Microenvironment

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

Detergency

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

Cloud Point Measurement

Cloud points are manifestations of solvation/desolvation phenomena in nonionic surfactant solutions.^[26,27] Cloud points of $C_{12}E_6$ (1%, w/v) solutions were determined by visually noting the temperature at which turbidity was observed when the surfactant solutions were slowly heated under constant stirring.^[28] The temperature at which the turbidity disappeared on slow cooling was also noted. The cloud points presented are the averages of appearance and disappearance temperatures, which did not differ by more than 0.4°C.

RESULTS AND DISCUSSIONS

The micellization of surfactants is dependent on temperature, additives, and solvent.^[29] Intramolecular interactions in mixed surfactants are studied at the cmc, where their effect on mixed micelle formation can be measured.^[30] In our present study, the cmcs of $C_{12}E_6$ /MES mixed surfactants, where the mole ratio of the two components were varied, were determined at different temperatures. The cmc data are presented in Table 1.

The cmcs of ionic and nonionic surfactants are functions of temperature. For the nonionic surfactant, the cmc decreases with increasing temperature as has generally been observed in the literature.^[31,32] In the case of MES, with increasing temperature (30–45°C), the cmc increases. The cmc values of MES obtained by conductivity are in good agreement with those reported in literature.^[16] The hydrophobic interactions are responsible for micelle formation. The hydration of hydrophobic groups in nonionic surfactant decreases as the temperature increases and thus the disturbance of water structure around the hydrophobic group results in increasing hydrophobic interaction and consequently the cmc decreases. Moreover, the hydration of oxyethylene groups also decreases as temperature increases resulting in lower cmc. The ionic repulsive forces are responsible for higher values of cmc for ionic surfactants.^[29] In the case of $C_{12}E_6$ /MES mixed systems, the cmc values were evaluated by surface tension measurements only, as conductance did not show any break. We have failed to understand the reason. Thus we decided that this nonionic-anionic surfactant mixture behaves as a nonionic

Table 1. Critical micelle concentration (mM) values of $C_{12}E_6$ /MES mixed surfactant system in aqueous media at different temperatures

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

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

^bConductivity data

Table 2. The thermodynamic parameters of micellization of C₁₂E₆/MES mixed surfactant systems

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

one i.e., mixed micelles are nontonic in nature. The cmc's of binary combinations of C₁₂E₆ and MES fall between the individual cmc values of the components (C₁₂E₆, MES). The cmc values of MES obtained by surface tension and conductance do differ at low temperature (Table 1). Repeated experimentation confirmed this result. However, no explanation is forthcoming.

The standard thermodynamic parameters of micellization can be determined from the temperature dependence of the cmc.^[33] The standard free energy of micellization for a nontonic surfactant is given by the relation^[31]

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

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

The ΔG_m° values are presented in Table 2. It is evident from Table 2 that the ΔG_m° values become more and more negative with increasing temperature, suggesting spontaneity in micelle formation with rising temperature. The standard enthalpy ΔH_m° and standard entropy ΔS_m° of micellization were evaluated from ΔG_m° to T plots. The slope and intercept gave ΔS_m° and ΔH_m° ,

respectively. The micellization process is endothermic, except for MES, where it is exothermic. This indicates that the micellization process is purely entropy dominated for C₁₂E₆ and mixed systems, though not exactly so for MES, that is, micellization is specific to surfactants and temperature.^[34-36] The entropy of micellization ΔS_m° values are positive, and large values of entropy were obtained, which is seen quite often.^[37] The entropy changes are so large that it may be considered as a change of phase.

The surface excess concentration under the conditions of surface saturation (Γ_{max}) can be used as a measure of maximum extent of adsorption of surfactants at the air/water interface using the Gibbs adsorption equation^[7,38] The Γ_{max} and A_{min} values thus calculated are presented in Table 3. It is observed that Γ_{max} increases with increasing temperature for C₁₂E₆, whereas it decreases with increasing temperature for MES. The increase in Γ_{max} for C₁₂E₆ is due to decreasing hydration of ethoxy segments, leading to greater tendency to locate at the air/water interface. The decrease in Γ_{max} with rising temperature for MES may be due to higher solubility of MES in water, which opposes adsorption

Table 3. Maximum Surface Excess (Γ_{max}) and limiting surface area per molecule (A_{min}) of C₁₂E₆/MES mixed surfactant system

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

of surfactants at the air/water interface. The thermodynamic parameters of adsorption of surfactants at the air/water interface, evaluated using the relation,^[39]

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

are presented in Table 4, where N , Π_{cmc} , and A_{cmc} are Avogadro's number, surface pressure at cmc ($\gamma_o - \gamma_{cmc}$), and area per molecule at cmc, respectively. The second term in Eq (5) represents surface work involved in going from zero surface pressure to surface pressure at cmc (Π_{cmc}) at constant minimum surface area per molecule. The ΔH_{ad}° and ΔS_{ad}° values were evaluated from a ΔG_{ad}° to T plot. It is clear from Table 4, that ΔG_{ad}° values are negative throughout, indicating that adsorption at the air/water interface takes place spontaneously in pure and mixed surfactants. The ΔG_{ad}° values are more negative in comparison to ΔG_m° values suggesting that, when a micelle is formed, more work has to be done to transfer the surfactant molecules in its monomeric form at the surface to the micellar stage in bulk. The ΔH_{ad}° values in most cases is positive, suggesting adsorption of surfactants is an endothermic process. The standard entropy of adsorption ΔS_{ad}° values are largely positive, reflecting greater freedom of movement of hydrocarbon chains at the air/water interface. However the study of adsorption of surfactants has proven not to be straightforward,^[40] as can be seen from our results where any regularity is difficult to observe.

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

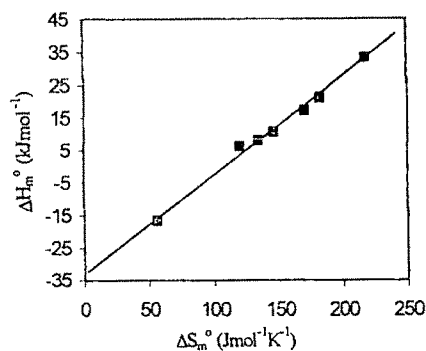


Figure 4. Plot of entropy (ΔS_m°) vs enthalpy (ΔH_m°).

The values of interaction between the surfactant molecules in the mixed micelle (β^m) evaluated using Rubingh's equation^[44] are presented in Table 5. The interaction parameter (β^m) values are all negative at all mole fractions of $C_{12}E_6$ /MES system indicating an attractive interaction between the MES and $C_{12}E_6$ head-groups in the mixed micelle, leading to electrostatic stabilization. As can be seen from Table 1, the cmc of MES seems to differ when surface tension or conductance methods are used. Hence, to calculate β^m , the micellar interaction parameter, we used both types of cmc data for MES. It can be seen from Table 5, that the calculated β^m values do not differ much (maximum about 10%) and the interaction is always attractive in nature. The composition of the micelle seems to remain exactly the same. The maximum difference in X_1 values by using different cmc values (i.e., either conductance or surface tension) was $\sim 7\%$ though, in most cases, it was less than 2%. This indicates that the composition of mixed micelle is without much error. It is suggested that nonionic surfactants of the poly(ethylene oxide) class have a weak cationic character resulting either from oxonium ion formation with protons from water or sharing of H of

Table 4. The thermodynamic parameters of adsorption of $C_{12}E_6$ /MES mixed surfactant systems

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

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

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

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

^aThe data after “/” was calculated using cmc of MES by ST measurement

water by hydrogen bond formation. Thus the attractive interaction is probably due to this weak cation with anionic surfactant, MES.^[45] The activity coefficient values were also evaluated using the relations:^[1]

$$\ln f_1 = \beta^m(1 - X_1^2) \quad (6)$$

$$\ln f_2 = \exp \beta^m(X_1^2) \quad (7)$$

where X_1 is mole fraction of surfactant 1 in the micelle and f_1 and f_2 are the activity coefficients of surfactants 1 and 2, respectively, in the mixed micelle. The f_1 and f_2 values are tabulated in Table 6.

