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STUDY ON MICELLIZATION AND INTERFACIAL ADSORPTION OF POLYOXYETHYLENE (30) LAURYL ETHER ($C_{12}E_{30}$) IN 0.01 M NACL AT AIR-WATER INTERFACE

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ABSTRACT

The surface properties of a polyoxyethylated octyl phenol [C_8H_{17}-$O(CH_2CH_2O)_{30}$-H] has been studied through surface tension measurements. The surface excess (G) and the corresponding interfacial parameters have been computed. The Gibbs free energy, enthalpy and entropy of micellization (ΔGG_m^0, ΔGH_m^0, ΔGS_m^0) and of adsorption at air-water interface (ΔGG_{ad}^0, ΔGH_{ad}^0, ΔGS_{ad}^0) have also been evaluated. An enthalpy-entropy compensation effect has been examined with an isostructural temperature of 292 K for both the micellization and interfacial adsorption processes. 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. The minimum area per surfactant molecule and critical micellar concentration divulge that both hydrophobicity and steric constraints of the surfactant play a pivotal role in micelle formation.

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INTRODUCTION

The surfactant molecules can organize themselves into aggregates when dissolved into aqueous medium. The micelle formation takes place above critical micelle concentration (cmc), below which surfactant molecules are present as monomers (Tanford, 1980 and Myers1992). The functions and properties of surfactant systems depend on their structural type, concentration and compositions, besides, temperature, pressure, pH, solvent and additives. There has been, recently, upsurge in commercial application of nonionic surfactants and the progress in basic research (Schick, 1982). Keeping in mind the properties of nonionic surfactants (Sulthana *et al.* 2000 and Koshy and Rakshit, 1991), we stretched our work, in continuation of our interest in the properties of polyoxyethylated octyl phenol to explore the interfacial and micellization properties of polyoxyethylated octyl phenol at different pHs to understand how acidity / alkalinity affect the behavior of the surfactant in aqueous solution (Dave *et al.* 2005). The effects of change of pH and temperatures of polyoxyethylene (10) lauryl ether [$C_{12}E_{10}$: CH_3 $(CH_2)_{11}(CH_2CH_2O)_{10}OH$] have been investigated (Sharma and Rakshit, 2004). The aggregation behavior of some polyoxyethylated alkyl ethers(Sahoo, 2002) and anionic surfactants (Sahoo *et al.* 2002) in aqueous medium using fluorescence spectroscopy. The effect of pH on other surfactants like dodecyldimethylamine oxide (DDAO) (Maeda, 1996), cationic hexadecyltrimethyl ammonium bromide (HTAB) (Behrends and Herranann, 2000) and amphoteric-anionic N,N-dimethyl N-lauroyl lysine (DMLL)-sodiumdodecyl sulphate (SDS) (Abe *et al.* 1989) have also been investigated. The results of pH on dimethyl dodecyl amine oxide (DDAO) showed that it behaves as nonionic at pH ^{3} 7, as cationic (DDHA^{+}) at pH £ 3 and as a nonionic-cationic mixture between pH 3 and 7 have been reported by Herrann (Herrmann, 1964).

In the present investigation, the effect of pH on surface excess (G), minimum area per molecule (A_{min}),surface pressure (P_{cmc}) and thermodynamics of micellization and adsorption of polyoxyethylated octyl phenol [C_8H_{17}-$O(CH_2CH_2O)_{30}$-H] at the air-water interface at different temperatures have been reported. The study of the effect of pH on micellization is important because of their ability to adsorb selectively on silica surface (Fu, 1987 and Patryka *et al.* 1984) and applications in processes such as detergency (Stensby, 1981),cosmetics (Idson, 1985), enhanced oil recovery (Fu, 1987) etc. The surface activity of this surfactant has been correlated with its structure.

METHODS

Reagents

Polyoxyethylated octyl phenol surfactant was procured from Nikko Chemicals, Japan under the commercial name OP-30. This surfactant was used as received. The absence of minimum in the surface tension vs. concentration plot confirmed the high purity (> 99 %) of this surfactant (Okano *et al.* 2000).

