Chapter IV A

Thermodynamics of Micellization and Interfacial Adsorption of Polyoxyethylene (10) Lauryl Ether ($C_{12}E_{10}$) in Water

The interfacial and micellization properties of nonionic surfactant, polyoxyethylene (10) lauryl ether [$C_{12}E_{10}$; $CH_3\ (CH_2)_{11}(OCH_2CH_2)_{10}OH$] at different *p*Hs and temperatures have been investigated from surface tension measurements. The surface excess (Γ) and the corresponding interfacial quantities have been evaluated. The Gibbs free energy, enthalpy and entropy of micellization (ΔG^{0}_{m}, ΔH^{0}_{m}, ΔS^{0}_{m}), and adsorption at the air/water interface (ΔG^{0}_{ad}, ΔH^{0}_{ad}, ΔS^{0}_{ad}) have also been computed. Both micellization and adsorption processes have been found to be endothermic at all *p*H. An enthalpy-entropy compensation effect has been observed with an isostructural temperature of 300 K for both the micellization and interfacial adsorption processes. The cloud point of $C_{12}E_{10}$ is not much affected by *p*H.

The interfacial and thermodynamic properties of surfactant in solution, both in presence and absence of additives, provide a wealth of information about solute-solute and solvent-solute interactions. Additives have significant effect on surfactant self- organization.[1] They can influence solvent structure and polarity and can also undergo direct interaction with the surfactants. Recently, there has been a rapid growth in commercial application of nonionic surfactants and the progress in basic research.[2] Hence in continuation of our interest in the properties of nonionic surfactants,[3,4,5] we extended our work to study the interfacial and micellization properties of poly oxyethylene (10) lauryl ether at different *p*Hs to understand how acidity/alkalinity affect the behaviour of the surfactant in aqueous solution. The effect of change of *p*H on stability, aggregation number and titration properties of dodecyldimethylamine oxide (DDAO) surfactant has been studied extensively[6]. The effect of *p*H on other surfactants like cationic[7] hexadecyltrimethyl ammonium bromide (HTAB) and amphoteric-anionic[8] N,N-dimethyl N-lauroyl lysine (DMLL)-sodiumdodecyl sulphate (SDS) have also been studied. Herrann[9] showed that dimethyl dodecyl amine oxide (DDAO), behave as nonionic at $pH \geq 7$, as cationic ($DDHA^+$) at $pH \leq 3$ and as a nonionic –cationic mixture between *p*H 3 and 7. However to our knowledge, no study dealing with the effect of *p*H on nonionic POE type surfactant have been done so far. We report herein the effect of *p*H on surface excess (Γ), minimum area per molecule (A_{min}), surface pressure (π_{cmc}) and thermodynamics of micellization and adsorption of $C_{12}E_{10}$ at the air/water interface at different temperatures. The study of the effect of *p*H on micellization is important because of increasing use of nonionic surfactants in drug delivery systems and also in emulsion formulation *e.g.* shampoo.

EXPERIMENTAL

Nonionic surfactant, Polyoxyethylene (10) lauryl ether, $C_{12}E_{10}$, $[CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH]$, molar mass = 626.85 (Sigma, USA) was used without any further purification. The surface tension *vs*. concentration plot did not show any minimum. All solutions were prepared using doubly distilled water having electric conductance 2-3 μScm^{-1}. A digital *p*H meter of Weltronix CM-100 was used, following calibration using buffer solutions of *p*H 4.0, 7.0 and 9.2 obtained from Qualigens fine chemicals, Glaxo, India. In the working solution, HCl was used to adjust the acidic *p*H while the alkaline *p*H was adjusted by using NaOH solution. The HCl and NaOH used were of analytical grade (Suvidhinath Lab., Baroda, India).

