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Physicochemical Studies of Nonionic Surfactants, $C_{12}E_{12}$ and $C_{12}E_{15}$: Effect of pH and NaCl

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Abstract- Aqueous micellar solutions of nonionic n-dodecyloligo ethyleneoxide surfactants, dodeca and pentadeca oxyethylene n-dodecylether, $C_{12}E_{12}$ and $C_{12}E_{15}$ [$CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_{12/15}OH$] have been investigated at different pH (acidic to alkaline) and in the presence of NaCl at different temperatures. The interfacial and micellization properties have been studied from surface tension measurements using du Nouy tensiometer. The cmc shows maximum value at neutral pH. With increase in the concentration of NaCl and also with the increase of temperature (35–50°C), the cmc decreases. Apart from the thermodynamic quantities of micellization as well as adsorption at air/water interface, the heat capacity ($\Delta C_{p,m}$), transfer enthalpy ($\Delta H_{m,tr}$), transfer heat capacities ($\Delta C_{p,m,tr}$), and Traube (σ) constant have been evaluated and discussed. Both micellization and adsorption processes have been found to be endothermic at all pH and in the presence of NaCl. An enthalpy-entropy compensation effect has been observed with an isostructural temperature from 299-315 K for both the micellization and interfacial adsorption processes. The CPs of $C_{12}E_{12}$ and $C_{12}E_{15}$ were significantly affected by the presence of NaCl but variation in pH does not have much effect. The micelle aggregation number (N_{agg}) has been measured by using steady state fluorescence quenching method at a total surfactant concentration ~ 10 mM at 30°C. The micropolarity and the binding constant (K_{sv}) for $C_{12}E_{12}$ and $C_{12}E_{15}$ in the presence of increasing concentration of NaCl (0.1, 0.25, 0.5, 0.75 and 1.0M) were determined from the ratio of the intensities of the first and the third vibronic peaks (I_1/I_3) of pyrene fluorescence emission spectrum. The micellar interiors were found to be reasonably polar.

Keywords : *Critical micelle concentration, nonionic surfactant, pH, aggregation number.*

INTRODUCTION

The interfacial and micellar properties of nonionic surfactants are governed by a delicate

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balance of hydrophobic and hydrophilic properties of the surfactant molecules. These properties of a surfactant are very sensitive and are influenced or controlled by the type of solvent and its polarity, temperature, pressure and also by presence of various foreign substances (cosolvent) [1-8]. They provide a wealth of information about solute-solute and solvent-solute interactions in aqueous solution, both in absence as well as in presence of additives. Additives have significant influence on surfactant self-organization [I]. They can influence solvent structure and polarity and can also undergo direct interaction with the surfactant.

Nonionic surfactant of the alkyl polyoxyethylene (POE) type are widely used in detergency, cosmetics, fabric softening, emulsion formulations like shampoo, paints, etc. as well as in pharmaceutical dosages and in drug delivery systems, which are pH sensitive phenomena. So we were interested to study the interfacial and micellization properties of POE surfactants at various pH to understand how acidity/alkalinity affect the behaviour of these surfactants in aqueous solution. The hydration of POE chains of these surfactants leads to the aqueous solubility of the molecules; their temperature induced dehydration is chiefly responsible for the inverse relationship between aqueous solubility and temperature, observed in these amphiphilic compounds. Maeda [9] emphasized the formation of hydrogen bonds between the cationic-nonionic and cationic-cationic species, where they studied the effect of change of pH on stability, aggregation number and titration properties of dodecyldimethylamine oxide (DDAO) surfactant. Herrmann [10] showed that DDAO behaved as a nonionic surfactant at $\text{pH} \geq 7$, a cationic (DDHA^+) at $\text{pH} \leq 3$ and a nonionic-cationic mixture between pH 3 and 7. The deinking of printed film by surfactant also depends on the pH [11]. Nonionic surfactant is effective above the cmc at very basic ($\sim \text{pH} 12$) condition [11]. The effect of salinity on the phase behaviour in microemulsion can be counter balanced by adjustment of pH [12,13]. The effect of pH on solutions of other surfactants like cationic cetyltrimethylammonium bromide (CTAB) [14], amphoteric-anionic N,N-dimethyl N-lauryl lysine (DMLL), anionic sodium dodecyl sulphate (SDS) [15] and fatty acid soap [16] were also studied. However to our knowledge, no study dealing with the effect of pH on nonionic POE type surfactant has been done so far. We report herein the effect of pH and salt on cmc, minimum area per molecule (A_{min}) and thermodynamics of micellization and adsorption at the air/water interface, of n-dodecyloligoethylene oxides $\text{C}_{12}\text{E}_{12}$ and $\text{C}_{12}\text{E}_{15}$ at different temperatures. We also determine the aggregation number of both the nonionic surfactants in the absence and in the presence of NaCl of different concentrations.

EXPERIMENTAL

Materials : $\text{C}_{12}\text{E}_{12}$ and $\text{C}_{12}\text{E}_{15}$, $[\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_{12/15}\text{OH}]$, MW 714 and 846 respectively were obtained from Lion Corp. Tokyo, Japan and used without any further purification. The surface tension vs concentration plot did not show any minimum. All

solutions were prepared by using doubly distilled water having specific conductance 2-3 $\mu\text{S cm}^{-1}$. HCl, NaOH and NaCl used for experiments were of analytical grade (Qualigens, India). Cetyl pyridinium chloride (Loba Chemie, Baroda, India) was recrystallized twice from benzene. Pyrene (Fluka, Germany) was recrystallized from cyclohexane.