The much lower mole fraction (X_1) of MES is reflected in its small activity coefficient (f_1) values, which suggests that MES in the mixed micelle is far away from the standard state. The (f_2) values of C₁₂E₆ are obviously higher (close to unity) which increase with increasing temperature, indicating that C₁₂E₆ in the mixed micelle is near its standard state.^[46,37]

The micellar aggregation numbers (N_{agg}) determined by steady state fluorescence quenching are represented in Fig. 5. It is evident from Fig. 5 that N_{agg} values of mixed

surfactant at all the mole ratios are different than those of single surfactants, though a regularity is difficult to visualize. This may be attributed to two competing factors (a) a decrease in steric interactions of C₁₂E₆ because of incorporation of MES into C₁₂E₆ micelles, and (b) a decrease in repulsive headgroup interactions in MES due to the presence of C₁₂E₆, and thus a larger mixed micelle is formed compared to C₁₂E₆ or MES.^[29,47]

The K_{SV} values calculated from Eq. (3) and given in Table 7 are the ratio of bimolecular quenching constant to unimolecular decay constant, and hence, we can say from the magnitudes of K_{SV} that the quenching is very efficient in these micelles. It should also be noted that K_{SV} is equal to the product of k_q , the rate constant quenching and τ , the actual lifetime of the fluorescing molecule in the absence of bimolecular quenching.^[48] We have not been able to determine the exact magnitude of τ . However, we can assume that τ for all mixed systems, presented in this paper and in pure MES, are almost same since k_q can be assumed to be similar. For C₁₂E₆ the fluorescence lifetime is much higher.

The effect of electrolytes like NaCl, NaBr, and non-electrolytes like polyethylene glycols (MW 200, 300, and

Table 6. Activity coefficient (f_1 and f_2) values of C₁₂E₆/MES mixed surfactant systems in aqueous media at different temperatures

N_{MES}	Temperature (K)			
	303	308	313	318
0.1	0.018 (0.933)	0.025 (0.975)	0.0297 (0.989)	0.0224 (0.982)
0.3	0.123 (0.988)	0.280 (0.99)	—	—
0.5	0.154 (0.964)	0.094 (0.92)	0.076 (0.917)	0.044 (0.825)
0.7	0.107 (0.743)	0.105 (0.79)	0.115 (0.858)	0.112 (0.876)
0.9	0.317 (0.764)	0.303 (0.79)	0.327 (0.862)	0.330 (0.889)

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

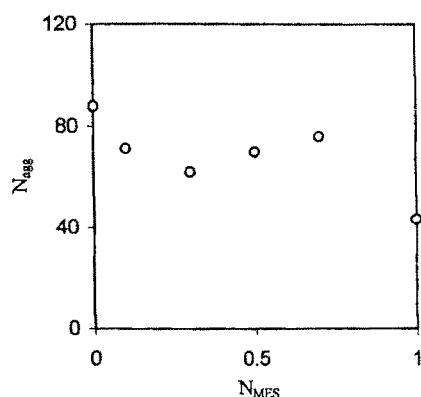


Figure 5. Plot of micellar aggregation number (N_{agg}) vs mole fraction of MES (N_{MES}) at room temperature ($\sim 25^\circ\text{C}$)

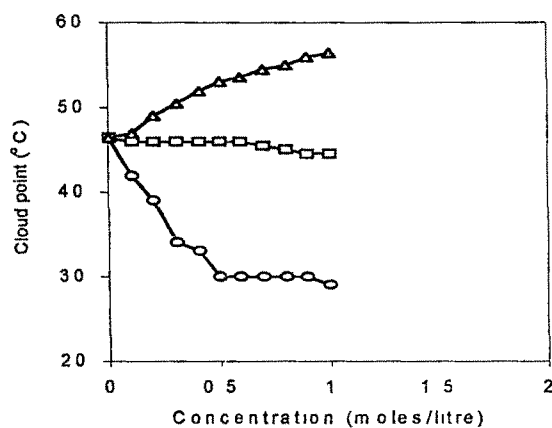


Figure 6. Plot of CP of $C_{12}E_6$ (1%, w/v) vs. concentration (mol L^{-1}) of electrolytes. Key: \circ , NaCl, Δ , NaI, \square , NaBr

400) on CP of $C_{12}E_6$ (1%, w/v) solution are represented in Figs. 6 and 7, respectively. The PEGs have negligible effect on the CP, though electrolytes have large but different type of effects within the concentration range studied. The CP of $C_{12}E_6$ (1%, w/v) is 46.5°C . NaBr does not affect the CP significantly. NaI increases the CP of $C_{12}E_6$ because of less hydrophobicity of I^- ions, which decreases the possibility

of two molecules coming together due to the presence of water, whereas CP decreases in the presence of NaCl, which may be due to high solvation of Cl^- ions and which leads to disruption of water around the micelles and hence easy approach to each other.

The relative viscosity values of surfactant solution of $C_{12}E_6$ (5%, w/v) in the presence of NaCl at different temperatures were determined (Table 8). The relative viscosity of $C_{12}E_6$ increased on addition of NaCl and was double than that of $C_{12}E_6$ in the absence of NaCl. The relative viscosity values of $C_{12}E_6$ in the presence of 0.2 M NaCl could be determined at 30°C , 35°C , and 40°C only, whereas as the η_{rel} were evaluated at 30°C and 35°C only for $C_{12}E_6 + 0.5$ M NaCl, as the solution became turbid because the CP was reached. The $|\eta|$ values of $C_{12}E_6$ in the presence of NaCl are higher ($\sim 200 \text{ cm}^3 \text{ g}^{-1}$), which is expected as the viscosity of concentrated surfactant solution increases in the presence of inorganic salt.^[49] Such a large change in viscosity may be due to changes in the micelle, because of the salting out effect of NaCl. The presence of NaCl leads to salting out of surfactant, which favors micellization.^[11] Also, the steric interactions in $C_{12}E_6$ may be reduced due to the presence of NaCl, resulting in the increase in micelle size and relative viscosity of $C_{12}E_6$ (5%, w/v).

The viscosity of 5% (w/v) $C_{12}E_6$ /MES mixed surfactant solution (Fig. 8) shows negative deviation from linearity. The η_{rel} values of $C_{12}E_6$ are much higher than those of MES. That $|\eta| = 2.5\text{--}4.0 \text{ cm}^3 \text{ g}^{-1}$ indicates globular particles.^[22] The intrinsic viscosity values of $C_{12}E_6$, MES, and $C_{12}E_6$ /MES mixed surfactant solution at all mole fractions are high. The lowest $|\eta|$ is $6.2 \text{ cm}^3 \text{ g}^{-1}$. Addition of MES to $C_{12}E_6$ reduced the viscosity (Fig. 8). The η_{rel} is independent of higher MES ratio. The η_{rel} values of $C_{12}E_6$ show a minimum at about 35°C with increasing temperature at low surfactant (0.25%, w/v), (Table 9). However, at high concentration (5%, w/v), η_{rel} increases with temperature. In the presence of NaCl, η_{rel} and $|\eta|$ both increase with temperature indicating formation of elongated micellar species.^[22] Temperature has no significant effect on the viscosity of MES and $C_{12}E_6$ /MES mixed surfactant solutions at higher MES ratio (Fig. 8).