Critical micelle concentration measurement

The critical micelle concentration (cmc) was determined by the surface tension (γ) measurement using a du-Noüy ring tensiometer (S. C. Dey and Co. Calcutta, India); measurements were taken at temperatures 308, 313, 318 and 323 K. The temperatures were maintained within ± 0.1 K by circulating thermostated water through a jacketed vessel containing the solution. Surface tension (γ) decreased with increasing surfactant concentration and reaching a plateau. The concentration of solution was varied by adding aliquots of a stock solution of known concentration with a Hamilton microsyringe to the known volume of solution taken in the jacketed vessel. For each set of experiments, the ring was cleaned by heating it in alcohol flame. The standard deviation of the mean in γ was ±0.5%. The measured surface tension values were plotted as a function of the logarithm of surfactant concentration and the critical micelle concentration (cmc) was estimated from the break point in the resulting curve.[10] The reproducibility of the surface tension concentration curve was checked with duplicate runs. The reproducibility in the cmc was found to be within ±1.0%, The required *p*H was maintained by adding aqueous HCl and NaOH for acidic and alkaline solution respectively. The *p*H of solution was determined before and after the completion of each run. It was found that there was a very small decrease in *p*H in all solutions except water (*p*H 6.8) in the presence of the surfactant. The change was of the order of 0.2 *p*H units within the experimental time span (~ 90min) and was thus neglected. However it is not very clear why this small change in *p*H occurred.

Cloud point (CP) measurement

The cloud points of polyoxyethylene (10) lauryl ether in all *p*H were determined. The total surfactant concentration was 1% (w/v). The experimental procedure was same as reported earlier[11]. The cloud points are presented in Table 1. These are the averages of the appearance and disappearance temperatures for the clouding, the maximum difference was not greater than 0.4°C. It can be hence seen that the CP is not much affected by the change of *p*H in the acidic range. The error in CP is 0.5%.

RESULTS AND DISCUSSION

Surface tension is a dependable and elegant method for the determination of cmc[12]. The cmc values of $C_{12}E_{10}$ at various *p*H and at different temperatures are presented in Table 1. It can be seen from the table that the critical micelle concentration values of polyoxyethylene (10) lauryl ether decrease with an increase in temperature at all *p*H, which is generally seen in case of nonionic surfactant. It is observed that at constant temperature, cmc increases with the *p*H of the solution, low *p*H favours the micellization of the surfactant.

Table :1 Critical micelle concentration (cmc) of polyoxyethylene (10)lauryl ether ($C_{12}E_{10}$) in aqueous solution as a function of *p*H, different temperature and its cloud point at different *p*H.

*p*H of the solution	Critical micelle concentration (cmc) / µm				Cloud point / °C
	Temperature / K				
	308	313	318	323	
2	6.0	5.9	5.4	4.3	86.9[†]
3	9.5	7.4	7.0	4.5	87.1[†]
4	10.0	8.1	7.9	5.0	87.3[†]
5	11.0	9.3	8.9	7.0	87.4[†]
6.8*	11.8	10.0	8.9	7.1	87.5[†]
9	13.1	11.2	11.0	10.9	88.4
11	14.1	13.1	11.2	11.1	89.0

* Ref.3

[†] These values are almost same. An average of 87.2 °C ± 0.1 can be taken as cp for these systems

The formation of micelle is controlled by hydrophobic interaction,[13] and the London dispersion force.[14] In the case of nonionic surfactants without any additive, the cmc decreases with increasing temperature due to the dehydration of the hydrophilic moiety of the surfactant molecules and also due to breaking of water structure[15]. The ether linkages in $C_{12}E_{10}$ chain can be protonated at low *p*H, making it positively charged to behave as a pseudo ionic surfactant. At alkaline or around neutral *p*H, this surfactant is expected to remain nonionic.

From Table 1, it is seen that with decreasing $[H^+]$, the cmc increases. Also lowering of temperature increases the cmc. Both H^+ and OH^- can form hydrogen bonds with water molecules and thereby promote water structure, which is also promoted by the hydrophobic group of the surfactant molecule. On increasing the temperature, the oxyethylene groups get dehydrated with decrease in hydrophilicity or increase in hydrophobicity causing lowering of cmc. The resultant cmc is governed by the effects of various factors, synergetic and /or antagonistic.