Methods : The critical micelle concentration (cmc) was determined by the surface tension (γ) measurement using a du-Nouÿ ring tensiometer (S. C. Dey and Co. Kolkata, India) at different temperatures, viz., 35, 40, 45 and 50°C. The temperature was maintained within $\pm 0.1^\circ\text{C}$ by circulating thermostated water through a jacketed vessel containing the solution. Other conditions were the same as reported in our recent papers. [5,17-19]. Representative plots of surface tension (γ) against $\text{Log}_{10} C$ (C in molarity) are shown in Fig. 1 and 2. The reproducibility in the cmc was found to be within $\pm 1.0\%$.

A digital pH meter of Weltronix CM-100, India was used, which was calibrated

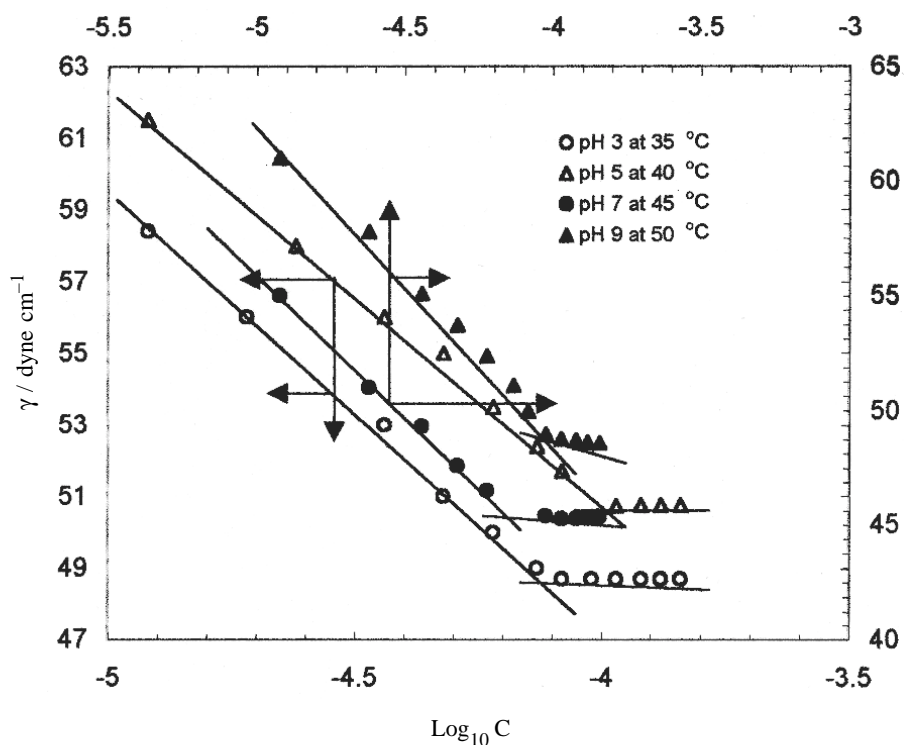


Fig. 1. Representative plots of Surface tension (γ) vs. logarithm of molar concentration (C) of $\text{C}_{12}\text{E}_{12}$ at different pHs.

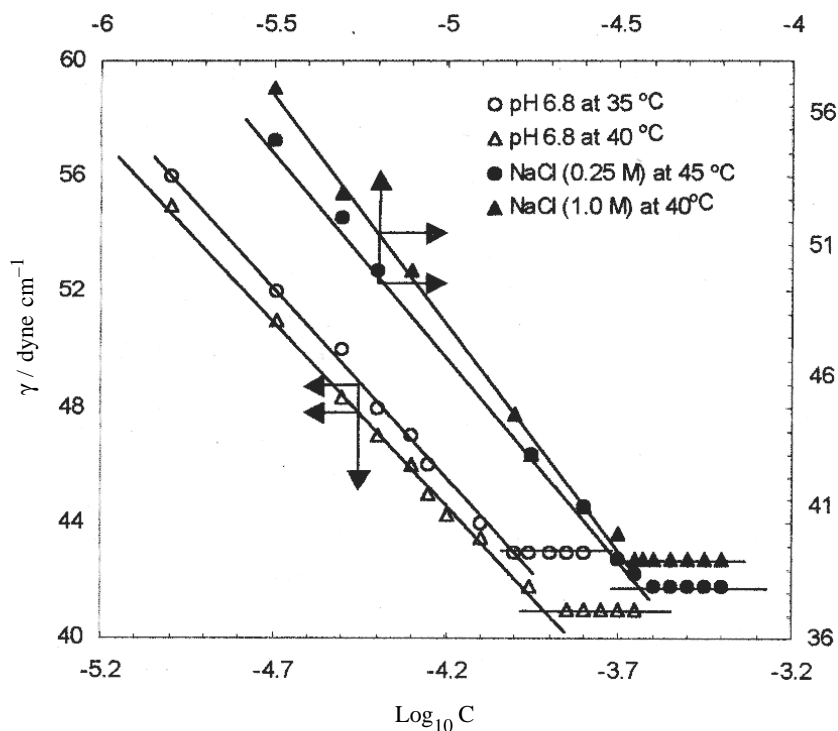


Fig. 2. Representative plots of Surface tension (γ) vs. logarithm of molar concentration (C) of $C_{12}E_{15}$ at different pHs and in the presence of NaCl

by using buffer solutions of pH 4.0, 7.0 and 9.2 obtained from Qualigens Fine Chemicals, India prior to pH measurements [20]. In the working solution, HCl was used to adjust the acidic pH while the alkaline pH was adjusted by using NaOH solution. The pH of solution was noted before and after the completion of each run, a negligible change in pH was observed at the end of each experiment which lasted for more than an hour.