Sodium chloride (Ranbaxy Fine Chemicals Ltd., India) for maintaining constant ionic strength was used without any further purification. The solutions of surfactants in triply distilled water having conductivity 2-3 £gScm^{-1} containing 0.01 M NaCl were prepared afresh for surface tension measurements. A digital pH meter of Systronics-335 was used, following calibration using buffer solutions of pH 4.0,7.0 and 9.2 obtained from S.D. Fine Chemicals Ltd., Borisar, India. In the working solution,0.01 M HCl and NaOH were used to adjust acidic and alkaline pH respectively.

Apparatus

The critical micelle concentration (cmc) was determined by the surface tension (γ) measurements using a du-Nouy ring tensiometer (S.C.Dey and Co. Calcutta, India) measurements were carried out at temperatures 303, 308,313 and 318 K. The temperatures were maintained within ± 0.1 K by circulating thermostated water through a jacketed vessel containing the solution. The surface tension measurements were done as reported by Dave *et al.* 2005. 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 (Song and Rosen, 1996). The cmc does not change with the addition of 0.01 M NaCl.

RESULTS AND DISCUSSION

Surface tension is a reliable and excellent method for determination of cmc (Menger and Keiper, 2000). The cmc values of polyoxyethylated octyl phenol [C_8H_{17}-$O(CH_2CH_2O)_{30}$-H] at various pHs and at different temperatures are depicted in Table1. It can be seen that at constant temperature, cmc increases with the pH of the solution, low pH conducive for the micellization of the surfactant. It is quite apparent from Table 1 that cmc values of polyoxyethylated octyl phenol decrease with an increase in temperature at all pH, a typical characteristic of nonionic surfactant.

From Table 1, it is emerged that with decreasing [H^+] or lowering of temperature increases the cmc. Both H^+ and OH^- can make hydrogen bonds with water molecules and thereby promote water structure, which is also promoted by the hydrophobic group of the surfactant molecule. On the other hand, increasing the temperature, the oxyethylene groups get dehydrated with decrease in hydrophilicity or increase in hydrophobicity causing lowering of cmc.

The standard free energy of micellization is associated to cmc by the following expression (Rosen,1988).

$$\Delta G_m^0 = RT \ln \left(\frac{cmc}{55.5}\right) \qquad \text{-------------------- (1)}$$

the values are given in Table 2.

The ΔG_m^0 values are all negative which manifests that the formation of micelle is a spontaneous process. Moreover, with increasing temperature the free energy of micellization is rather more negative revealing comparative spontaneity of the micellization process as temperature increases.

The ΔS_m^0 was enumerated from the slop of the ΔG_m^0 vs. T plots. The ΔH_m^0 had been computed from the expression (Attwood *et al.* 1985).

$$\Delta H_m^0 = \Delta G_m^0 + TDS_m^0 \qquad \text{--------------------} \ (2)$$

The free energy of micellization (ΔG_m^0) and the enthalpy of micellization (ΔH_m^0) are both positive denoting that the micellization process is entropy driven process. High entropy changes are generally associated with a phase change. The pseudophase micellar model is, therefore, opted over the mass action model. Furthermore, the poly(oxyethylene) moiety in [C_8H_{17}-$O(CH_2CH_2O)_{30}$-H] chain can be protonated at low pH, leads to increase in entropy of micellization, making it positively charged to behave as a pseudo ionic surfactant. At alkaline pH, decreasing entropy of micellization due to deprotonation, making it to remain nonionic.