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

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

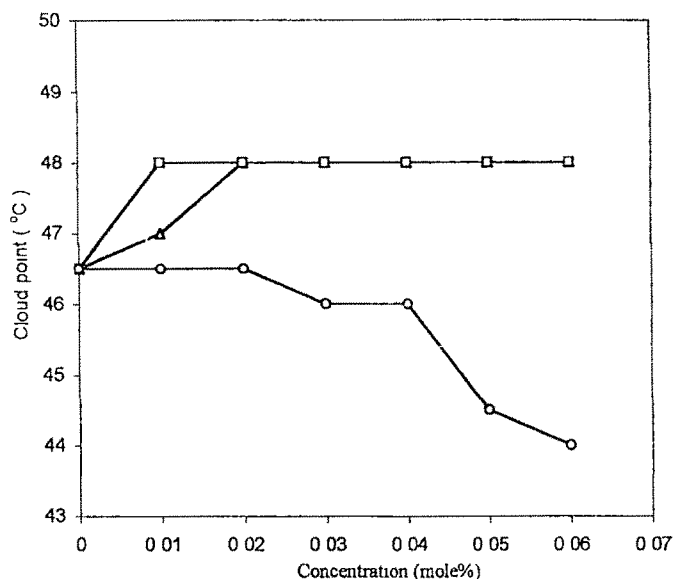


Figure 7. Plot of CP of $C_{12}E_6$ (1%, w/v) vs. concentration (mole%) of PEGs. Key: Δ , PEG 200; \square , PEG 300; \circ , PEG 400.

Foaming is an inherent property of surfactant-solutions. Nonionic surfactants containing poly(oxyethylene) groups produce both less foam and less stable foam than ionic surfactants. However, the foaming efficiency and stability of surfactants can be altered by addition of certain additives.^[1,50] We studied the foaming efficiency and foam stability of $C_{12}E_6$ in the presence of different mole fractions of MES at 30°C, 35°C, and 40°C. The foam heights indicative of foamability of $C_{12}E_6$ /MES mixed surfactant solutions were evaluated at different temperatures and are presented in Table 10. It is evident from Table 10 that these values are higher in most of mole fractions of mixed surfactants solutions than individual surfactants. Also, the foam heights increased with increasing temperature for pure as well as mixed surfactants, indicating better foaming efficiency at higher temperatures. In the case of mixed surfactants, there is a possibility of rapid variation of concentration at the

air/water interface, which is one of the main requirements for good foam-forming qualities,^[51] which is enhanced with rising temperature. Thus, higher foam heights for mixed surfactants indicate higher interfacial activity. Foams are very complex and it seems that a clear relation between foam height and variables does not exist. Moreover, drainage, evaporation, interaction with environment, etc. also affect foam stability.^[52]

Detergency of surfactant solutions was also studied using a dye removal method and is represented in Figs 9–12. The temperatures were maintained at 35°C and 50°C. For cotton fabric at 35°C, MES was found to be the most effective detergent at the initial point and the mixture the least effective. However, with time the mixture was a better detergent than the pure components. However, at 50°C, MES was more efficient at the starting point, with time the mixture as well as pure components had the same efficiency. For terry cotton $C_{12}E_6$ was an

Table 8. Viscosity study of $C_{12}E_6$ (5%, w/v) at different temperatures and in the presence of different amounts of NaCl

Concentration of NaCl (M)	η_{rel}				$ \eta \text{ cm}^3 \text{ g}^{-1}$			
	30	35	40	45	30	35	40	45
0.0	3.05	4.24	5.86	7.72	41	64.8	97.2	134.4
0.2	4.476	6.556	9.016	—	69.6	111.1	160.3	—
0.2	7.547	10.929	—	—	131	198.6	—	—

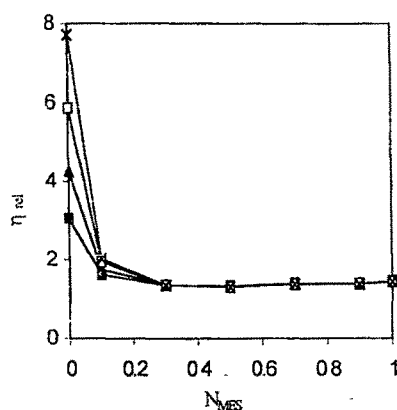


Figure 8. Plot of relative viscosity (η_{rel}) vs. mole fraction of MES (N_{MES}). Key: ■, 30°C; ▲, 35°C; □, 40°C; ×, 45°C

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

Temperature (°C)	η_{rel}	η_{abs} (poise)
30	0.986	0.00785
35	0.975	0.0070
40	0.997	0.0065
45	1.056	0.0063

efficient detergent both at 35°C and 50°C. The detergency efficiency of $C_{12}E_6$ was higher than MES, as nonionic surfactants, because of low critical micelle concentration are better solubilizing agents than ionics.^[53] The results did not show any synergistic behavior in this property in the mixed systems.

Table 10. Foam stability of $C_{12}E_6$ /MES mixed surfactant systems as a function of temperature

N_{MES}	Foam height (cm \pm 1 l)		
	30°C	35°C	40°C
0.0	12.6	14.3	17.1
0.1	14.3	15.7	17.5
0.3	15.5	19.6	23.2
0.5	22.5	27.1	31.5
0.7	20.8	24.0	28.8
0.9	18.9	22.4	26.5
1.0	16.8	20.5	25.0

Note: Total surfactant concentration was 5.8 mM, average of at least two runs

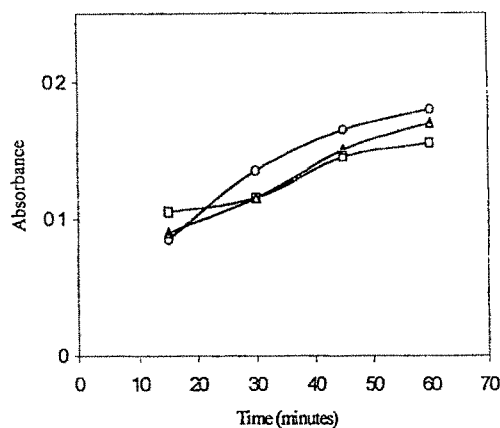


Figure 9. Plot of absorbance vs. time (min) at 35°C Key: □, MES; Δ, $C_{12}E_6$; ○, 5.5 $C_{12}E_6$:MES.

CONCLUSIONS

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

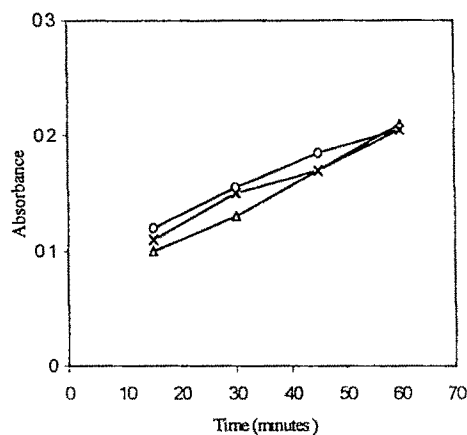


Figure 10. Plot of absorbance vs. time (min) at 50°C Key: ○, MES; Δ, $C_{12}E_6$; ×, 5.5 $C_{12}E_6$:MES

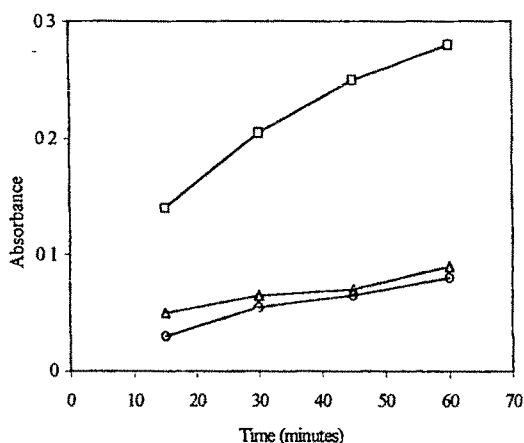


Figure 11. Plot of absorbance vs time (min) at 35°C Key Δ , MES, \square , $C_{12}E_6$; \circ , 5:5 $C_{12}E_6$:MES.