The micellar aggregation number (N_{agg}) of surfactant solutions was determined by steady state fluorescence quenching measurements. Pyrene was used as the probe and cetyl pyridinium chloride as the quencher. The fluorescence emission spectra of pyrene monomers in the surfactant solutions were determined with a Shimadzu RF-5301 PC spectrofluorimeter at the excitation and emission wavelengths, 335 and 385 nm respectively. Excitation and emission band pass were 3 and 1.5 nm respectively. Each spectrum had five vibronic peaks from shorter to longer wavelengths (Fig. 3). All fluorescence measurements were carried out at room temperature, (~ 30 °C).

An aliquot of the stock solution of pyrene in ethanol was transferred into a flask

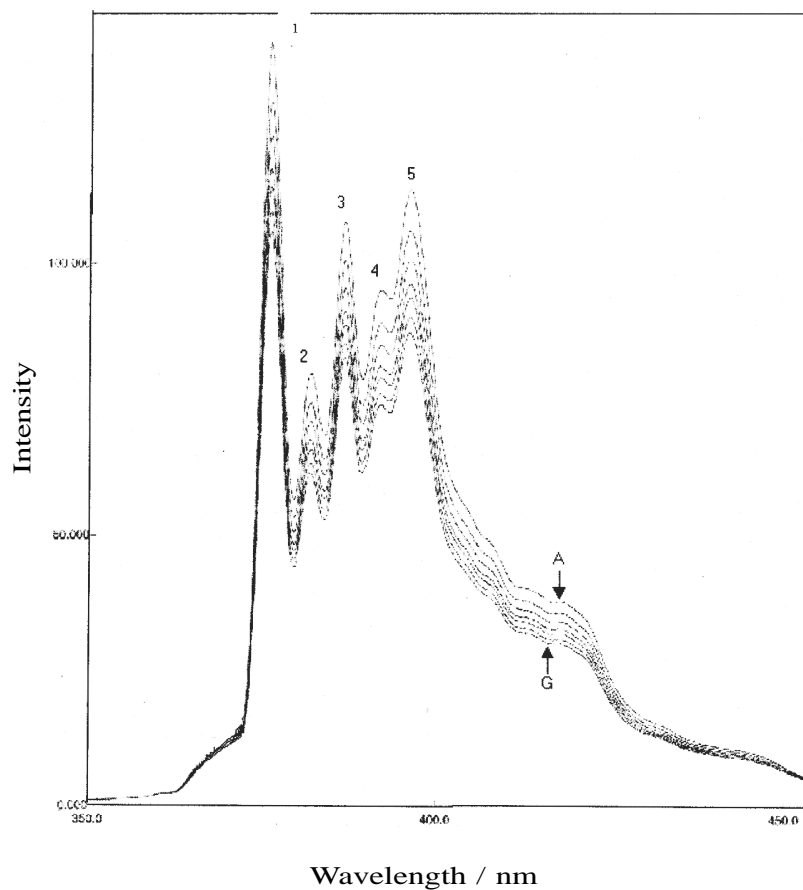


Fig. 3. Representative fluorescence (emission) spectra of 10^{-5} M pyrene in aqueous micellar solution of $C_{12}E_{12}$ in presence 0.25 M NaCl at various quencher concentrations. From top to bottom A (zero), B (1.8×10^{-5} M), C (3.3×10^{-5} M), D (4.6×10^{-5} M), E (5.7×10^{-5} M), F (6.6×10^{-5} M) and G (7.5×10^{-5} M) respectively.

and the solvent was evaporated with nitrogen. The surfactant solution (10 mM) was added and pyrene concentration was kept constant at 10^{-6} M. The quencher concentration was varied from 0 to 8×10^{-5} M.

The micellar aggregation number (N_{agg}) was deduced from the equation [21,22],

$$\ln I = \ln I_0 - \frac{(N_{agg} [Q])}{([S] - cmc)} \quad (1)$$

where [Q] and [S] are the concentrations of the quencher and the total surfactant respectively. The ratio of the intensities of the first (I_1 , 375 nm) and the third (I_3 , 395 nm) vibronic peaks, i.e., I_1/I_3 of the monomeric pyrene fluorescence emission spectrum in presence of surfactants is considered to be the index of micropolarity of the system, i.e., it gives an idea of the microenvironment in the micelle. A low value of this ratio ($I_1/I_3 < 1$) is generally taken as the pyrene having nonpolar surroundings whereas higher value ($I_1/I_3 > 1$) suggests that pyrene has polar surroundings [23].

The CP of surfactant concentration (1% w/v) in presence of NaCl (0.5-4.0 M) and at all pH were determined. The experimental procedure was the same as reported earlier [8]. The CP presented here are the averages of the appearance and the disappearance temperatures of the cloud. The experiments were repeated twice and the error was about 0.5%.