The enthalpies and entropies of micellization process, as presented in Table 2,were plotted against each other and an excellent linear compensation effect was observed as suggested by Lumry and rajender (Lumry *et al.* 1970). The slop of the line is the compensation temperature has been found to be 292 K, close to the expected values between 270 and 294 K in aqueous medium (Lumry *et al.* 1970). The existence of such enthalpy-entropy compensation effect was also observed earlier for many physicochemical processes including monolayer and micellization (Sharma and Rakshit, 2004; Lumry, and Rajendra, 1970; Lumry and Rajendra, 1970; Singh and Singh, 1984 and Leffler *et al.* 1963).

In order to calculate the amount of surfactant adsorbed per unit area at air-water interface, these surface pressure ($P_{cmc}= g_0-g_{cmc}$, where g_0 and g_{cmc} are the surface tension of solvent and the surface tension of surfactant solution at cmc respectively) is fitted to the Gibbs adsorption equation. Assuming the adsorption density of water to be zero, the Gibbs adsorption equation (Defay *et al.* 1966) may be written as:

$$d\Pi = \Gamma dm$$

$$d\Pi = \Gamma RT \, d \ln C \qquad \text{--------------------} \ (3)$$

Where, $d\Pi$= the change in the surface pressure in the solution,

Γ = the adsorption density of the surfactant,

$d\mu$ = the change in the chemical potential of the surfactant,

R = universal gas constant,

T = absolute temperature,

C = concentration of the surfactant in aqueous solution.

Since the surfactant solutions are dilute, the activity is easily replaced by concentration. Eq. 3 can be written as;

$$\Gamma = \left(\frac{1}{RT}\right)\left(\frac{d\Pi}{d \ln C}\right) \qquad \text{--------------------} \ (4)$$

Manimum adsorption density is calculated by limiting the concentration in the above equation to cmc of the surfactant

$$\Gamma = \frac{1}{2.303RT} \lim it_{c \to cmc} \left(\frac{d\Pi}{d \log C}\right)_T \qquad \text{--------------------} \ (5)$$

$$A_{min} = \frac{10^{20}}{N\Gamma_{max}} \qquad \text{--------------------} \ (6)$$

Where N is the Avogadro number.

It is seen from Table 3, the surface excess increases with increase in temperature due to dehydration of the surfactant molecule. This is ascribed to compact adsorption at the air-water interface, two forces are operating; the hydrophobic interaction of the alkyl chain and the cross sectional area of the poly(oxyethylene) unit (as the surfactant anchors at the interface through hy-

Table 1

Critical micelle concentration (cmc) of polyoxyethylated octyl phenol [C_8H_{17}-$O(CH_2CH_2O)_{10}$-H] in 0.01 M NaCl solution as a function of pH at different temperatures

pH of the solution	Critical micelle concentration (cmc),M at			
	303 K	308 K	313 K	318 K
3	8.3´10^{-4}	7.8´10^{-4}	7.1´10^{-4}	6.3´10^{-4}
5	9.1´10^{-4}	8.5´10^{-4}	7.9´10^{-4}	7.0´10^{-4}
6.8*	10.0´10^{-4}	9.3´10^{-4}	9.1´10^{-4}	8.4´10^{-4}
9	12.3´10^{-4}	11.5´10^{-4}	10.3´10^{-4}	9.5´10^{-4}

* Ref.10

Table 2

Thermodynamic parameters of micellization of polyoxyethylated octyl phenol [C_8H_{17}-$O(CH_2CH_2O)_{10}$-H] in 0.01 M NaCl solution at different pHs and temperatures

pH of the solution	- ΔG_m^0 /KJ mol^{-1} at				ΔH_m^0/	ΔS_m^0/
	303 K	308 K	313 K	318 K	KJ mol^{-1}	J $mol^{-1}K^{-1}$
3	27.99	28.61	29.32	30.10	14.81	141
5	27.76	28.39	29.04	29.83	14.15	138
6.8	33.32	28.16	28.67	29.34	54.27	265
9	27.00	27.62	28.35	29.02	13.91	135

Table 3

Surface excess and area per molecule of polyoxyethylated octyl phenol [C_8H_{17}-$O(CH_2CH_2O)_{10}$-H] in 0.01 M NaCl solution at different pHs and temperatures.