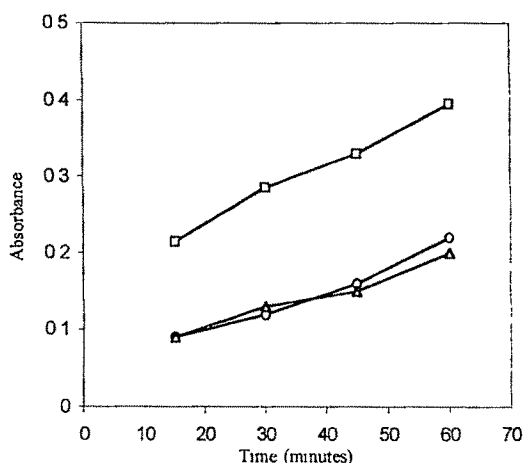


Figure 12. Plot of absorbance vs time (min) at 50°C Key \circ , MES, \square , $C_{12}E_6$, Δ , 5:5 $C_{12}E_6$:MES

foaming efficiency for mixed surfactant was superior than those of single surfactants. From the intrinsic viscosity values, the mixed micelles at all mole fractions were suggested to be elongated.

ACKNOWLEDGMENT

Financial assistance from Lion Corporation, Tokyo, Japan is gratefully acknowledged. Dr. T. Mukherjee of BARC, Mumbai, deserves our grateful thanks for fluorescence measurements.

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Received July 22, 2002

Accepted December 26, 2002

Study of the cloud point of $C_{12}E_n$ nonionic surfactants: effect of additives

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Received 4 June 2002; accepted 30 December 2002

Abstract

Nonionic surfactants are useful in the formation of emulsions. The aqueous solutions of these surfactants show complex phase behaviour including liquid–liquid phase separation at higher temperature. Addition of foreign substance to surfactant solutions does change the temperature at which the clouding phenomena occurs. In this article, we report the effect of electrolytes as well as nonelectrolytes on the cloud point (CP) of a series of nonionic surfactants of the poly(oxyethylene)ether type $C_{12}E_n$ ($n = 6, 9, 10$). It was observed that NaI and KI have different effect on the CP from that of NaCl, NaBr, KCl and KBr. Tetra butyl ammonium iodide (TBAI) acts differently on the CP from the Tetra methyl ammonium bromide (TMAB). Overall the electrolytes and nonelectrolytes have a large amount of effect on CP of nonionic surfactants, because of their effect on water structure and their hydrophilicity.

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Keywords Nonionic surfactants; Cloud Point; Electrolytes, Nonelectrolytes, Hydrophilicity

1. Introduction

Nonionic surface active agents are prepared by reacting a water insoluble material, such as an alkyl phenol with ethylene oxide to give a product which has an oil soluble group attached to a water soluble polyoxyethylene chain. The high water solubility of polyoxyethylene chain is due to hydrogen bonding between the solvent and the ether oxygen atoms in the chain. Since hydrogen bonding is temperature sensitive phenomenon, for

each nonionic emulsifier molecule, there exists a temperature at which the degree of hydration of the hydrophilic portion is just insufficient to solubilize the remaining hydrocarbon portion, which is called the 'Cloud Point' [1]. At this temperature, surfactant is no longer soluble in water and solution becomes hazy or cloudy. This instant separation of nonionic surfactant upon heating into two phases, one surfactant rich and other aqueous, containing surfactant close to cmc at that temperature is the characteristic of non-ionic surfactant which differentiates it from ionic surfactant. Nonionic surfactants are widely used as solubilizers, emulsifiers and detergents in many industrial processes. Therefore, the cloud point data are of considerable practical interest. For

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instance, the stability of O/W emulsions solubilized by nonionic surfactant has been related to CP [3–5]. In preparing emulsions, the CP is very important in selection of the most suitable surfactant for a given oil [3,6,7]. Moreover, pharmaceutical dosage forms consist of nonionic surfactant as stabilizer [8]. Several factors have been considered to be responsible for the CP phenomenon like structure of surfactant molecule, concentration, temperature and a third component (additive). CP is very sensitive to the presence of additives in a system, even at a very low concentration. The additives modify the surfactant–solvent interactions, change the cmc, size of micelles and phase behavior in the surfactant solutions [9]. Many efforts have been made to investigate the effect of various additives e.g. inorganic electrolytes [10,12–20], organic compounds [7,8,11,21–25], ionic surfactants [10,24–29], cationic surfactants [24,29] and zwitterionic surfactants on the cloud point of a nonionic surfactant. Some authors have also reported the CP of ionic surfactants [30–32]. This paper presents experimental results of the effect of various additives like inorganic electrolytes (NaX, KX, $\text{Ca}(\text{NO}_3)_2$ where X is halide ion) and nonelectrolytes (PEG-4000, carboxy methyl cellulose, glucose, sucrose) on the cloud points of aqueous solutions of a series of C_{12}E_n ($n=6, 9, 10$) nonionic surfactants. We have also determined the cloud point of C_{12}E_9 and $\text{C}_{12}\text{E}_{10}$ in presence of Triton X-100 (TX-100), which is widely used as a detergent in molecular biology [33].

2. Materials and methods

Hexa oxyethylene monododecylether, C_{12}E_6 – $[\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_6\text{OH}]$, and nona oxyethylene mono dodecylether, C_{12}E_9 – $[\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_9\text{OH}]$, of Lion Corporation, Tokyo, Japan were used as received. Deca oxyethylene monododecylether, $\text{C}_{12}\text{E}_{10}$ – $[\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}]$, and Triton X 100 of Sigma, USA were used without further purification. The electrolytes used in all experiments were of analytical grade. Glucose and sucrose were obtained from Qualigens, India.

Carboxy methyl cellulose (M.W. $\sim 100,000$) and PEG-4000 (M.W. 4000) were obtained from Suvidinath Laboratories, Baroda, India. Doubly distilled water was used to prepare sample solutions.

Cloud points of surfactant solutions were determined visually by noting the temperature at which the turbidity was observed. The temperature at which the turbidity disappeared on cooling was also noted. Cloud points presented in this article are averages of the appearance and disappearance temperatures of the clouds. These temperatures did not differ by more than 0.4 °C.

3. Results and discussion

In Fig. 1 the variation of CP as a function of $\text{C}_{12}\text{E}_{10}$ concentration are shown. For $\text{C}_{12}\text{E}_{10}$ (1% w/v) solution the CP is 88 °C [2,34]. The cloud point increases as concentration decreases from dilute to very dilute solution (less than 1%, inset in Fig. 1). However CP decreases as the concentration becomes greater than 1% up to about 10% (w/v). Above 10% (w/v), the CP increases with increasing concentration (Fig. 1). A number of studies of CP of aqueous nonionic surfactants are reported but most of them are limited to reasonably dilute solutions [1]. The decrease in CP with increase in $\text{C}_{12}\text{E}_{10}$ concentration is due to increase in micelle concentration. The phase separation results from micelle–micelle interaction. However,

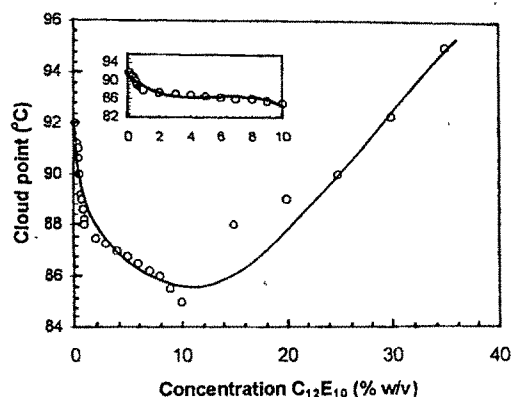


Fig. 1. Cloud point of $\text{C}_{12}\text{E}_{10}$ as a function of wt % of $\text{C}_{12}\text{E}_{10}$ in solution.

at higher concentration (> 10%) the CP increases. This is because, at high surfactant concentration, a structured water surfactant system is present [10,35]. With increase in temperature, this structure breaks, though the molecules are not free of the surfactant effect. That is, some water molecules are not attached to a micelle in particular, but to micelle system in general, forming buffers between micelles. It has been suggested earlier that in polyglycol ether surfactant systems, the water molecules are available for total tenside molecules [36]. Thus higher temperature is required to remove these 'floating' water molecules which are barriers for micellar interaction. Thus CP is a higher temperature and at this temperature the bridge water molecules are released [10].