RESULTS AND DISCUSSION

Critical micelle concentrations

Effect of pH : Surface tension is a dependable and an elegant method for the determination of cmc [24]. The cmc values of $C_{12}E_{12}$ and $C_{12}E_{15}$ at various pH and in presence of NaCl of different concentrations at different temperatures are presented in Table 1. It is evident from the Table 1 that, the cmc values of these POE surfactants decrease with an increase in temperature at all pH, which is expected for nonionic surfactants of POE class. This is due to the dehydration of the hydrophilic moiety of the surfactant molecules and also due to the breaking of water structure [5]. As the dielectric constant of water decreases with temperature, hydration of POE chains diminishes when the solution is heated. It is observed that at a given temperature, the pH vs. cmc plot shows a maximum at pH ~ 7 . As the hydrophilicity of POE nonionic surfactant (number of POE units) increases, the cmc increases, thus $C_{12}E_{15}$ has higher value of cmc than $C_{12}E_{12}$ at neutral pH. The formation of micelle is controlled by hydrophobic interaction and the London dispersion forces [25]. The ether linkages in $C_{12}E_{12}$ and $C_{12}E_{15}$ chain can be protonated at low pH, and thus the surfactants acquire a weak cationic character and behave as a pseudo ionic surfactant. At alkaline or around neutral pH these surfactants are expected to remain nonionic.

It is seen that in the acidic region with decreasing $[H^+]$, the cmc increases. With increase in alkalinity the cmc decreases. 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, i.e., there is a decrease in hydrophilicity or an increase in hydrophobicity causing the lowering of cmc. The resultant cmc is governed by the effects of various factors, synergistic and/or antagonistic. It is however obvious that the presence of excess H^+ or OH^- induces early

TABLE 1

Critical micelle concentrations of $C_{12}E_{12}$ and $C_{12}E_{15}$ in aqueous solution as a function of pH and different concentrations of NaCl at various temperatures.

	Critical micelle concentration $\times 10^5$ M							
	$C_{12}E_{12}$				$C_{12}E_{15}$			
pH	35	40	45	50°C	35	40	45	50°C
1.0	8.3	7.9	70.0	6.6	5.4	4.4	4.1	5.2
3.0	8.3	8.1	7.9	7.6	9.1	8.70	8.1	7.2
5.0	9.9	9.3	8.6	8.2	9.8	7.41	6.0	6.66
6.8	10.2	9.8	9.1	8.5	12.8	10.2	9.5	8.5
9.0	8.3	7.6	6.9	6.3	7.4	4.7	5.4	4.9
11.0	7.4	5.9	6.3	5.8	6.5	5.7	5.4	5.2
NaCl / M	$C_{12}E_{12}$				$C_{12}E_{15}$			
0.10	7.9	7.0	6.0	5.8	6.5	5.2	4.9	4.5
0.25	7.0	6.0	6.0	5.2	4.9	4.4	4.0	3.7
0.50	5.8	5.5	4.8	3.8	4.5	3.8	4.1	2.8
1.00	4.8	4.0	4.6	3.3	4.1	3.3	2.9	2.7

micellization probably because of more structured solvent.

Effect of Salt : The effect of salt on the cmc's of the POE nonionic surfactants are expected to be less complicated, due to the absence of charge-charge interactions. However, such studies have been less systematic and the nature of the effect has been attributed to various phenomena. The cmc's of $C_{12}E_{12}$ and $C_{12}E_{15}$ also decreased by the added NaCl. Various interpretations have been proposed for the observed effects. According to Shinoda et.al [26], the change in cmc is due to the decreased hydration of the surfactant resulting in an increase in their effective concentration. This is due to the amount of added salt, and their hydration. Hsiao et. al [27] attributed the lowering in cmc to the decrease in hydration of the EO chain, caused by added electrolytes, and probably due to the breaking of hydrogen bonds. Becher [28] first interpreted the lowering of the cmc due to decrease in the water activity, but later discounted this possibility. Schick [29] attributed the effect to the salting out of the EO chains. However, Mukerjee [30] concluded that the salting out of the hydrocarbon moiety of the surfactant is responsible for the lowering of cmc and not of the hydrophilic head group as proposed by Schick [29]. However we feel that probably both Schick's and Mukerjee's suggestions hold good. This is be-

cause NaCl is certainly going to affect the amount of water available for the surfactants. The hydrophilic group will therefore have less amount of water though the iceberg structure around the hydrophobic groups will be completely devoid of water, both resulting in an early micelle formation.

Thermodynamics of micellization and adsorption

The Gibbs free energy of micellization (ΔG_m^0) for a nonionic surfactant is related to the cmc (expressed in mole fraction scale) by the following relation [31],

$$\Delta G_m^0 = RT \ln \text{cmc} \quad (2)$$

the standard state being the hypothetical ideal solution of surfactant at unit mole fraction. Standard free energy of micellization, ΔG_m^0 , thus evaluated from eqn. 2 are presented in Table 2. It is evident from Table 2 that the free energy of micellization is relatively more

TABLE 2

The free energy (ΔG_m^0), enthalpy (ΔH_m^0) and entropy (ΔS_m^0) of micellization of $C_{12}E_{12}$ and $C_{12}E_{15}$ at different pHs and different concentrations of NaCl.