The Gibbs free energy of micellization (ΔG^{0}_{m}) for a nonionic surfactant is related to the cmc (expressed in mole fraction scale) by the following relation[16],

$$\Delta G^{0}_{m} = RT \ln \text{cmc} \qquad \ldots(1)$$

The initial standard state being the hypothetical ideal solution of unit mole fraction though behaving as if at infinite dilution and the final state being the micelle itself. In Table 2, the Gibbs free energy, enthalpy and entropy of micellization ΔG^{0}_{m}, ΔH^{0}_{m} and ΔS^{0}_{m} respectively at the standard state of unit mole fraction are reported. The free energy of micellization is relatively more negative with increasing temperature indicating relative spontaneity of the micellization process as temperature increases.

Table 2 Thermodynamic parameters of micellization of $C_{12}E_{10}$ at different *p*H, and temperature.

*p*H of solution	$-\Delta G^{0}_{m}$ / kJmol^{-1} Temperature / *K* 308	313	318	323	ΔH^{0}_{m} / kJmol^{-1}	ΔS^{0}_{m} / Jmol^{-1}K^{-1}
2	41.0	41.8	42.7	44.0	20.1	198
3	39.9	41.2	42.0	43.8	37.2	250
4	39.8	41.0	41.7	43.6	34.8	242
5	39.5	40.6	41.4	42.7	24.6	208
6.8	39.3	40.4	41.4	42.6	27.8	218
9	39.0	40.1	40.8	41.5	11.4	164
11	38.9	39.7	40.7	41.4	13.5	170

The ΔS^{0}_{m} was computed from the slope of the reasonably linear ΔG^{0}_{m} vs. *T* plots. The ΔH^{0}_{m} was then calculated from the equation[16]

$$\Delta H^{o}_{m} = \Delta G^{o}_{m} + T\Delta S^{o}_{m} \qquad \ldots (2)$$

The entropy of micellization (ΔS^{o}_{m}) values are all positive and large indicating that the micellization process is entropy controled. The micellization process is endothermic in nature. High entropy changes are generally associated with a phase-change. The pseudophase micellar model is thus prefered over the mass action model. Rosen[17] has stated that the presence of hydrated oxyethylene groups of the surfactant introduces structure in the liquid phase and that the removal of the surfactant via micellization results in an increase in the overall randomness [18] and hence an increase in entropy. The hydrated surfactant molecules release the water molecules during micellization on the consequence of which the entropy of the process increases.

A good linear correlation between ΔH^{o}_{m} and ΔS^{o}_{m} values has been observed. On a general basis, such a compensation has been suggested by Lumry and Rajender[19]. The slope of the line i.e. the compensation temperature has been found to be 300 K, close to the expected values between 270 and 294K in aqueous medium[19]. Thus, the micellization is a function of the bulk structure of the solvent. The small variations, observed here as well as those observed earlier[20] may be due to the difference in the bulk structural property of the solution from that of water. However deviations from Lumry *et.al* observation are well known. As mentioned by Krug *et al.*[21] error in the data may also lead to such compensation.

The air/water interface of a surfactant solution is well populated[22] by the adsorbed amphiphile molecules. The Gibbs surface excess (Γ) for dilute solution of a nonionic surfactant is given by the adsorption equation[23]

$$\Gamma = (-1/RT)\,(d\gamma/d\ln C) \qquad \ldots (3)$$

where Γ, γ, R, T and C are the surface excess, surface tension, gas constant, absolute temperature and concentration, respectively. The slope of the tangent at the given concentration of the γ *vs.* log C plot has been used to calculate Γ by using curve fitting to a polynomial equation of the form, $y=ax^2+bx+c$ in microsoft excel program. The R^2 (Regression coefficient) value of the fit lies between 0.9583 and 0.9957. The surface excess is an effective measure of the molecular adsorption at the air / liquid interface. The Γ values are presented in Table 3.

Table 3 Surface excess and area per molecule of $C_{12}E_{10}$ at different *p*H and temperature.