In Fig. 2, the effects of NaF, NaCl, NaBr and NaI on the cloud point of $C_{12}E_9$ and $C_{12}E_{10}$ (1% w/v) are reported. NaF, NaCl and NaBr decrease the cloud point of both surfactants, whereas NaI increases the cloud point. In the lyotropic series, it is expected that the effect of $F^- > Cl^- > Br^- > I^-$ on the decrease in CP, because the ionic sizes increase along the group consequently decreasing the formal charge density on anion, thus lowering the attraction on anion and thereby lowering the attraction of water. However, NaI is considered as water structure breaker, resulting in an increase in CP. Similar results for $C_{12}E_6$ were observed earlier

also [37]. However, there is not much difference in the CPs of $C_{12}E_9$ and $C_{12}E_{10}$ both in the presence and absence of electrolytes. This is probably because of the polydispersity in these surfactants. The error in CPs being less than 2%.

Fig. 3 represents the change in cloud point, ΔCP ($^{\circ}C$) of $C_{12}E_6$, and $C_{12}E_{10}$ (1% /v) in presence of KCl, KBr and KI. These electrolytes also had similar impact on the CP as did NaF, NaCl, NaBr and NaI had on $C_{12}E_6$, $C_{12}E_9$, and $C_{12}E_{10}$. NaX has more pronounced effect than KX, barring an exception of KBr, which decreased the CP to a large extent compared to NaBr.

Figs. 4 and 5 represent the effect of tetra butyl ammonium iodide (TBAI) and tetra methyl ammonium bromide (TMAB) on the cloud points of $C_{12}E_n$ ($n = 6, 9, 10$), respectively. It is clear from Fig. 4 that CP of $C_{12}E_n$ increases with increase in concentration of TBAI. The cloud point increase in this case is attributed to the mixed micelle formation of TBAI with nonionic surfactant predominating over water structure formation. Thus the mixed micelles with their cationic components have greater intermicellar repulsions and stronger interaction with water and consequently higher cloud point than the corresponding POE nonionic micelle [16]. TMAB however, decreases the CP of all three surfactants. TMAB is water structure former, thereby decreases the availability of non-

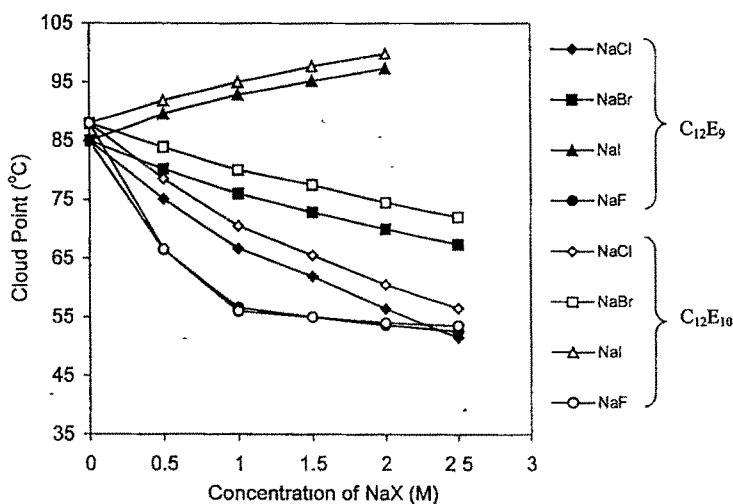
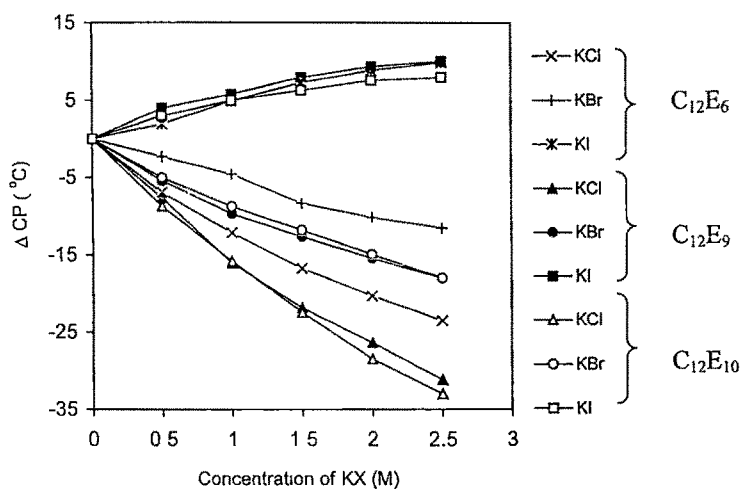
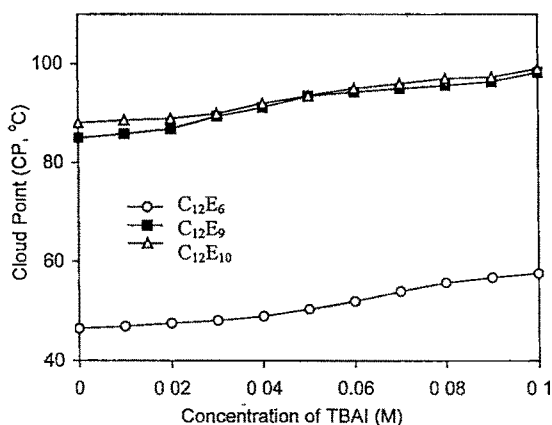
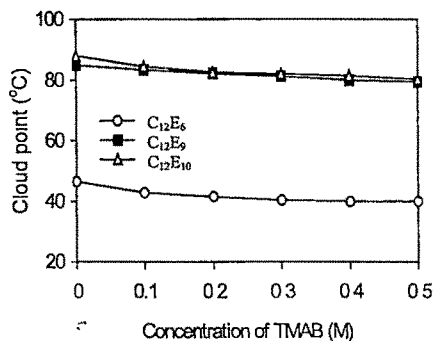


Fig. 2 Cloud point of $C_{12}E_9$ and $C_{12}E_{10}$ (1% w/v) in presence of NaX.

Fig. 3. Change in cloud point (ΔCP , $^{\circ}C$) of $C_{12}E_n$ in presence of KX.Fig. 4. Cloud point of $C_{12}E_n$ (1% w/v) in presence of tetra butyl ammonium iodide.

associated water molecules to hydrate the ether oxygens of the POE chain [2] and thus lowering the cloud point.