	$C_{12}E_{12}$						$C_{12}E_{15}$					
	$-\Delta G_m^0$ kJmol ⁻¹				ΔH_m^0 kJmol ⁻¹	ΔS_m^0 Jmol ⁻¹ K ⁻¹	$-\Delta G_m^0$ kJmol ⁻¹				ΔH_m^0 kJmol ⁻¹	ΔS_m^0 Jmol ⁻¹ K ⁻¹
pH	35	40	45	50°C			35	40	45	50°C		
1.0	34.4	35.1	35.9	36.6	12.9	153	35.4	36.6	37.3	37.3	3.73	128
3.0	34.3	34.9	35.5	36.3	4.3	125	34.1	34.8	35.5	36.4	12.8	152
5.0	34.0	34.6	35.4	36.1	9.4	141	33.9	35.2	36.3	36.6	22.6	184
6.8	33.8	34.5	35.2	36.0	11.2	146	33.2	34.4	35.1	35.9	20.9	176
9.0	34.3	35.1	35.9	36.8	15.4	161	34.6	36.4	36.6	37.4	18.0	172
11.0	34.6	35.8	36.2	37.0	22.9	186	34.9	35.9	36.6	37.3	13.7	158
NaCl (M)												
0.1	34.4	35.3	36.3	37.0	18.2	171	34.9	36.1	36.8	37.7	21.1	182
0.25	34.8	35.7	36.3	37.3	15.3	163	35.7	36.6	37.4	38.2	15.4	166
0.5	35.3	36.0	36.9	38.1	18.6	174	35.9	36.9	37.3	38.9	19.4	180
1.0	35.8	36.8	37.0	38.5	21.7	186	36.1	37.3	38.2	39.0	25.6	200

negative with increasing temperature, indicating relative spontaneity of the micellization process as the temperature increases. The free energy of micellization, ΔG_m^0 values are more negative in presence of NaCl of different concentrations as compared to that in pure water, suggesting that the micellization of both the surfactants is more favoured in presence of NaCl.

The standard entropy of micellization (ΔS_m^0) and enthalpy of micellization (ΔH_m^0) were computed from the slope and the intercept respectively of linear ΔG_m^0 vs. T plots. The entropy of micellization values are all positive and large indicating that the micellization process is entropy controlled. Overall micellization process for both the surfactants at different pH and in presence of NaCl is endothermic in nature. High entropy changes are generally associated with a phase-change; the pseudophase micellar model is thus preferred over the mass action model and has been used by us. Rosen [4] 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 molecules via micellization wherein the hydrated surfactant molecules release the water molecules resulting in an increase in overall entropy of the system.

Linear correlation between enthalpy and entropy, i.e., enthalpy-entropy compensation phenomenon for micellization process is observed for both the surfactants (Fig. 4). Such a compensation was suggested by Lumry and Rajender [32] and the slope of the line, i.e., the compensation temperature was found to be 300 K for micellization, which is close to the expected values between 270 and 294K in aqueous medium [32]. The observed value is a little higher than the suggested value and this may be due to the effect of additives. Moreover, the small variations, we observe here as well as those observed earlier [7] may be due to the differences in the bulk structural property of the solution from that of water.

The heat capacities for the micelle formation ($\Delta C_{p,m}$) were also evaluated from the plot of ΔH_m vs T, the slope being $\Delta C_{p,m}$. (Table 3). The variation of heat capacities with both pH and concentration of NaCl did not show any regularity; this was observed earlier in calorimetric studies [33]. The transfer enthalpies ($\Delta H_{m,tr}$) and transfer heat capacities ($\Delta C_{p,m,tr}$) of micelle from water to aqueous solution were obtained using the relations [34],

$$\Delta H_{m,tr} = \Delta H_m(\text{aq.additive}) - \Delta H_m(\text{aq.}) \quad (3)$$

$$\Delta C_{p,m,tr} = \Delta C_{p,m}(\text{aq.additive}) - \Delta C_{p,m}(\text{aq.}) \quad (4)$$

The transfer enthalpies of micelle were found to be negative (Table 3) but few are positive also. Such transfer enthalpies were also reported for the transfer of NaCl and amino acids from water to aqueous urea solution by Ahluwalia et. al [33b]. It shows that transfer of hydrophilic (OE) groups from water (pH 6.8) to acidic or basic solution is exothermic, whereas that of hydrophobic group is endothermic. The transfer heat capaci-

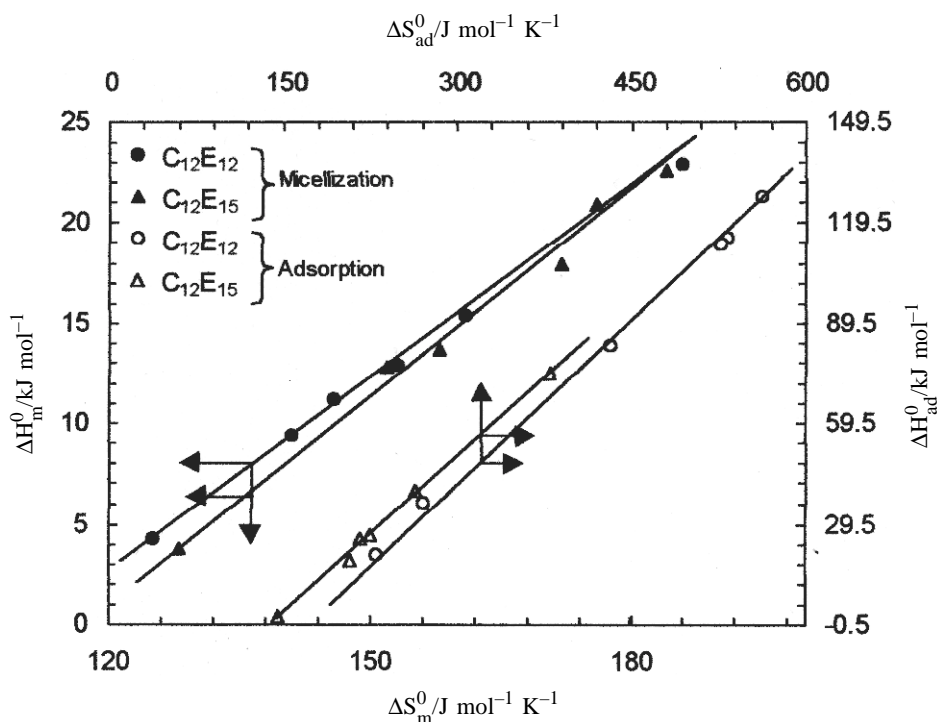


Fig. 4. Enthalpy-entropy compensation plot for micellization and adsorption taking all systems together.

ties of micellization $\Delta C_{p,m.tr.}$ for the transfer of micelle from water (pH 6.8) to acidic or basic solution are negative indicating increased hydration of micelles due to greater extent of hydrogen bonding between OE and additives present in the solution. The $\Delta C_{p,m.tr.}$ values remain more or less constant throughout for all the systems indicating no obvious structural transition.