pH of the solution	$\Gamma \times 10^6$ (mol.m^{-2}) at				A_{min}(A^{o2}) at			
	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K
3	1.11	1.09	1.01	0.99	14.9	15.2	16.4	16.8
5	1.18	1.15	1.09	1.03	14.1	14.4	15.2	16.2
6.8^*	1.25	1.18	1.12	1.08	13.3	14.0	14.8	15.4
9	1.31	1.28	1.23	1.17	12.6	13.0	13.5	14.2

* Ref.10

Table 4

Thermodynamic parameters of micellization of polyoxyethylated octyl phenol [C_8H_{17}-$O(CH_2CH_2O)_{10}$-H] in 0.01 M NaCl solution at different pHs and temperatures.

pH of the solution	- ΔG_{ad}^{0} /KJ mol^{-1} at				Δ_{Had}^{0}/	ΔS_{ad}^{0}/
	303 K	308 K	313 K	318 K	KJ mol^{-1}	J mol^{-1}K^{-1}
3	65.10	66.41	70.11	71.72	441	69.41
5	62.67	64.22	67.12	69.83	477	82.70
6.8	66.28	67.55	65.45	67.49	543	42.71
9	58.45	59.81	61.85	64.23	385	60.13

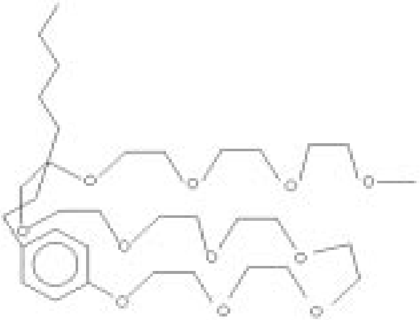

Fig.1 Schematic diagram illustrating arrangement of poly (oxyethylene) units on the water surface

drogen bonding between poly (oxyethylene) unit and the water molecule as shown in Fig. 1. This is also supported from the fluorescence behavior of pyrene in the presence of polyoxyethylated alkyl phenol (Sahoo *et al.* 2002 & Sahoo and Misra, 2001). The effect of temperature on Γat different pH is a complex phenomenon. This is influenced by the interaction of H^+ and OH^- ions with water as well as with the surfactant. The nature of interaction is complicated.

The A_{min} values of polyoxyethylated octyl phenol [C_8H_{17}-$O(CH_2CH_2O)_{30}$-H] at cmc are exhibited in Table 3. The magnitudes of A_{min} are of the order of 1.0´10^2 (A$^{\circ 2}$) or less, indicating that the surface is a close packed one which refers that the orientation of the surfactant molecules is perpendicular to the surface[31]. The value of free energy of adsorption at air-water interface (ΔG^0_{ad}) has been obtained using the expression (Rakshit and Narayan, 1986).

$$\Delta G^0_{ad} = \Delta G^0_{m} - NP_{cmc}A_{min} \qquad \text{--------------------} \ (7)$$

In Table 4, the thermodynamic parameters of adsorption viz. G^0_{ad}, ΔH^0_{ad} and ΔS^0_{ad} of polyoxyethylated octyl phenol at the air-solution interface at various pHs are shown. The standard entropy (ΔS^0_{ad}) and (ΔH^0_{ad}) of adsorption have been calculated from the slope of the reasonably linear ΔG^0_{ad} vs. T plot. The ΔH^0_{ad} has been obtained from the thermodynamic relation (Eq.2). The free energy of micellization, ΔG^0_{m} was less negative than the free energy of adsorption, ΔG^0_{ad} 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.

CONCLUSION

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 (Sulthana *et al.* 1996; Koshy and Rakshit, 1991; Rakshit and Narayan, 1986 and Del Rio *et al.* 1995).The compensation temperature has been found to be 275K, some what different from 292 K obtained for micellization phenomenon, but within the expected range for aqueous systems (270-294 K) (Lumry and Rajendra, 1970).

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