In Fig. 6, the cloud point of $C_{12}E_n$ (1% w/v) solution in presence of glucose, sucrose and $Ca(NO_3)_2$ is illustrated. It is clear that, glucose and sucrose both decrease the cloud point, whereas $Ca(NO_3)_2$ has negligible effect on the CP of $C_{12}E_n$. This indicates that glucose and sucrose remove nearby water molecules surrounding the micelle and helping the micelles to approach each

Fig. 5. Cloud point of $C_{12}E_n$ (1% w/v) in presence of tetra methyl ammonium bromide

other easily. It was suggested by Kjellander and Florin [38] that, appearance of cloud point is entropy dominated. The ethylene oxide group of POE nonionic surfactant is highly hydrated. When the additives (glucose and sucrose) are added, the water of hydration of the micelles decreases, as these additives compete for water molecules associated with the micelle. Thus with two relatively less hydrated micelles approaching each other, the hydration spheres overlap and some of the water molecules are freed to increase the entropy of the system. At the cloud point, the water molecules get totally detached from the micelles. However, some researchers [3] have suggested that the hydropho-

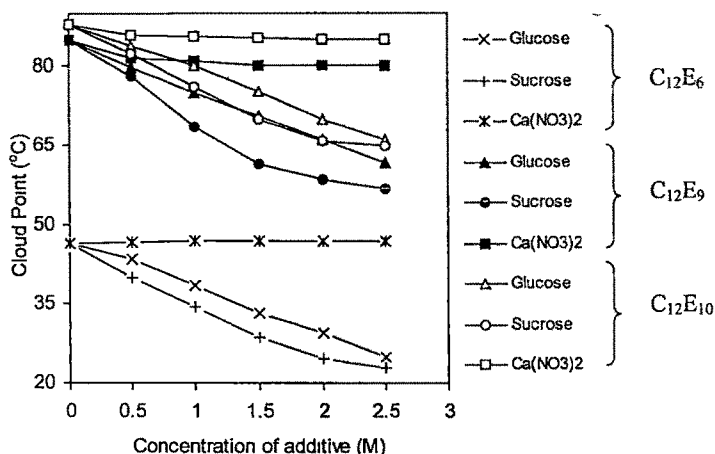


Fig. 6. Cloud point of C₁₂E_n (1% w/v) in presence of different additives.

bic and hydrophilic parts of the micelle interact with water differently where temperature dependent interaction parameters come in to play. At CP the hydrophobicity has relative dominance over hydrophilicity and complete removal of water may not be necessary. With our study it is difficult to make a choice between the two ideas. In any case the overall entropy is high and hence the free energy change is relatively more negative and the appearance of cloud point is facile [39].

In Table 1, the cloud points of C₁₂E₆, C₁₂E₉ and C₁₂E₁₀ (1% w/v) as function of concentration of KSCN are presented. It is evident that, thiocyanate anion being a very soft lewis base and water structure breaker increases the cloud point by

making more water molecules available to interact with POE chain.

We have also determined the CP of C₁₂E₉ and C₁₂E₁₀ mixed with TX-100 i.e. nonionic–nonionic surfactant system. Also the CP of C₁₂E₁₀/TX-100 (1:1, 1% w/v) mixture in presence of NaX and KX (Fig. 7) were determined.

The cloud points of C₁₂E₉/TX-100 (2% w/v) as well as C₁₂E₁₀/TX-100 (2% w/v) mixed in various mole ratios are presented in Table 2. It is clear that, the CP of mixed surfactant system at all mole fractions in both the systems are intermediate

Table 1
Cloud point for C₁₂E₉/TX-100 and C₁₂E₁₀/TX-100 (2% w/v) as a function of mole fraction of TX-100

N _{TX-100}	Cloud point (°C)	
	C ₁₂ E ₉ /TX-100	C ₁₂ E ₁₀ /TX-100
0.0	84.2	88
0.1	82.4	84
0.3	80	80.4
0.5	77.2	77
0.7	73.6	72.5
0.9	72.8	70
1.0	65.4	65.4

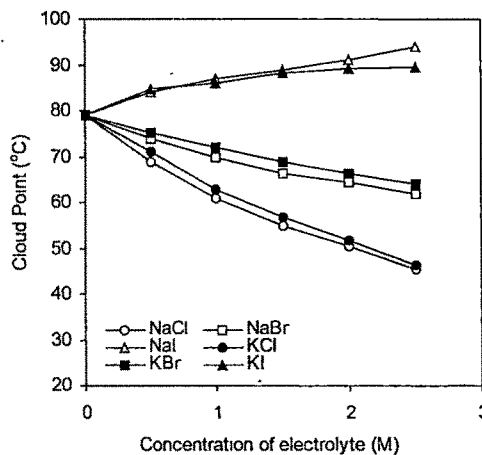


Fig. 7. Cloud point of C₁₂E₁₀/TX-100 (1:1, 1% w/v) in presence of electrolytes

Table 2
Cloud point of $C_{12}E_n$ in presence of KSCN

Concentration of KSCN (M)	Cloud point (°C)		
	$C_{12}E_6$	$C_{12}E_9$	$C_{12}E_{10}$
0.0	46.5	85	88
0.1	48	87.2	89
0.2	50.6	89	91
0.3	52.8	90.2	92.5
0.4	54.2	91.6	93.3
0.5	55.4	92.8	94

between either of the pure surfactant. From Fig. 7, it is evident that the cloud point of $C_{12}E_{10}/TX-100$ mixed surfactant system in presence of NaX and KX (where $X = Cl^-$, Br^-) decreases CP whereas in presence of NaI and KI the CP increases. This is expected, because the mixed nonionic–nonionic micelle formed by adding TX-100 to $C_{12}E_{10}$ is chargeless similar to that of a pure nonionic surfactant. Thus the addition of NaX and KX will have similar effect on the CP of mixed nonionic–nonionic surfactant system, as it had on pure nonionic surfactants. Reasons for such behaviour have been described earlier in this article.

We also investigated the effect of carboxy methyl cellulose and PEG-4000 on the CP of $C_{12}E_n$ (1% w/v) solution (Table 3, Fig. 8a and b). It was suggested earlier that the solutes, which get solubilized in the POE mantle of the micelle decrease the cloud point [40]. Hence we believe that, both carboxy methyl cellulose and PEG-4000 do enter the core of the micelle, consequently decreasing the cloud point. Similar result for TX-

114 on addition of PEG-200, -300 and -400 has been reported earlier [10]. However, as carboxy methyl cellulose and PEG-4000 are expected to be reasonably hydrated it is difficult to visualize these molecules in core of the micelle which is oil type but may be present at the palisade layer. Moreover, they will affect the water structure as well as the number of water molecules available for POE groups of the surfactants to be hydrated and hence the CP decreases (cf. discussion of the effect of glucose, sucrose etc., Fig. 6).

Clouding phenomenon is dependent on the structure of poly oxyethylenated nonionic surfactant. The results reported in this article also support the above-mentioned hypothesis. We have studied the effect of various foreign substances on the CP of $C_{12}E_6$, $C_{12}E_9$ and $C_{12}E_{10}$. That is, the hydrophobic group is same, only the ethylene oxide content is changing ($n = 6, 9, 10$). Higher the percentage of oxyethylene (hydrophilic) group, higher will be the cloud point, though the relation between oxyethylene percentage and cloud point is not linear. Hence the decreasing order of cloud point of CP is $C_{12}E_{10} > C_{12}E_9 > C_{12}E_6$ [2].