The air/water interface of a surfactant solution is well populated [33] by the adsorbed amphiphile molecules. The surface excess concentration, Γ_{max} , of the surfactant molecules in the surface layer compared to the bulk and the area per molecule, A_{min} in the surface monolayer were calculated by the standard procedure [4,34]. The slope of the tangent, at a given concentration of the γ vs. $\text{Log}_{10}C$ plot has been used to calculate Γ_{max} , by fitting a curve to a polynomial equation of the form, $y = ax^2 + bx + c$ in Microsoft excel. The regression coefficient (R^2) value of the fit, lies between 0.9645 and 0.9968. The effect of temperature on Γ_{max} at different pH did not show any regular variation (data not given), thus the interaction seems not to be straightforward. This may be guided by

TABLE 3

The heat capacities ($\Delta C_{p,m.}$) and the transfer enthalpies ($\Delta H_{m.tr.}$) and heat capacities ($\Delta C_{p,m.tr.}$) of Micellization of $C_{12}E_{12}$ and $C_{12}E_{15}$ in Aqueous Solutions of various pH and NaCl concentrations at 45°C.

pH	$C_{12}E_{15}$			$C_{12}E_{15}$		
	$\Delta C_{p,m.}$ ($Jmol^{-1}K^{-1}$)	$\Delta H_{m.tr.}$ ($kJmol^{-1}$)	$\Delta C_{p,m.tr.}$ ($Jmol^{-1}K^{-1}$)	$\Delta C_{p,m.}$ ($Jmol^{-1}K^{-1}$)	$\Delta H_{m.tr.}$ ($kJmol^{-1}$)	$\Delta C_{p,m.tr.}$ ($Jmol^{-1}K^{-1}$)
1.0	0.005	1.52	-0.001	-0.062	-17.47	-0.048
3.0	-0.007	-6.98	-0.013	0.012	-8.03	0.026
5.0	-0.001	-1.79	-0.007	-0.056	1.33	-0.042
6.8	0.006	0.0	0.0	-0.014	0.0	0.0
9.0	-0.005	4.07	-0.011	0.028	-2.78	0.042
11.0	0.034	11.72	0.28	-0.024	-7.43	-0.01
NaCl (%)						
0.10	0.001	6.85	-0.005	-0.008	0.29	0.006
0.25	0.001	4.3	-0.005	-0.004	-5.48	0.01
0.50	-0.012	7.2	-0.018	-0.008	-0.93	0.006
1.00	0.02	10.92	-0.014	-0.01	4.53	0.004

(The error in the data is <2%)

the interaction of H^+ and OH^- ions with water as well as the surfactant. The increase in the temperature (in presence of H^+ or OH^-) hinders the adsorption of surfactants at air/water interface. This is because of (i) the changed nature of water due to presence of H^+ and OH^- ions and (ii) the possibility of interaction between the surfactant and the H^+ ions, due to the presence of unpaired electrons on the oxygen of oxyethylene groups.

The $A_{min.}$ values of $C_{12}E_{12}$ and $C_{12}E_{15}$ at cmc are presented in Table 4. The magnitudes are of the order of ~ 1.0 nm² 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 [35]. The effectiveness of a surface active molecule is measured by the surface pressure (π_{cmc}) at the cmc, i.e., $\pi_{cmc} = \gamma_o - \gamma_{cmc}$ where γ_o and γ_{cmc} are the surface tension of pure solvent and the surface tension of the surfactant solution at cmc respectively.

The value of free energy of adsorption of the surfactant at the air/water interface

TABLE 4.

Minimum area per molecule A_{\min} of $C_{12}E_{12}$ and $C_{12}E_{15}$ at different pHs and different concentrations of NaCl.

A_{\min} (nm ²)								
System	$C_{12}E_{12}$				$C_{12}E_{15}$			
pH	35	40	45	50°C	35	40	45	50°C
1.0	0.58	0.90	0.83	0.99	0.62	0.74	0.53	0.84
3.0	0.75	0.79	0.85	0.84	0.73	0.69	0.84	0.92
5.0	0.60	0.66	0.83	0.76	0.70	0.80	0.76	0.51
6.8	0.82	0.89	0.98	0.83	0.71	0.72	0.80	0.89
9.0	0.71	0.98	0.73	0.70	0.85	0.52	0.69	0.63
11.0	0.86	0.89	1.03	1.03	0.73	0.58	0.68	0.66
NaCl / M								
0.10	1.03	1.11	1.11	1.20	0.77	0.84	0.83	0.78
0.25	1.03	0.90	0.92	1.08	0.83	0.84	0.83	0.76
0.50	1.40	1.09	0.70	0.80	0.90	0.85	0.77	0.80
1.00	1.14	0.87	1.14	1.03	0.81	1.10	1.10	1.00

(ΔG_{ad}^0) was calculated using the relation [36],

$$\Delta G_{\text{ad}}^0 = RT \ln \text{cmc} - N\pi_{\text{cmc}} A_{\min} \quad (5)$$

The standard state for the 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_{m}^0) was less negative than the free energy of adsorption, ΔG_{ad}^0 values at air/water interface at all temperatures, suggesting 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 5, the thermodynamic parameters of adsorption, i.e., ΔG_{ad}^0 , ΔH_{ad}^0 and ΔS_{ad}^0 of $C_{12}E_{12}$ and $C_{12}E_{15}$ at the air/solution interface, at various pHs and in NaCl solutions of different concentrations are presented.