*p*H of solution	$\Gamma \times 10^{10}$ / mol cm^{-2}				$A_{min} \times 10^{2}$ / nm^{2}			
	Temperature / *K*							
	308	313	318	323	308	313	318	323
2	2.8	2.0	1.8	3.7	59.3	83.0	92.2	44.9
3	2.5	4.1	2.2	2.3	66.4	40.5	75.5	72.2
4	2.6	2.9	3.1	3.6	64.6	56.6	54.4	45.4
5	4.0	1.0	1.7	4.8	41.5	166.0	97.6	34.6
6.8	2.3	2.4	3.3	3.6	72.2	69.2	50.3	46.1
9	4.2	2.9	3.3	4.4	40.0	57.2	50.3	37.7
11	2.8	2.8	2.3	2.8	58.3	58.9	72.2	59.3

The surface excess increases with increase in temperature (at *p*H 6.8) due to the dehydration of the surfactant molecule. This has not been observed at lower and higher *p*H. In some cases (*p*H 2, 5 and 9) a minimum has been observed. At *p*H 4 and 11 there has been only a slight decrease with temperature. The effect of temperature Γ at different *p*H is a complex phenomenon. This is guided by the interaction of H^+ and OH^- ions with water as well as with the surfactant. The nature of interaction is not straightforward.

From the surface excess quantity, it is possible to calculate the minimum area per molecule (A_{min}), by the relation.

$$A_{min}\,(\mathrm{nm}^2) = 10^{14}/N\Gamma_{max} \qquad \ldots(4)$$

where N is the Avogadro number. The magnitudes of $A_{\min}$ are of the order of 1.0 x 10^2 nm^2 or less, suggesting that the surface is a close packed one which means that the orientation of the surfactant molecules is almost perpendicular to the surface.[24] The $A_{\min}$ values of $C_{12}E_{10}$ at cmc are also presented in Table 3.The effectiveness of a surface active molecule is measured by the surface pressure (π_{cmc}) at the cmc i.e. $\pi_{cmc} = \gamma_0 - \gamma_{cmc}$ where γ_0 and γ_{cmc} are the surface tension of solvent and the surface tension of surfactant solution at cmc respectively. The value of free energy of adsorption at air/water interface (ΔG^o_{ad}) has been calculated using the relation[25],

$$\Delta G^o_{ad} = \mathrm{R\,T} \ln \mathrm{cmc} - N \pi_{cmc} \mathrm{A}_{\min} \qquad \ldots (5)$$

The standard state for adsorbed surfactant here is a hypothetical monolayer at its minimum surface area/molecule but at zero surface pressure. As expected, the free energy of micellization, ΔG^o_m was less negative than the free energy of adsorption, ΔG^o_{ad} values at air/water interface at all temperatures, indicating that when a micelle is formed, work has to be done to transfer the surfactant molecules in the monomeric form at the surface to the micellar stage through the aqueous medium. In Table 4, the thermodynamic parameters of adsorption i.e. ΔG^o_{ad}, ΔH^o_{ad} and ΔS^o_{ad} of $C_{12}E_{10}$ at the air/solution interface at various pH are presented. The standard entropy (ΔS^o_{ad}) and enthalpy (ΔH^o_{ad}) of adsorption have been obtained from the slope of the reasonably linear ΔG^o_{ad} Vs T plot. The ΔH^o_{ad} has been obtained from the thermodynamic relation (Eq.2). It can be seen from Table 2 and 4 that the derived enthalpy and entropy quantities have irregular relationship with pH. The error associated with these quantities is ±7%. It is difficult to say from the available data as to whether irregularity is due to this error or genuine. Hence no reasoning is preferred. Direct measurement would give better answer. However as mentioned in an earlier paragraph adsorption at air/water interface in these systems seems to be very much a complex phenomenon.

Table 4 Thermodynamic parameter of adsorption of polyoxyethylene (10) lauryl ether at different *p*H, and temperature.

