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INTERACTION OF PEO-PS-PEO BLOCK COPOLYMERS WITH IONIC SURFACTANTS IN AQUEOUS SOLUTION

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ABSTRACT

The formation of polyelectrolyte type complex by the interaction between ionic (anionic and cationic) surfactant and block copolymer in water was observed from viscosity measurements. Interaction between the two was also examined from conductance and surface tension measurements were two transitions, one below and one above the critical micelle concentration, CMC, of the surfactants were observed. A possible mechanism for such an interaction is proposed.

INTRODUCTION

Complexes formed between polymers and surfactants in aqueous solution have been critically examined in recent years for wide varieties of applications of mixed systems [1-5]. The most common system investigated in the past is polyethylene oxide (PEO) as a nonionic polymer with ionic surfactants which forms association complexes in aqueous media [4-9]. Some of these studies make it obvious that the surfactant adsorbs onto the polymer and the resultant complex exhibits polyelectrolytic behavior. Interaction between block copolymer and ionic surfactants have also been reported and some studies involve systems in which both polymer and surfactant are capable of associating individually [10-13]. Hydrophobic-hydrophilic block copolymers have been known to form micellar aggregates in aqueous solutions and, therefore, it is interesting to study the interaction of micelle forming block copolymers with ionic surfactants. Bahadur *et al.* [13-15] have discussed colloidal and aggregation behavior of hydrophobic-hydrophilic block copolymer and their interaction with ionic surfactants. This paper is a part of our studies on three triblock copolymers of the type poly(ethylene oxide)-polystyrene-poly(ethylene oxide), (PEO-PS-PEO), with two ionic surfactants (sodium dodecyl benzene sulfonate, $NaC_{12}BS$, anionic and hexadecyl pyridinium bromide, $C_{16}PyBr$, cationic). The formation of a polyelectrolyte type complex by the interaction between ionic (anionic and cationic) surfactant and block copolymer in water was observed from viscosity measurements. Conductivity and surface tension measurements have been used to study the interaction between block copolymers and ionic surfactants, where two breaks in the curves can be detected: the first one at $C_{surf.} = C_1 < CMC$ and second one at $C_{surf.} = C_2 > CMC$. Viscosity behavior of a comparison of the relative strengths of binding of anionic and cationic surfactants to copolymer were observed. A possible mechanism for such an interaction is proposed.

EXPERIMENTAL

Materials

The cationic surfactant hexadecyl pyridinium bromide ($C_{16}PyBr$) was a product of Sigma Chemical Co. (U.S.A.) and anionic surfactant sodium dodecylbenzene sulphonate ($NaC_{12}BS$) was supplied by Dr. A. K. Goswami, Mathura, as a pure chemical. Both these surfactants were recrystallized several times until no minimum in the surface tension-concentration plots was observed and their critical micelle concentration, CMC, agreed with literature values [16].

Three triblock copolymers of the type poly(ethylene oxide)-polystyrene-poly(ethylene oxide), PEO-PS-PEO, used were supplied by Professor G. Riess. These were synthesised on a laboratory scale by an anionic polymerization method [17] and had the characteristics shown in Table 1.

The water used was always triple distilled (the final distillation was carried out in an all pyrex glass - fit assembly); the conductivity of water used was always less than 0.5×10^{-6} ohm^{-1} cm^{-1}.

TABLE 1. Molecular Characteristics of Peo-Ps-Peo Block Copolymer

Block copolymer	**Mn total**	**% PS**	**Mn PS**
Cop. 49	8600	21.0	1800
Cop. 45	8800	18.4	1600
Cop. 51	19800	9.1	1800

Methods

The conductance of solutions was measured using a digital conductivity meter (Toshniwal, India) and dipping type conductivity cell with platinized electrodes. The reproducibility of conductance data was checked by repeating the measurements several times.

A modified drop volume technique was used for all measurements of surface tension using an 'Agla' micrometer syringe (Burroughs Wellcome, England), which can deliver liquids accurate up to + 0.0002 ml in volume. The average drop time was three minutes. The average volume of not less than six drops was used in conjuction with the correction due to Harkins and Brown [18] to calculate surface tension value. The results are good to slightly better than ±0.5%.