The standard entropy (ΔS_{ad}^0) and enthalpy (ΔH_{ad}^0) of adsorption were obtained from the slope and intercept respectively of the reasonably linear ΔG_{ad}^0 vs T plot. The ΔS_{ad}^0 values are all positive and greater than those of ΔS_{m}^0 values, reflecting greater freedom

TABLE 5

The free energy (ΔG_{ad}^0), enthalpy (ΔH_{ad}^0) and entropy (ΔS_{ad}^0) of adsorption and Traube's constant ($\times 10^{-7}$) $C_{12}E_{12}$ and $C_{12}E_{15}$ at different pHs and different concentrations of NaCl.

pH	$C_{12}E_{12}$						$C_{12}E_{12}$					
	$-\Delta G_{ad}^0$ kJmol ⁻¹				ΔH_{ad}^0	ΔS_{ad}^0	$-\Delta G_{ad}^0$ kJmol ⁻¹				ΔG_{ad}^0	ΔG_{ad}^0
	35	40	45	50°C	kJmol ⁻¹	Jmol ⁻¹ K ⁻¹	35	40	45	50°C	kJmol ⁻¹	Jmol ⁻¹ K ⁻¹
1.0	48.3 (15.5)	53.4 (81.6)	53.7 (66.2)	57.1 (172)	114.8	532.2	42.8 (1.81)	44.6 (2.78)	43.8 (1.6)	49.4 (9.8)	74.7	380
3.0	51.1 (46.4)	51.9 (45.9)	54.8 (100)	53.9 (52.1)	20.1	231.4	41.1 (0.93)	43.1 (1.6)	43.4 (1.4)	44.6 (1.6)	25.1	216
5.0	45.8 (5.87)	47.0 (6.98)	53.9 (71.4)	52.9 (35.9)	127.3	561.6	42.3 (1.49)	45.7 (4.2)	45.9 (3.5)	46.0 (2.8)	26.3	226
6.8	47.3 (10.5)	53.5 (84.8)	58.0 (337)	53.0 (37.3)	83.3	431.2	41.9 (1.28)	43.1 (1.6)	44.9 (2.4)	45.7 (2.5)	39.4	264
9.0	47.6 (11.8)	54.7 (135)	52.0 (34.8)	51.3 (19.8)	35.6	271.3	46.5 (7.7)	44.9 (3.1)	47.8 (7.1)	49.0 (8.4)	18.6	208
11.0	48.0 (13.8)	52.1 (49.5)	56.1 (164)	55.5 (94.5)	113.3	526.8	44.0 (2.9)	42.1 (1.1)	44.9 (2.4)	45.5 (2.3)	1.9	146
NaCl (M)												
0.10	42.2 (1.44)	54.8 (140)	60.0 (718)	62.6 (1330)	173.5	717.4	45.5 (5.2)	49.0 (15.1)	50.0 (16.3)	50.9 (17.0)	59.7	344
0.25	57.5 (565)	54.1 (107)	55.5 (131)	59.2 (375)	125.0	570.0	46.4 (7.4)	46.7 (6.2)	47.4 (6.1)	50.2 (13.1)	28.7	242
0.50	47.7 (12.3)	565 (269)	52.8 (47.1)	53.1 (38.7)	61.8	355.4	49.5 (24.8)	47.3 (7.8)	50.5 (19.7)	47.7 (5.18)	62.6	44
1.00	59.4 (1190)	60.1 (1070)	62.2 (1650)	58.4 (278)	26.5	279.0 36.7	50.5 84.8	53.5 337	58.0 58.3	54.2 44.4	312	

*The values in the parentheses are Traube's constant

of motion of the hydrocarbon chain at the planar air/water interface compared to that in the cramped interior beneath the convex surface of micelle [36]. It is evident from Tables 2 and 5 that the derived enthalpy and entropy quantities have irregular variation with pH. However, in the presence of NaCl, the enthalpy and entropy of micellization increase while for adsorption of surfactant at air/water interface, the corresponding values decrease

on increasing the concentration of NaCl. The error associated with the values of these quantities is $\pm 5\%$.

Like micellization process, the adsorption of surfactant at air/water interface has also been found to be endothermic in nature. The endothermic character of micellization and adsorption are specific to the surfactant, the additive and the temperature of micellization [37-41]. The ΔH_{ad}^0 vs ΔS_{ad}^0 compensation plot of the adsorption phenomenon is observed for both the surfactants and is illustrated in Fig. 4. The compensation temperature is observed to be 305 and 315K for $C_{12}E_{12}$ and $C_{12}E_{15}$ respectively, slightly different from 300K obtained for the micellization phenomenon, but around the expected region for aqueous systems (270-294K) [32].

