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SURFACE AND THERMODYNAMIC PROPERTIES OF POLYACRYLIC ACID IN PRESENCE OF AQUEOUS TRITON X-100 AT VARIOUS TEMPERATURES

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ABSTRACT

Surface and thermodynamic properties of micellization and adsorption at liquid-air interface for non-ionic surfactant Triton X-100 (TX-100) and Triton-X-100-Polyacrylic acid (PAAc) polymer-surfactant system have been obtained using surface tension data. It has been found that the PSP values are higher than the CMC of pure surfactant (TX-100); the PSP values for polymer-surfactant system increases with increase in polymer concentration as well as the temperature. From the thermodynamic parameter it has been observed that the free energy values indicates spontaneous micelle formation. The enthalpy and entropy of micellization of TX-100 in presence of PAAc is exothermic.

Key words :- Triton-X-100 (TX-100), Polyacrylic acid (PAAc), Surface Tension, P-S System (Polymer-surfactant system), CMC (Critical Micelle Concentration), PSP (Polymer Saturation Point), CAC (Critical Aggregation Concentration).

INTRODUCTION

Surface and thermodynamic studies of aqueous polymer surfactant system provide valuable information regarding the mechanism of interaction between unlike molecules[1-9], Polymer-surfactant interaction has been'studied by various methods[10,11]. All these studies indicates that polymers interact with surfactants by inducing micellization of surfactants on the polymer chain and after getting saturated with micelles, the excess of surfactant form free micelles[12]. The polymer-surfactant interactions consider the effect of polymer molecule on surfactant self assembly through micelle formation. At lower concentration individual surfactant molecule get attached to the polymer segment. The phenomenon of aggregation of surfactant in presence of polymer can be characterized by the critical aggregation developed by Chu & Thomas[13]. Further addition of surfactant leads to polymer saturation point (PSP) or critical micelle concentration (CMC) of the surfactant in presence of the polymer.

In this paper we presents the results of polymer-surfactant system containing polyacrylic acid (PAAc) and non-ionic surfactant Triton X-100 at 303K, 308K, 313K and 318K temperatures. The surface and thermodynamic properties associated with P-S system have been computed.

MATERIALS AND METHODS

The water soluble polymer polyacrylic acid was the product of Sigma, USA (Mol. Wt = 4,000,000). It was dialysed to remove low molecular weight fractions and other associated electrolytic impurities. Non-ionic surfactant, Tritox X-100 was obtained from

Fluka chemie and it was used as received.

Doubly distilled water (specific conductance 2-4x10^{-6}5cm^{-1}) at 303K was used in all preparations. The CMC & PSP of polymer-surfactant system was obtained by surface tension measurement using a du-Nouy tensi-ometer[14] at 303, 308, 313 and 318 K. The concentration of surfactant was varied by adding concentrated stock solution to known volume of polymer solution in the jacketed beaker with the help of a micro-syringe. The temperature of polymer solution was maintained constant by circulating thermdstated water through a jacketed beaker containing the polymer solution.

Thermodynamic parameters associated with micellization are evaluated, at CAC & PSP of the the polyactylic acid-TX-100 system.

Table-1. Critical aggregation concentration (CAC) and Polymer saturation point (PSP) at different temperatures by surface tension measurement

Polymer Concentration	CAC (mm)				PSP (mm)			
% (W/V)	303 K	308 K	313 K	318 K	303 K	308 K	313 K	
0.01	0.100	0.097	0.099	0.096	0.255	0.270	0.280	0.295
0.02	0.098	0.097	0.100	0.099	0.258	0.272	0.282	0.298
0.03	0.100	0.100	0.102	0.104	0.262	0.276	0.284	0.302
0.04	0.102	0.103	0.100	0.105	0.267	0.280	0.290	0.306

RESULTS AND DISCUSSION

Table-1 gives the CAC and PSP values for polymer TX-100 system from the surface tension measurement of different temperatures

From the above surface tension data it is indicated that the PSP values increases with increase in polymer concentration as well as the temperature of the P-S system. This due to availability of more binding sites for the surfactant to interact resulting into higher PSP value[15]. In the present P-S system the PSP values are comparatively higher than CMC of TX-100. Saito *et al.*,[16] reported similar data for polyacrylic acid and non-ionic surfactant. The plot of surface tension against the log of surfactant concentration shows two break points.