*p*H of solution	$-\Delta G^{o}_{ad}$ / kJmol^{-1} Temperature / *K* 308	313	318	323	ΔH^{o}_{ad}/ kJmol^{-1}	ΔS^{o}_{ad} / Jmol^{-1}K^{-1}
2	46.2	44.5	50.4	46.6	2.1	142
3	48.1	44.6	46.7	49.5	11.2	186
4	44.5	45.2	46.9	46.9	10.3	178
5	42.3	46.9	47.1	46.0	25.7	226
6.8	42.7	43.7	43.8	44.8	-3.4	128
9	43.9	45.1	45.5	46.3	2.8	152
11	44.8	45.7	46.8	47.4	10.0	178

Like the micellization process, the adsorption at the air/water interface has been found to be also endothermic. The endothermic character of micellization and adsorption are specific to the surfactant, the additive and the temperature[4, 5, 26, 27]. The compensation temperature has been found to be 284K, somewhat different from 300K obtained for micellization phenomenon, but within the expected range for aqueous systems (270-294K) [19].

The cloud points are the manifestation of the solvation /desolvation phenomena of the nonionic surfactant in solution. The desolvation of the hydrophilic groups of the surfactant leads to phase separation i.e. clouding in the surfactant solution. It is seen that the *p*H has mild effect on the cloud point of $C_{12}E_{10}$, it increases only by 2°C for a change of *p*H from 2 to 11 (Table 1), and at the acidic region there is no effect at all.

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Chapter IV B

Study of the Cloud Point of $C_{12}E_n$ Nonionic Surfactants: Effect of Additives

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=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 Tetramethyl ammonium bromide (TMAB). Overall the electrolytes and non-electrolytes have a large amount of effect on CP of nonionic surfactants, because of their effect on water structure and their hydrophilicity.

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 nonionic 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 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 eg. 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, $Ca(NO_3)_2$ where X is halide ion) and non-electrolytes (PEG-4000, carboxy methyl cellulose, glucose, sucrose) on the cloud points of aqueous solutions of $C_{12}E_n$ (n=10) nonionic surfactant. We have also determined the cloud point of $C_{12}E_{10}$ in presence of TX 100, which is widely used as a detergent in molecular biology [33].

MATERIALS AND METHODS

Deca oxyethylene monododecyl ether, $C_{12}E_{10}$ - $[CH_3\ (CH_2)_{11}(OCH_2CH_2)_{10}OH]$, 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. ~ 100,000) & 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.

RESULTS AND DISCUSSION

In Fig. 1 the variation of CP as a function of $C_{12}E_{10}$ concentration are shown. For $C_{12}E_{10}$ (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 $C_{12}E_{10}$ concentration is due to increase in micelle concentration. The phase separation results from micelle-micelle interaction. However 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].

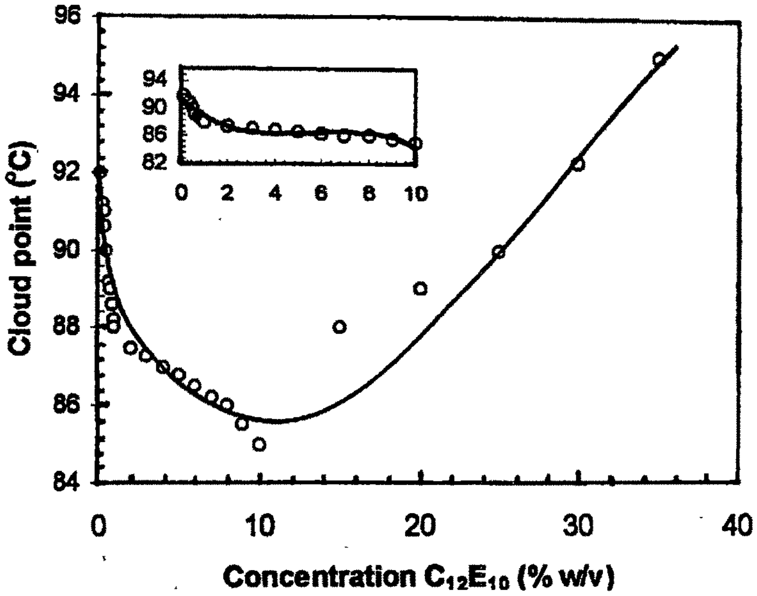

Fig. 1. Cloud point of $C_{12}E_{10}$ as a function of weight % of $C_{12}E_{10}$ in solution.