Viscosity measurements were made using an Ubbelohde suspended level viscometer. Solvent flow times in the range 120-360 s were obtained, thus no kinetic correction was necessary. When at least three consecutive flow times agreeing within ±0.2 s were recorded, the average flow time was taken. Shear corrections were not taken because the intrinsic viscosities obtained were less than 3 dlg^{-1}. The flow volume of the viscometer used was greater than 5 ml making drainage errors unimportant.

In studies involving polymer-surfactant interactions the solutions were kept overnight at a temperature of 30°C to ensure complete interaction.

RESULTS AND DISCUSSION

Surface tension and conductivity measurements have been used extensively to study the interactions between block polymer and ionic surfactant.

In aqueous surfactant solutions, the micellization is revealed by a break in the plot of specific conductance (or surface tension) as a function of surfactant concentration. Insets in Figures 1 and 2 report representative plots for $C_{16}PyBr$ by the two techniques which reveal CMC value as 0.7 mM at 30°C which agree well

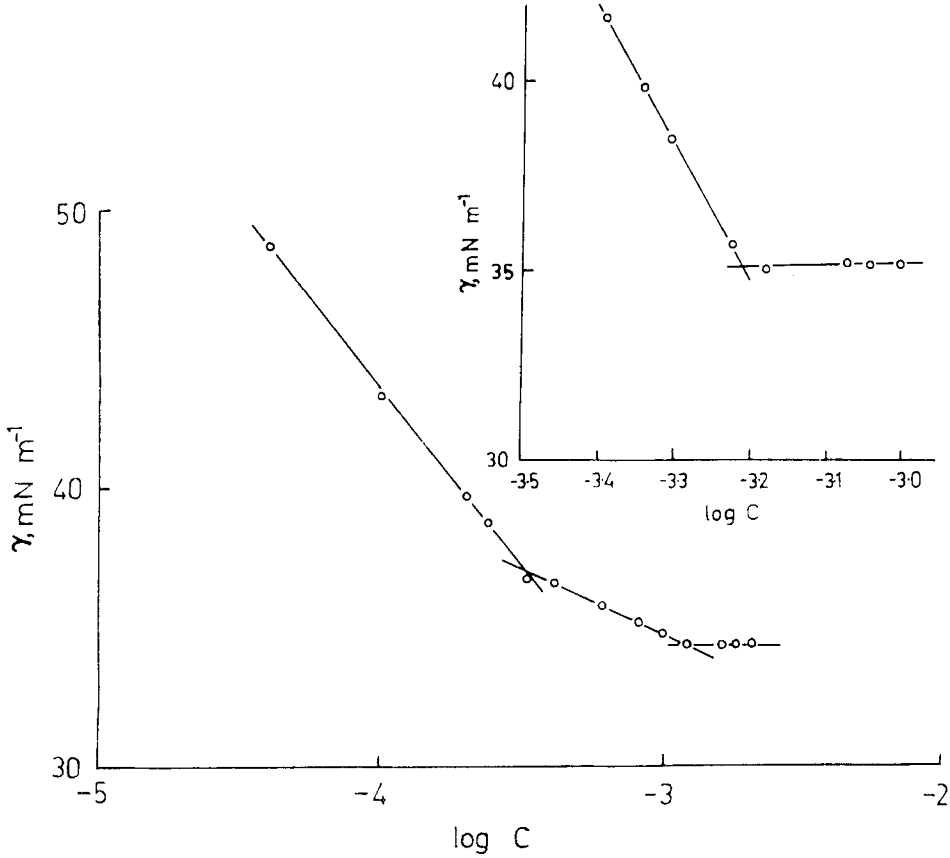

Figure 1. Surface tension behavior of aqueous cetylpyridinium bromide solution in presence of block copolymer PEO-PS-PEO ($\overline{Mn}$ = 8800, %PS = 18.4) at 30°C (in the inset is shown the plot in the absence of block copolymer).

with the literature values [16]. Similarly, for $NaC_{12}BS$ the CMC was around 0.75 mM which is close to that of $C_{16}PyBr$. Thus, these two different types of surfactants provide a good choice to compare the interaction of polymers with anionic and cationic type surfactants.