4. Conclusion

The effects of various electrolytes and nonelectrolytes on the cloud points of $C_{12}E_6$, $C_{12}E_9$ and $C_{12}E_{10}$ were studied. The CP of $C_{12}E_{10}$ showed a minimum in variation with concentration. Sucrose, glucose, KCl, KBr, NaCl, NaI, $(CH_3)_4NBr$ and $(C_4H_9)_4NI$ do change the cloud point to a large extent. Water structure breaking property of

Table 3
Cloud point (°C) of $C_{12}E_n$ in presence of CMC and PEG-4000

CMC (% w/v)	Cloud point (°C)			PEG-4000 (% w/v)	Cloud point (°C)		
	$C_{12}E_6$	$C_{12}E_9$	$C_{12}E_{10}$		$C_{12}E_6$	$C_{12}E_9$	$C_{12}E_{10}$
0.0	46.5	85	88	0.0	46.5	85	88
0.1	41.4	83.8	85	0.01	37.4	82.4	87
0.2	41.4	83.4	84.5	0.02	34.2	81	86.4
0.3	41.4	83	84	0.03	29.6	80.4	86
0.4	41.2	82.6	83	0.04	24	79.8	85.7
0.5	41	81.4	82.5	0.05	18.8	78.8	85.4

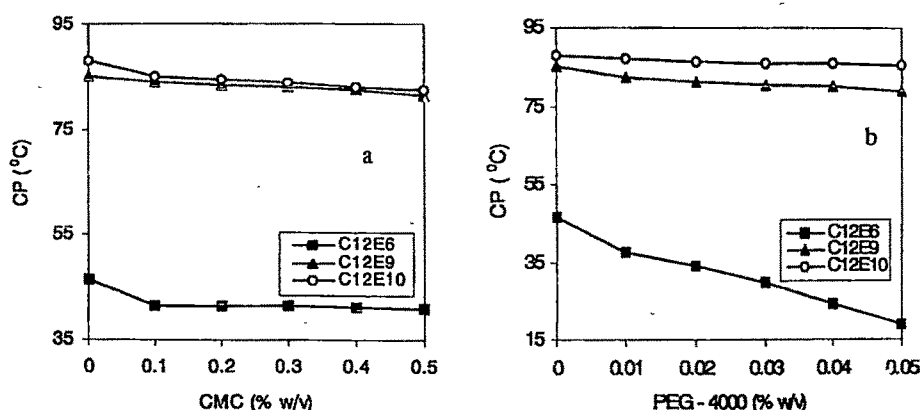


Fig. 8. (a) Cloud point of $C_{12}E_n$ in presence of CMC; (b) cloud point of $C_{12}E_n$ in presence of PEG-4000.

NaI and KI makes its effect different from that of NaCl, NaBr as well as KCl and KBr. $(C_4H_9)_4NI$ has different effect on CP than $(CH_3)_4NBr$, because of mixed micelle formation of $(C_4H_9)_4NI$ with nonionic surfactant predominating over water structure formation. Mixed nonionic–nonionic surfactant system shows clouding phenomenon at temperatures, which are intermediate to that of corresponding pure surfactants.

Acknowledgements

Lion Corporation, Tokyo, Japan and IUC-DAEF, Mumbai, are gratefully acknowledged for providing financial assistance.

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Physicochemical properties of anionic-nonionic surfactant mixture : α -sulfonatomyristic acid methyl ester (MES) – nonaoxyethylene monododecyl ether ($C_{12}E_9$)[†]

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Manuscript received 20 September 2002

We report the interfacial, thermodynamic and performance properties of the binary mixture of α -sulfonatomyristic 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 (Nagg.) have been determined. The mixed micellar composition and interaction parameter (β^m) are 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 are 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, showing 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-organizing behavior 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 with interaction of nonaoxyethylene monododecyl ether ($C_{12}E_9$) with α -sulfonatomyristic acid methyl ester (MES) in aqueous solution, with refer-

ence 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 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 cmc values for aqueous solution of single and binary surfactant systems of different mole fractions at 30, 35, 40 and 45° are presented in Table 1. The cmc values of MES obtained by conductance measurements are in good agreement with those reported in literature¹¹, though the cmc values obtained by surface tension and conductance measurement 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 – $C_{12}E_9$, the cmc values decrease with increase in temperature, which has generally been observed earlier also^{17,18}. The cmc values of $C_{12}E_9$ /MES mixed surfactant system were evaluated by surface tension measurement only as specific conductance-concentration plot did not show any break. Thus we treated $C_{12}E_9$ /MES surfactant

[†]Dedicated to Professor R. P. Rastogi.

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) ^b	(0.641)	(0.646)	(0.656)

^aConductivity data. ^bValues in parenthesis are the degree of ionization of micelle of MES.

mixture as a nonionic one, i.e. mixed micelles are nonionic in nature.

Thermodynamics of micellization and adsorption :

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. α was computed from the ratio between slopes of the post-micellar and pre-micellar regions of the specific conductance – concentration profile of MES¹⁹. The ΔG_m⁰ values are presented in Table 2. The ΔG_m⁰ values are all negative and become more negative with increase in temperature, suggesting that formation of micelles becomes relatively more spontaneous. The standard enthalpy ΔH_m⁰ and standard entropy ΔS_m⁰ of micellization were evaluated from ΔG_m⁰ – T

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

N _{MES}	–ΔG _m ⁰ (kJ mol ⁻¹) at				ΔH _m ⁰ kJ mol ⁻¹	ΔS _m ⁰ J K ⁻¹ mol ⁻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

plot. The slope and intercept gave ΔS_m⁰ and ΔH_m⁰, respectively. The overall micellization process is endothermic except for MES, where it is exothermic. The ΔS_m⁰ values are positive indicating that micellization is entropy-dominated²⁰.

The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of the surfactant at the air/water interface were evaluated using Gibb's adsorption equation²¹ and are presented in Table 3. The lower values of A_{min} in the mixed systems may be due to closer packing at the air-water inter-

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

N _{MES}	Γ _{max} × 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	2.46	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

face owing to the decreased repulsion between the oriented headgroups of surfactants. The thermodynamic parameters of adsorption of surfactants at the air/water interface were evaluated using the relation²²,

$$\Delta G_{ad}^0 = \Delta G_m^0 - N \Gamma_{cmc} A_{cmc}$$

where N, Γ_{cmc} and A_{cmc} are Avogadro number, surface pressure at cmc (γ₀ – γ_{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. The standard enthalpy, ΔH_{ad}⁰ and standard entropy, ΔS_{ad}⁰ values were evaluated from ΔG_{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

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

N _{MES}	–ΔG _{ad} ⁰ (kJ mol ⁻¹) at				ΔH _{ad} ⁰ kJ mol ⁻¹	ΔS _{ad} ⁰ J K ⁻¹ mol ⁻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

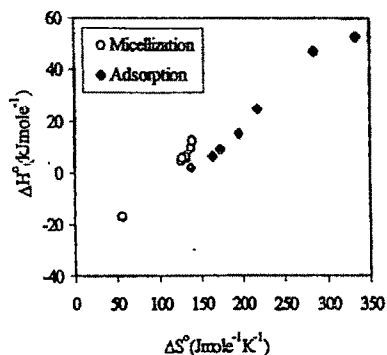


Fig. 1. Enthalpy-entropy compensation plot.

surfactants (Table 4). 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 and ΔH_m^0 as well as ΔS_{ad}^0 and ΔH_{ad}^0 (Fig. 1) was observed for this system which was suggested by Lumry and Rajender²³. The compensation temperature for micellization and adsorption processes are 314 and 281 K, respectively. Such behavior was observed earlier also²⁴ and it implies that at 314 K, the micellization process is independent of structural changes in the system and is dependent only on enthalpic factors²⁵. The β^m values, a measure of interaction between the surfactant molecules in the mixed micelle, are presented in Table 5. β^m values are all negative at all mole fractions of $C_{12}E_9$ /MES system

Table 5. Interaction parameter (β^m) values of $C_{12}E_9$ /MES mixed surfactant system in aqueous media at different temperatures*

N_{MES}	$(\beta^m)^a$			
	303	308	313	318 K
0.1	-	-	-	-
0.3	-1.87/-1.57 ^b (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 'l' was calculated using cmc of MES by ST measurement.

except $N_{MES} = 0.1$, where the iteration did not coalesce. The negative β^m values suggest an attractive interaction

between the MES and $C_{12}E_9$ headgroups in the mixed micelle leading to electrostatic stabilization. It is evident from Table 1, that the cmc of MES seems to differ when surface tension or conductance methods are used. It is clear that calculated β^m values do differ (maximum ~15%) but the interaction is always attractive in nature.