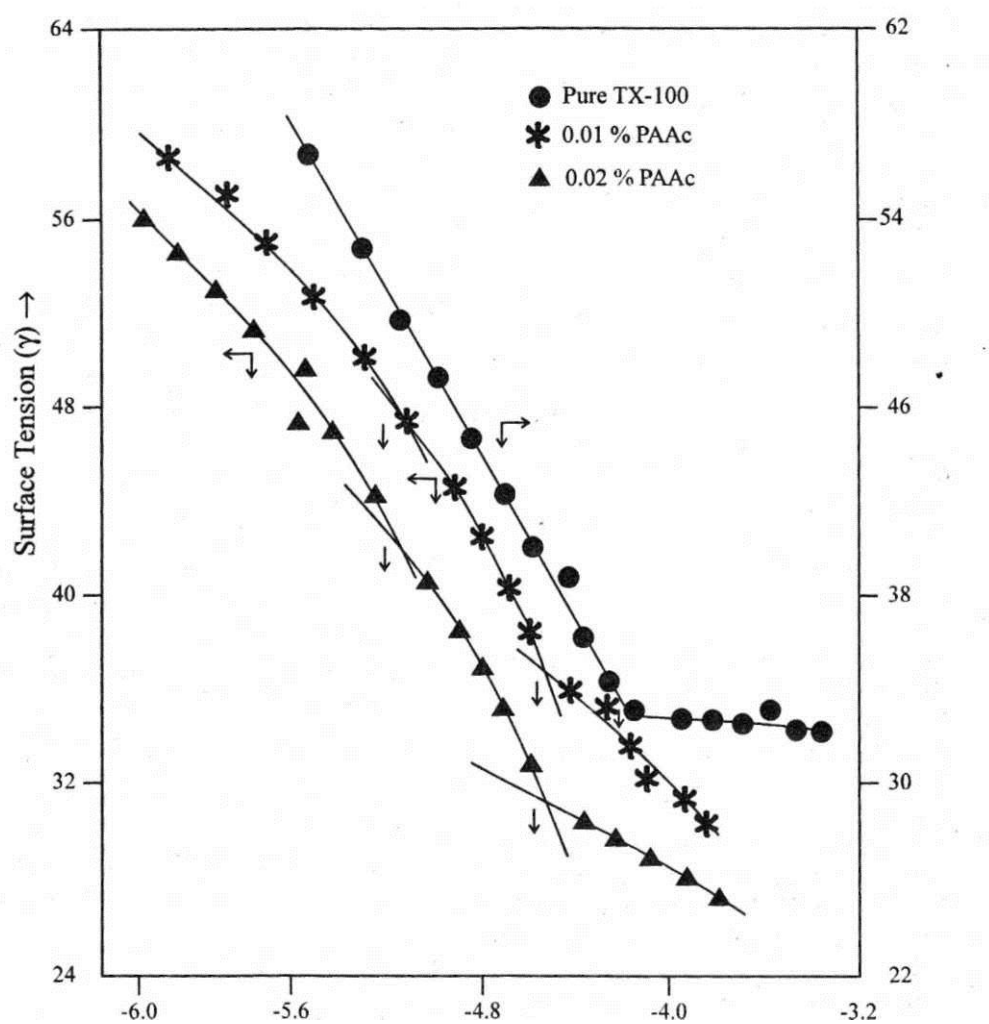
Generally in case of non-ionic surfactants, CMC decreases with increasing temperature[17,18]. This lowering in CMC may be due to the changes in water structure, water-surfactant interaction, dehydration of the oxyethylene moiety of the surfactant molecule.

Thermodyanamic parameters associated with micellization for pure surfactant and at the CAC and PSP of polymer-surfactant system are calculated. The free energy of micellization at PSP, $\Delta G°_{PSP}$ for a non-ionic system is obtained by[18].

$$\Delta G°_{PSP} = RT \ln C_{PSP}$$

Table-2. Standard free energy, entropy and enthalpy at PSP for Polyacrylic acid TX-100 system-

Polymer Concentration	$-\Delta G°_{PSP}$ (KJ mole^{-1})				$\Delta H°_{PSP}$ (KJ mole^{-1})	$\Delta S°_{PSP}$ (KJ mole^{-1} K^{-1})
% (W/V)	303K	308K	313K	318K		
0.01	31.3	31.6	31.8	32.2	7.2	79.2
0.02	31.2	31.5	31.8	32.1	7.6	79.4
0.03	31.0	31.3	31.7	32.2	8.0	80.8
0.04	31.2	31.6	31.9	32.3	8.4	80.5



Surfactant concentration Log C (M)—>

Fig. 1. Plot of Surface Tension-Log C(M) at 313 K

Table-2. gives the free energy, enthalpy and entropy values for PAAc-TX-100 system.

In case of pure TX-100, the free energy values became more negative with increase in temperature, indicating formation of spontaneous micelle. In presence of polymer the $\Delta G°_{PSP}$ values become more negative with increase in temperature. The $\Delta G°_{PSP}$ are always found to be much more negative as compared to $\Delta G°_{M}$ values indicating micelle formation in presence of the polymer is more favourable compared to normal micelle formation.

The enthalpy and entropy of micelle formation in presence of polymers are evaluated by using following relationship

$\Delta G°_{PSP} = \Delta H°_{PSP} - T\Delta S°_{PSP}$ From the data given in table-2 it is indicated that the micellization of TX-100 in presence of PAAc is exothermic.

CONCLUSIONS

By surface tension measurement two criticalconcentrations were obtained. The first break point is known as critical aggregation concentration (CAC) and the second break point is the polymer saturation point (PSP). For this P-S system, the PSP values are higher than the CMC of pure TX-100. The PSP values of the P-S system increases with increasing the temperature and polymer concentration since more number of polymer sites are available for binding.

The free energy values indicates spontaneous micelle formation, the enthalpy and entropy of micellization of TX-100 in presence of PAAC is exothermic. Exothermicity and endoothermicity are specific to the nature of surfactant and additive.

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