Interaction between three PEO-PS-PEO block copolymers (with varying molecular characteristics) and $C_{16}PyBr$ (or $NaC_{12}BS$) was examined by conductance, surface tension and viscosity results. The typical plots of surface tension results (Figure 1) and conductance results (Figure 2) were used to obtain interaction parameters as detailed below which are recorded in Table 2.

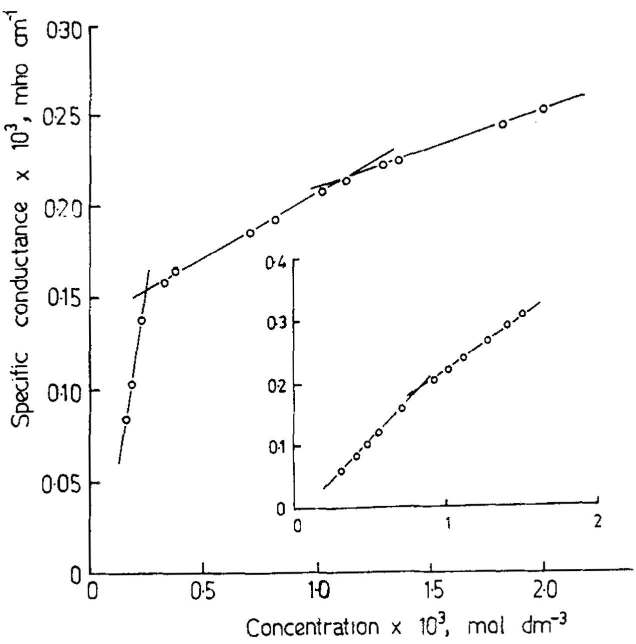

Figure 2. Conductance behavior of aqueous cetylpyridinium bromide solution in presence of (0.3 gdl^{-1}) block copolymer PEO-PS-PEO ($\overline{Mn}$ = 8600, %PS = 21.0) at 30°C (in the inset is shown the plot in the absence of block copolymer).

In the presence of interacting polymers, two breaks in the surface tension (and conductivity) versus concentration plots are often detected: the first one, at $C_{surf.} = C_1 < CMC$, is the critical aggregation concentration (CAC), generally considered the onset of the binding of surfactant onto the copolymer [19]; the second one, at $C_{surf.} = C_2 > CMC$, is assumed [20] to correspond to the polymer saturation concentration (PSP) by surfactant.

In the PEO-PS-PEO + $C_{16}PyBr$ system, when the solution of copolymer contains sufficiently low concentration of $C_{16}PyBr$ such that a critical level is not exceeded (i.e. below CAC), most of the surfactant molecules apparently exist freely in the solution. When the $C_{16}PyBr$ concentration exceeds the CAC, complex formation occurs over a broad surfactant concentration range in which a substantial amount of surfactant is bound in the form of aggregates to the copolymer chain, although a part of surfactant will still be present in the free form. In the presence of the copolymer, the CAC values are substantially lower than the CMC of pure

TABLE 2. Interaction Data for Peo-Ps-Peo Block Copolymer (0.3 Gdl^{-1}) With Ionic Surfactant At 30°C

Copolymer	**Surfactant/ Method**	**First Critical Concentration (or CAC) C_1 mmol dm^{-3}**	**Critical Micelle Concentration CMC mmol dm^{-3}**	**Second Critical Concentration (or PSP) C_2 mmol dm^{-3}**
	C_{16}PyBr			
Cop. 49	Conductance	0.24	0.70	1.13
	Surface-tension	0.26	0.70	1.06
	C_{16}PyBr			
Cop. 45	Conductance	0.50	0.70	1.42
	Surface-tension	0.42	0.70	1.20
	$NaC_{12}BS$			
Cop. 45	Conductance	0.48	0.75	1.75
	Surface-tension	0.46	0.73	1.80
	$NaC_{12}BS$			
Cop. 51	Conductance	0.62	0.75	1.00
	Surface-tension	0.63	0.73	0.96