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 f_1 and f_2 are the activity coefficients of surfactants 1 and 2, respectively, in the mixed micelle. The f_1 and f_2 values are presented in Table 6.

Table 6. Activity coefficient (f_1, f_2) values of $C_{12}E_9$ /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 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 $C_{12}E_9$ are higher which increase with increase in

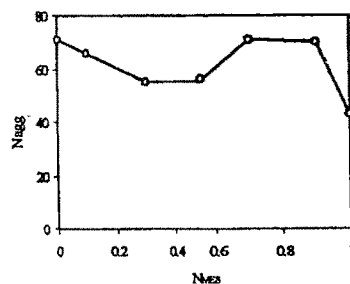


Fig. 2. Micellar aggregation number (N_{agg}) for $C_{12}E_9$ /MES mixed surfactant system

temperature, indicating that C₁₂E₉ in the mixed micelle is near its standard state^{3,5} (Table 6).

Micellar aggregation number and microenvironment :

Micellar aggregation number (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 behavior 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.

Table 7. Micropolarity (I_1/I_3) and binding constant (K_{SV}) for C₁₂E₉/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
$K_{SV} \times 10^{-4}$ (dm ³ mol ⁻¹)	1.2	1.03	0.85	0.82	0.74	1.22	1.10

The ratio of the 1st and 3rd vibronic 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 (Table 7) 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,

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

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

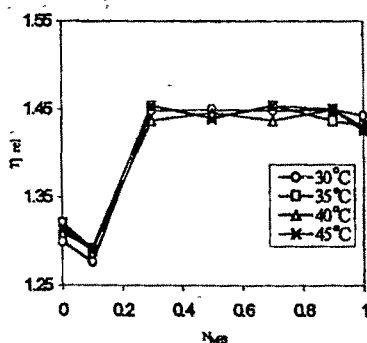


Fig. 3. Plots of relative viscosity vs N_{MES} for C₁₂E₉/MES system.

similar magnitude.

In Fig. 3, the relative viscosity (η_{rel}) values for 5% (w/v) C₁₂E₉/MES mixed surfactant solutions as a function of molefraction of MES is plotted. The η_{rel} for C₁₂E₉ is low. Initially η_{rel} decreases at $N_{MES} = 0.1$ and then suddenly increases and shows a maximum at $N_{MES} = 0.3$. The maximum in viscosity arises due to the formation of mixed micelle. In general, η_{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,

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

where limit to zero concentration indicates that intermolecular interactions are absent. In this study we have calculated $|\eta|$ without taking the zero concentration limit. The intrinsic viscosity values (Table 8) of C₁₂E₉/MES mixed surfactant system at all mole fractions indicate that micelles

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

N_{MES}	303 K	308 K	313 K	318 K
0.0	8.8	8.6	8.6	8.4
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	6.0	6.4	6.2	6.3

are nonspherical as $|\eta|$ should be 2.5–4 cm³ g⁻¹ for spherical systems²⁷ and the lowest $|\eta|$ for this 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 Söni *et al.*²⁹ also reported observations pertaining to the 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. It is clear that, foaminess in single as well as mixed surfactant system 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 mole fractions are higher

Table 9. Foam stability of $C_{12}E_9$ /MES mixed surfactant system as a function of temperature (average of at least two runs)

N_{MES}	Foam height (cms ± 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

compared to $C_{12}E_9$, 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. However, it seems that the mixed surfactant layer is a rigid one. Moreover, drainage, evaporation, interaction between environment and foams etc. determine the foam stability³¹.

Experimental

Nonaoxyethylene monododecyl ether [$CH_3(CH_2)_{11}(OCH_2CH_2)_9OH$], i.e. $C_{12}E_9$ and α -sulfonatomyristic acid methyl ester - $C_{12}H_{25}CH(SO_3Na)COOCH_3$, i.e. (MES) (Lion Corporation, Tokyo) were used without further purification. Cetylpyridinium chloride (Loba Chemie, India) was crystallized twice from benzene prior to use. Pyrene (Fluka, Germany) was recrystallized from cyclohexane. All solutions were prepared using double-distilled water.

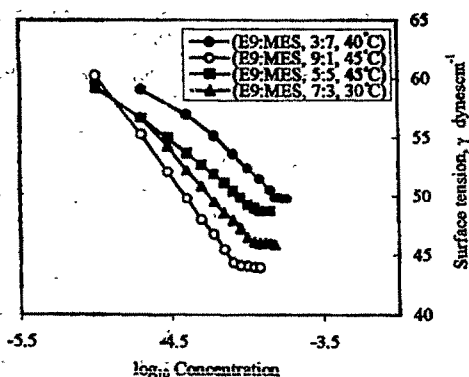


Fig. 4. Representative plot of surface tension vs log concentration.

The critical micelle concentration were determined using surface tension measurements as described earlier⁵. Error in cmc values is less than $\pm 1\%$. Representative plots of

surface tension (γ) vs logarithm of surfactant concentration ($\log C$) are shown in Fig. 4.

Conductance (κ) were measured with an Equiptronics (India) conductivity-bridge. A dip type cell of cell constant 1.01 cm^{-1} was used. The conductance of different solutions which were obtained on addition of aliquot of a known concentrated surfactant solution to a given volume of the

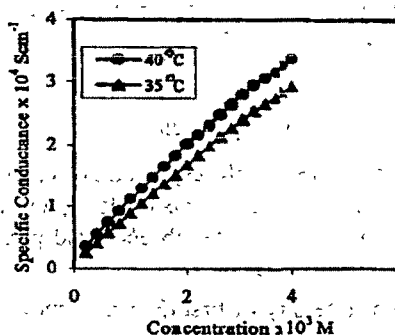


Fig. 5. Representative plot of specific conductance (κ) vs concentration of MES.

thermostated solvent were measured. Specific conductance (κ) vs concentration of surfactant plots are shown in Fig. 5 for pure MES only, and 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 cetylpyridinium chloride as quencher. The excitation and emission wavelengths were 335 and 385 nm, respectively. All the fluorescence measurement was carried out at room temperature ($\sim 25^\circ$) using a Hitachi F-4010

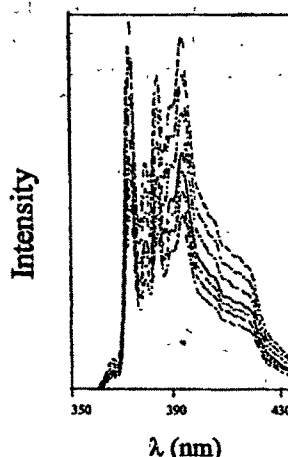


Fig. 6. Representative fluorescence (emission) spectra of 10^{-6} M pyrene in aqueous micellar solution of $C_{12}E_9$: MES (5 : 5).

spectrophotometer. Each spectrum had one to five vibronic peaks from shorter to longer wavelengths (Fig. 6). 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,

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

where [Q], [M] and [S] are the concentrations of quencher, micelle and total surfactant, respectively, I_0 and 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 measured using Ubbelohde suspended level viscometer at 30, 35, 40 and 45°C ($\pm 1^\circ$) in a thermostated bath.

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

Acknowledgement

Financial support from Lion Corporation, Tokyo, Japan, is gratefully acknowledged. Dr. T. Mukherjee of BARC deserves our grateful thanks for fluorescence measurements.

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