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 $C_{12}E_{10}$ (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 $C_{12}E_{10}$ 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%

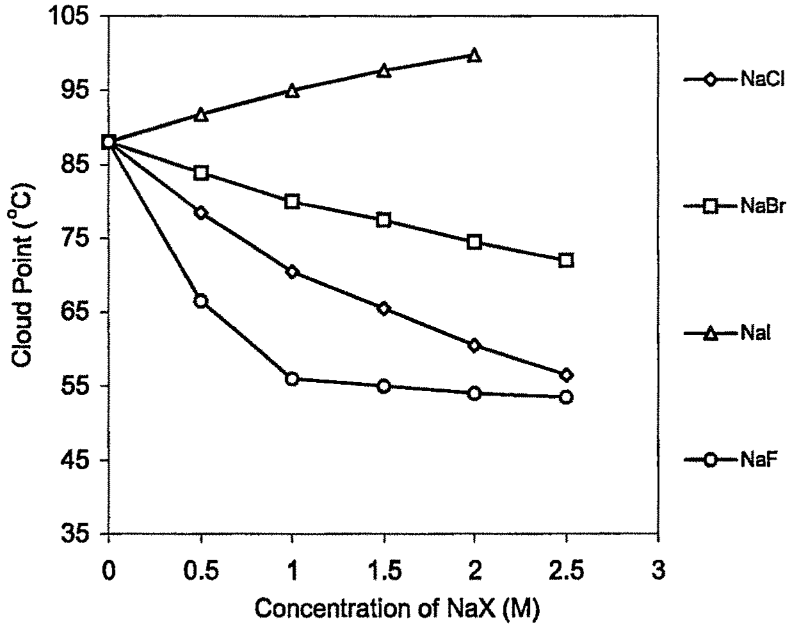

Fig. 2. Cloud point of $C_{12}E_{10}$ (1% w/v) in presence of NaX.

Fig. 3 represents the change in cloud point, Δ CP (°C) of $C_{12}E_{10}$ (1%w/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 $C_{12}E_{10}$. NaX has more pronounced effect than KX, baring an exception of KBr, which decreased the CP to a large extent compared to NaBr. Fig. 4 and Fig. 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= 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 nonassociated water molecules to hydrate the ether oxygens of the POE chain [2] and thus lowering the cloud point.

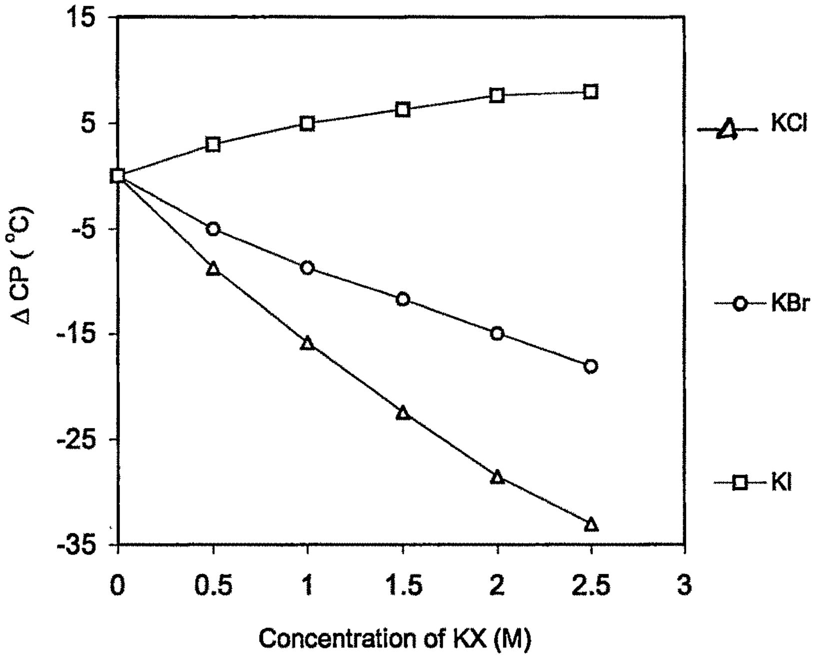

Fig. 3. Change in cloud point (Δ CP, °C) of $C_{12}E_{10}$ in presence of KX.