C_{16}PyBr solution. Above the concentration, at which the copolymer has become saturated with surfactant micelles (i.e. above PSP), the concentration of free micelles increases in the bulk solution. The critical concentration points obtained by both the methods were almost same. Furthermore, an interesting feature is that the extent of interaction mainly depended upon the molecular weight of polystyrene block in the PEO-PS-PEO block copolymer; that is, with increasing hydrophobicity, the adsorption of the surfactant aggregates on to the copolymer is increased. Very weak or no detectable interaction between cationic surfactants and nonionic polymers like PEO, PVP and PVA homopolymer has been observed [21]. Clear interaction, however, observed between C_{16}PyBr and PEO-PS-PEO interaction appears to be influenced by the hydrophobic PS moiety.

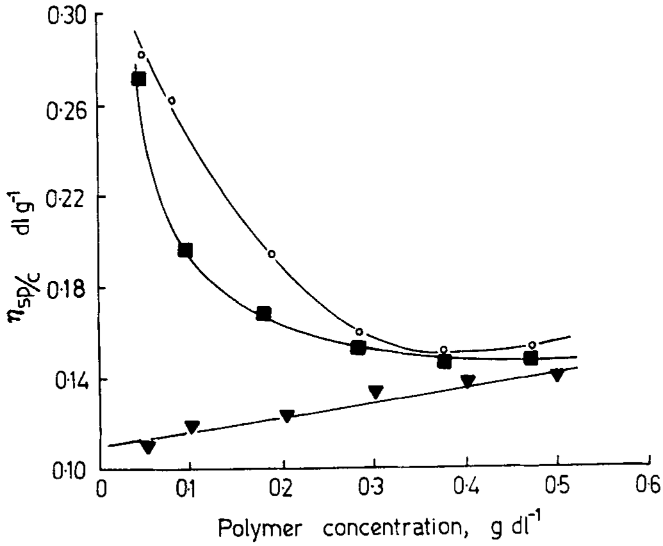

Figure 3. Reduced viscosity versus block copolymer PEO-PS-PEO ($\overline{Mn}$ = 8800, %PS = 18.4) concentration plot with and without surfactant (1 mmol dm^{-3}) at 30°C.

▼ No surfactant, ● NaC$_{12}$BS, O C$_{16}$PyBr

Some comparisons were made to ascertain the formation of the polymer-surfactant complex under different conditions. Data on Cop. 45 (and Cop. 49) with C$_{16}$PyBr show stronger interaction of the surfactant with Cop. 49 as is shown by lower CAC value. Similarly, for Cop. 45 (and Cop. 51) and NaC$_{12}$BS, the interaction was stronger with Cop. 45. These results clearly demonstrate that higher percentage of the hydrophobic PS block enhances the interaction.

The viscosity of solutions containing surfactant-copolymer complexes yields valuable information about the nature of the complex. Viscosity measurements are carried out for the copolymer in aqueous surfactant solutions. Figure 3 shows curves obtained by plotting specific viscosity divided by concentration of copolymer (i.e. reduced viscosity); as a function of copolymer concentration. This is the conventional way of representing viscosity behavior during complex formation. In the absence of surfactant the viscosity of the copolymer solution decreased linearly with the copolymer concentration and it was possible to determine the intrinsic viscosity. But, the viscosity behavior of the copolymer in presence of 1 mmol dm^{-3} surfactant concentration (around CMC) showed an upswing which is