It has been suggested by Weiner and Zografis [41] that,

$$\Delta G_{ad}^0 = -RT \ln \sigma \quad (6)$$

where ' σ ' is known as Traube's constant and is defined by the relation

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

This means σ is the rate of change of surface pressure per unit concentration change at infinite dilution. The σ values are given in Table 5. It can be noted that the σ of the pure $C_{12}E_{12/15}$ is similar to the data given in Table 4 of Meguro et.al [42] thereby suggesting that our adsorption data are reasonable. We computed the effect of different pH and NaCl concentration on σ where unfortunately, no regularity was observed.

Micellar aggregation number (N_{agg})

The micellar aggregation numbers of $C_{12}E_{12}$ and $C_{12}E_{15}$ evaluated using steady state fluorescence quenching measurements with varying NaCl concentration are tabulated in Table 6. It is evident that, the N_{agg} of $C_{12}E_{12}$ is higher than that of $C_{12}E_{15}$. However, in presence of NaCl, though the N_{agg} changes, there is no regular change with increasing NaCl concentration. A minimum is observed for both the surfactants, though at different NaCl concentrations. However, at higher concentration of NaCl, the N_{agg} increases due to the decrease in the steric hindrance between ethylene oxide moieties of the polyoxyethylene chain due to the presence of NaCl. Table 6 also illustrates the intensity ratio of the first and the third vibronic peaks (I_1/I_3) in the monomeric pyrene fluorescence emission spectrum, which is sensitive to the local polarity around the probe (pyrene). It is evident that, all the values of I_1/I_3 are > 1 suggesting polar environment around pyrene. However I_1/I_3 values are almost constant ($I_1/I_3 \sim 1.30$) for both the surfactants irrespective of NaCl concentration in the present study. This indicates that by the presence of NaCl there is no significant change in polarity around pyrene.

TABLE 6

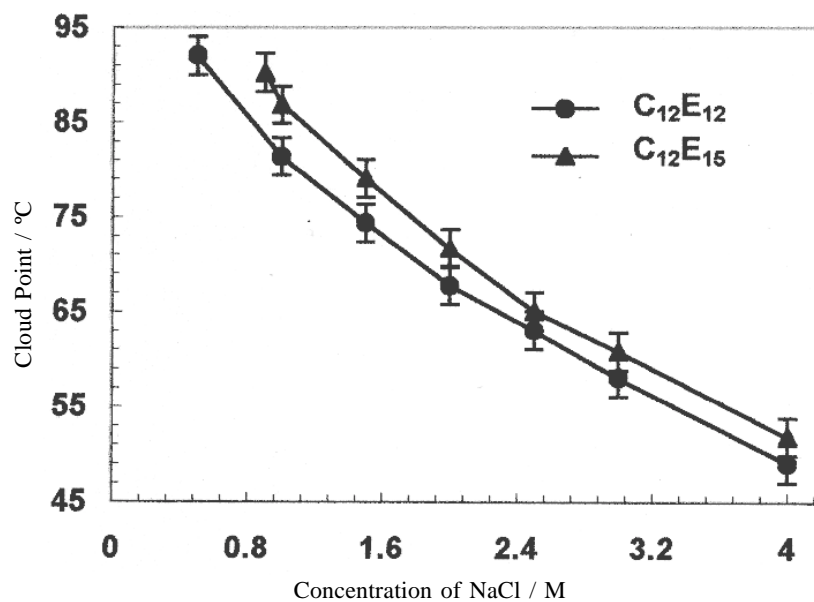
 Aggregation number (N_{agg}) and micropolarity (I_1/I_3) of $C_{12}E_{12}$ and $C_{12}E_{15}$ in the presence of NaCl at 30°C.

Concentration of NaCl / M	Aggregation number (N_{agg})	
	$C_{12}E_{15}$	$C_{12}E_{12}$
0.00	74 ± 4 (1.30)	51 ± 3 (1.30)
0.10	51 ± 3 (1.30)	46 ± 2 (1.31)
0.25	33 ± 2 (1.31)	57 ± 3 (1.30)
0.50	46 ± 2 (1.31)	56 ± 3 (1.31)
1.00	53 ± 3 (1.30)	58 ± 3 (1.31)

Micropolarity values are given in in parentheses

Cloud points

Cloud points are the manifestation of the solvation/desolvation phenomena in nonionic surfactant solution. The desolvation of the hydrophilic groups of the surfactant


 Fig. 5. Cloud point vs NaCl concentration plot for $C_{12}E_{12}$ and $C_{12}E_{15}$ surfactants.

leads to the formation of cloud in the surfactant solution. It is seen that pH does not have any effect on the cloud points of $C_{12}E_{12}$ and $C_{12}E_{15}$ but NaCl being a water structure maker, lowers the CP of POE surfactants by decreasing the availability of water molecule to hydrate the ether oxygen of the POE chain (Fig 5). Similar results were also observed with other $C_{12}E_n$ ($n=9,10$) surfactants [43]. However, it has been stated that when temperature dependent interaction parameters exist, the hydrophilic and hydrophobic parts of micelles interact with water in different ways [44]. Clouding of surfactant is thus dependent on balance of hydrophobicity and hydrophilicity. Hence at CP, hydrophobicity is more dominating than hydrophilicity and the complete removal of water from the molecule is not essential. Therefore we can say that the H^+ and Cl^- ions affect the hydrophobicity or hydrophilicity to the same extent but in opposite direction which is also true for Na^+ and OH^- ions. Hence the CP does not change on changing the pH. However the effect of Na^+ and Cl^- are not of same magnitude and hence there is a change in CP.

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