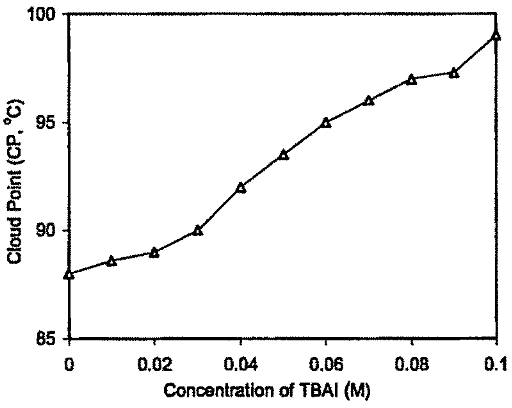

Fig. 4. Cloud Point of $C_{12}E_{10}$ (1% w/v) in presence of Tetra butyl ammonium iodide.

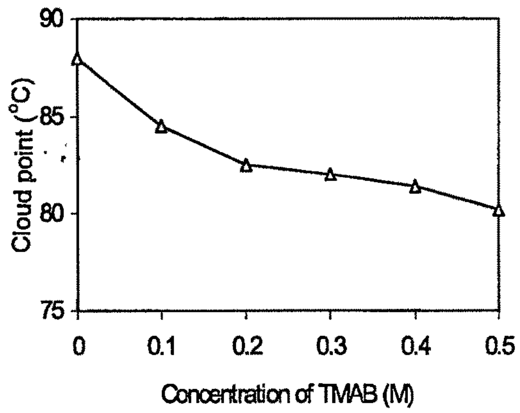

Fig. 5. Cloud Point of $C_{12}E_{10}$ (1% w/v) in presence of Tetra methyl ammonium bromide.

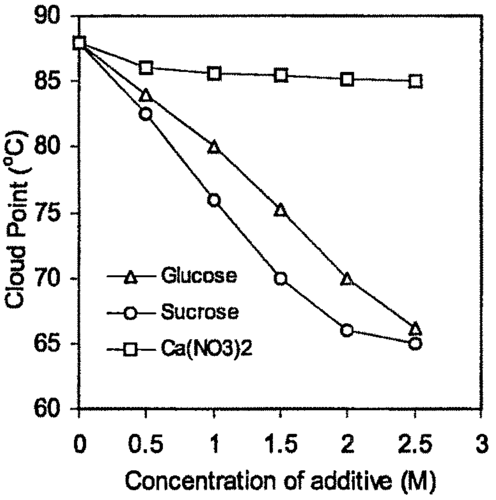

Fig. 6. Cloud Point of $C_{12}E_{10}$ (1% w/v) in presence of different additives.

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 other easily. It was suggested by Kjellander et al [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 hydrophobic 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 $C_{12}E_{10}$ (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 $C_{12}E_{10}$ mixed with Triton X 100 i.e. nonionic-nonionic surfactant system. Also the CP of $C_{12}E_{10}$/TX 100 (1:1, 1% w/v) mixture in presence of NaX and KX (Fig. 7) were determined.

Table 1. Cloud Point of $C_{12}E_n$ in presence of KSCN.

Concentration of KSCN (M)	Cloud Point (°C)
	$C_{12}E_{10}$
0.0	88
0.1	89
0.2	91
0.3	92.5
0.4	93.3
0.5	94

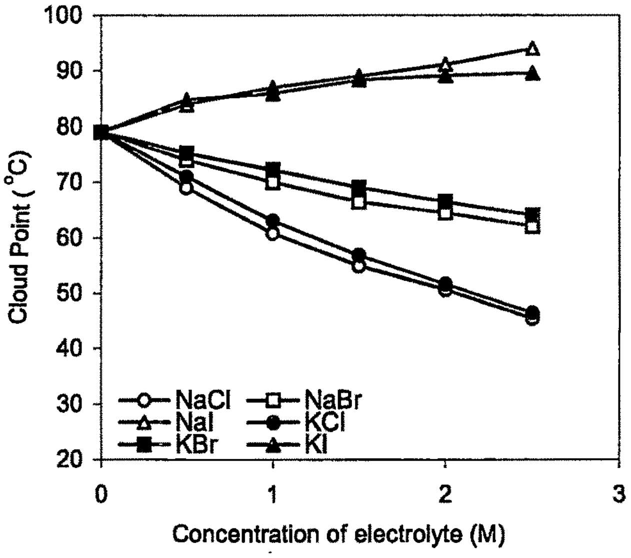

Fig. 7. Cloud Point of $C_{12}E_{10}$/TX 100 (1:1, 1%w/v) in presence of electrolytes.