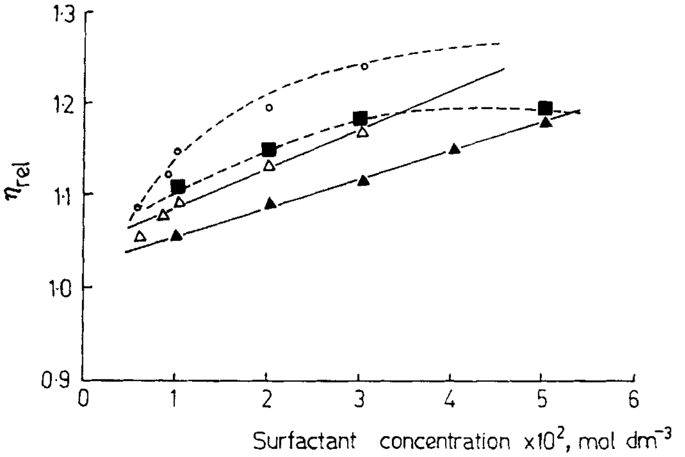

Figure 4. Relative viscosity versus surfactant concentration plot with and without PEO-PS-PEO (0.3 gdl^{-1}) block copolymer ($\overline{Mn}$ = 8800, %PS = 18.4) at 30 °C.

▲, ■ NaC$_{12}$BS; Δ,O C$_{16}$PyBr; —— , in the absence of polymer and ---- in the presence of polymer.

clearly a manifestation of the polyelectrolyte effect. In such cases, it is difficult to extrapolate the reduced viscosity to zero concentration for precise determination of intrinsic viscosity.

A comparison of the relative strengths of binding of anionic and cationic surfactant to copolymer is difficult to make and not very meaningful but some estimate can be attempted. The polyelectrolyte complex type behavior of viscosity of copolymer solution in the presence of anionic and cationic surfactants is shown in Figure 3. The curves for copolymer-anionic surfactant are much steeper than similar curves for copolymer-cationic-surfactant solution (Figure 3), indicating stronger interaction of anionic surfactant with copolymer than that of cationic surfactant. The data recorded in Table 2, also demonstrate the strong interaction between copolymer-anionic surfactant than that of cationic surfactant. The reason for this is quite complex but can be found by considering the volume change on micellization of cationic and anionic surfactant [22]. The change in solution volume for the micellization of cationic surfactant is less than that for an anionic surfactant of comparable chain length. Hence, the hydrophobic interaction for copolymer-cationic surfactant may be less than that for copolymer-anionic surfactant.

The relative viscosity is used rather than the more usual reduced viscosity ($\eta_{sp/C}$) since the concentration of the complex is unknown. Relative viscosities were determined at a fixed copolymer concentration of 0.3 gdl^{-1} as a function of surfactant concentration. The data shown in Figure 4 demonstrates a maximum value of relative viscosity and this is attributed to the association of surfactant molecules with poly(ethylene oxide) (PEO) chains in the block copolymer, and as a result the PEO segments are expanded. Above the concentration at which the PEO has become saturated with surfactant micelles, the concentration of free micelles increases as well as that of singly dispersed molecules in the bulk solution. The ionic strength is increased and as expected for a polyelectrolyte, the relative viscosity (η_{rel}) values are reduced. Nagarajan [12] reported such type of viscosity behavior for polymer-surfactant complexes.

Various topologies [12, 23] have been proposed for polymer-surfactant complexes. The nature of forces responsible for complex formation depends on the type of both, polymer and surfactant. Based on the results obtained, two possible explanations have been proposed for the copolymer-surfactant interaction. Styrene-ethylene oxide block copolymers form polymolecular micelles in water with a swollen core of polystyrene block surrounded by flexible fringes of soluble poly(ethylene oxide) chains. From the dependence of extent of interaction on concentration and nature of copolymer, it is thought that hydrophobic block of copolymer and hydrophobic moiety of surfactants are responsible for the formation of a "polyelectrolyte type complex" as shown in viscosity measurements. The other mode of interaction between copolymer and surfactant is the formation of mixed micelles by a phenomenon similar to solubilization, where the flexible poly(ethylene oxide) chains of the block copolymer micelle wrap around the surfactant micelles.

CONCLUSION

The two breaks in surface tension (or conductivity) versus surfactant concentration plots clearly revealed the interaction between PEO-PS-PEO block copolymers and ionic surfactants ($C_{16}PyBr$ and $NaC_{12}BS$) in water. Such an interaction is dominated by hydrophobic interaction and thus depends upon the molecular characteristics of copolymers and surfactants. The polyelectrolyte like behavior as observed from viscosity results further confirms the interaction between the copolymer and surfactants.

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