The cloud points of $C_{12}E_{10}$/TX100 (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 between either of the pure surfactant. From Fig. 7, it is evident that the cloud point of $C_{12}E_{10}$/TX100 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.

Table 2. Cloud point for $C_{12}E_{10}$/TX-100 (2% w/v) as a function of mole fraction of TX-100

$N_{\text{TX-100}}$	Cloud Point (°C)
	$C_{12}E_{10}$/TX-100
0.0	88
0.1	84
0.3	80.4
0.5	77
0.7	72.5
0.9	70
1.0	65.4

This is expected, because the mixed nonionic-nonionic micelle formed by adding TX100 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 $C_{12}E_{10}$ (1%w/v) solution (Table 3, Fig. 8a and 8b). 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 TX114 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.

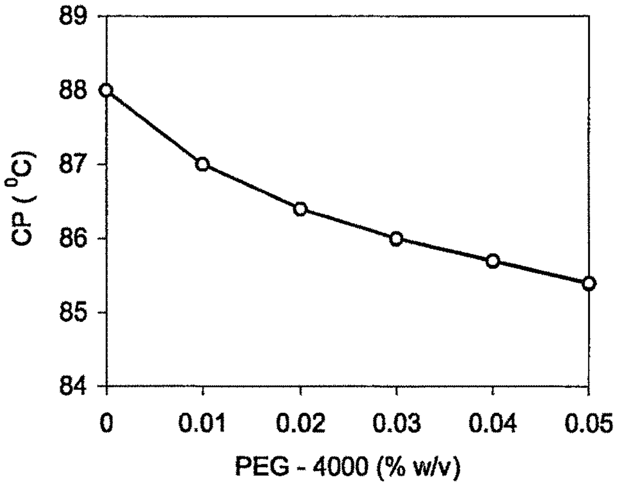

Fig. 8b. Cloud Point of $C_{12}E_{10}$ in presence of PEG – 4000.

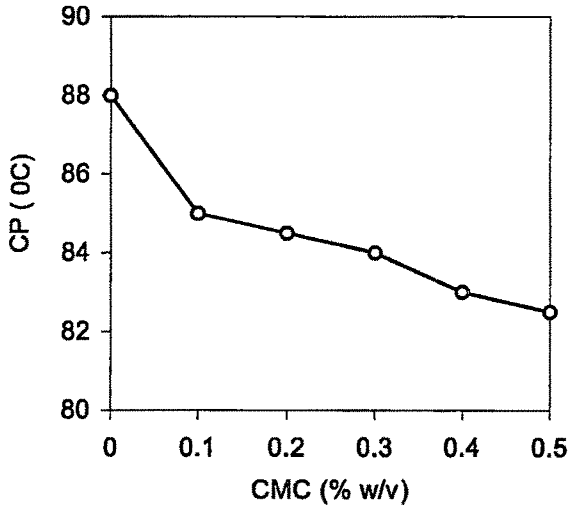

Fig. 8a. Cloud Point of $C_{12}E_{10}$ in presence of CMC.

Table 3. Cloud Point (°C) of $C_{12}E_{10}$ in presence of Carboxy methyl cellulose

(CMC) and PEG-4000

CMC (% w/v)	Cloud Point (°C)	PEG- 4000 (% w/v)	Cloud Point (°C)
0.0	88	0.0	88
0.1	85	0.01	87
0.2	84.5	0.02	86.4
0.3	84	0.03	86
0.4	83	0.04	85.7
0.5	82.5	0.05	85.4

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 $C_{12}E_{10}$.

CONCLUSION

The effects of various electrolytes and non-electrolytes on the cloud points of $C_{12}E_{10}$ 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 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.

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