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A study of the effect of biopolymer on the aggregation behaviour of cationic surfactants in aqueous medium

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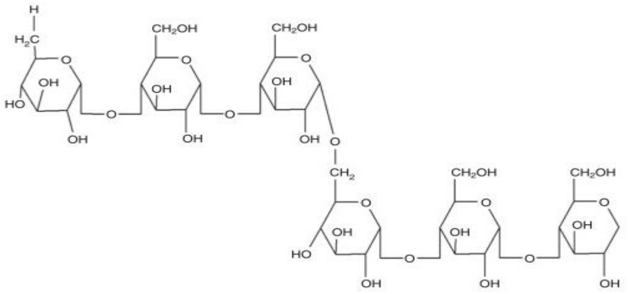
Abstract

The interaction of biopolymer pullulan with different surfactants have been studied in aqueous medium by tensiometry, conductometry and spectrophotometry at 298 K. Here conventional surfactants are used for the investigation of polymer-surfactant system. Using these physicochemical techniques, a surface parameter, CMC (a certain concentration at which and above micelles are formed) of the surfactants is determined in presence of polymer. From conductometric plot counter ion binding (β) has been calculated. Micropolarity index is also determined from fluorescence spectra. Dual influence of hydrophobic and electrostatic interactions plays important role in this system. This system provides a insight towards solubilization of protein, drug etc. in associative atmosphere of surfactants.

Keywords: Biopolymer, surfactant, CMC, counter ion binding, micropolarity index.

1. Introduction

Surfactant is one of the most important chemical entities possessing the special property of micelle formation through molecular aggregation in both aqueous and non-aqueous solvents at a definite concentration known as cmc or critical micelle concentration [1,2]. They have both hydrophobic and hydrophilic part and thus can reduce air-liquid interfacial tension. Now-a-days they are extensively used in soap, cosmetics, paper making, gene transfection, drug delivery, pharmaceuticals, oil recovery, vesicle formation etc. [3-6]. Recently Polymer- surfactant interactions have been drawn a great deal of attention as a composite due to wide range of applications in many fields like industrial, pharmaceutical, medicinal, laundry and cosmetics [7-9]. Complex formation between polymer and charged surfactants has been a field of interest in recent colloid chemistry [10,11]. The hydrophobic interaction between lipophilic domain of polymer and hydrophobic tail part of surfactant plays the major role in such areas. Cellulose is most abundant biopolymer found in nature. It is a polysaccharide (H: O = 2: 1) which is made of a linear chain of several hundred to many thousands of β (1→4) linked D-glucose monomeric unit. Carbohydrate -based polymers receive special attraction due to their biodegradable, biocpmpatible and low immunogenic nature [12]. Pullulan is a water soluble, neutral linear polysaccharide consisting of α-1,4 and α-1,6 glycosidic linkages [13]. This is found as an intermediate between the amylose and dextran structure. The unique structure of pullulan (Scheme 1) is responsible for its high solubility in water and flexibility, as a result of the low degree of H-bonding in its crystal form. It is produced from starch by the fungus Aureobasidium pullulans. With upto 35% ethanol in water it is used as hair fixative agents with enhanced drying times. As the reports of interaction of pullulan in presence of surfactant are limited in literature, an effort has been made to study the interaction between pullulan with cationic amphiphile, cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium p-toluenesulfonate (CTAT) in aqueous medium using tensiometry, conductometry and spectrometry in this presentation.



Scheme 1. Structure of pullulan

2. Materials and Methods

2.1. Materials: Pullulan was AR grade product and obtained from Sigma Aldrich (USA). CTAB (99%) and CTAT (99%) were purchased from SRL, Mumbai, India and used without purification. Double distilled deionized water was used during the whole experiment.

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2.2. Methods

Tensiometry: A calibrated du Noüy tensiometer (Krüss, Germany) was employed with the platinum ring detachment method for surface tension measurement at 298 K. Stock surfactant solution was prepared ~ 15 times above the CMC [14]. Using a Hamilton micro syringe, a concentrated stock solution of surfactants in an aqueous media was added to water gradually. Each measurement was preceded by a 5-minute equilibration period. To ensure accuracy, each measurement was carried out three times. The method's accuracy was 0.1 mN.m^{-1}. The detailed process was carried out as per literature [15-17]. Surface tension (γ) vs. log[surfactant] was plotted to determine the CMC, and from the breaks in the plot, the CMC was calculated [18].

Conductometry: An Eütech (Singapore) was used to measure electrical conductivity (cell constant is 1 cm^{-1}). The temperature of the solution was kept constant at 298 K using a water bath with precision of a ± 0.1 K. Using a Hamilton micro syringe, stock solution prepared in the specific solvent (about ~15 times the CMC) was progressively added to a container containing 6 mL of the solvent. After each addition, followed by homogeneous mixing, the value of the specific conductance (κ) was recorded. Each measurement was carried out three times, and the average result was recorded with an error of 2 s. The CMC values were calculated like early works [19-20] from the breakpoints in the specific conductance (κ) vs. surfactant concentration graphs.

Fluorimetry: Steady state fluorescence study was done by Perkin Elmer LS 55 fluorescence spectrophotometer attached with a Peltier facility keeping temperature constant at 298 K . An amount of 2.5 mL solution of (0.1g and 0.05g) % Pullulan was taken in transparent quartz cuvette and surfactant (concn ~15 times above CMC in aqueous medium) was added gradually by the Hamilton micro syringe. Pyrene used as a probe was excited at 335 nm and its emission was recorded in the wavelength range of 350 – 550 nm with an emission band pass of 4 nm. Anisotropic measurement for emission was monitored at 374 nm and 384 nm which corresponds to the first and third vibrational peaks of pyrene, respectively. The excitation and emission slits were 15 and 2.5 nm respectively. The probe concentration was kept small (1μL) to avoid eximer formation. The ratio of first (I$_1$) to third (I$_3$) vibrational peak vs.[surfactant] in the absence and presence of surfactant is presented in Fig. 3.

3. Results and discussion

3.1. Surface tension measurement

Observable change in surface tension value depends upon the balance of surface-active species at the interface and in the bulk. A sharp break in the surface tension (γ) vs. log [surfactant] plot is obtained from tensiometric measurement indicates the term critical micelle concentration (CMC). The value of CMC in tensiometry is the minimum concentration of surface-active agent required to saturate the air/solution interface. Both the systems showed a noticeable decrease in surface tension value at very low concentration of the surfactants indicating the polymer-surfactant interaction (Fig. 1). Those values are tabulated in the following Table 1. In the pullulan-surfactant system, the values of CMC increase with increasing the polymer concentration due to the very strong electrostatic as well as hydrophobic interaction between neutral polymer (pullulan) with the cationic surfactant than that of pure surfactant in water. This complex is solubilized or partially solubilized in the micellar media and a new prominent break appears that denotes as CMC after which only free surfactants micelle is formed. Such types of noticeable change in CMC values in case of pullulan-surfactant system are very rare in literature. CTAT shows a lower CMC value (0.381) than CTAB (1.032 mM). So CTAT has stronger binding sites than CTAB. With increasing the

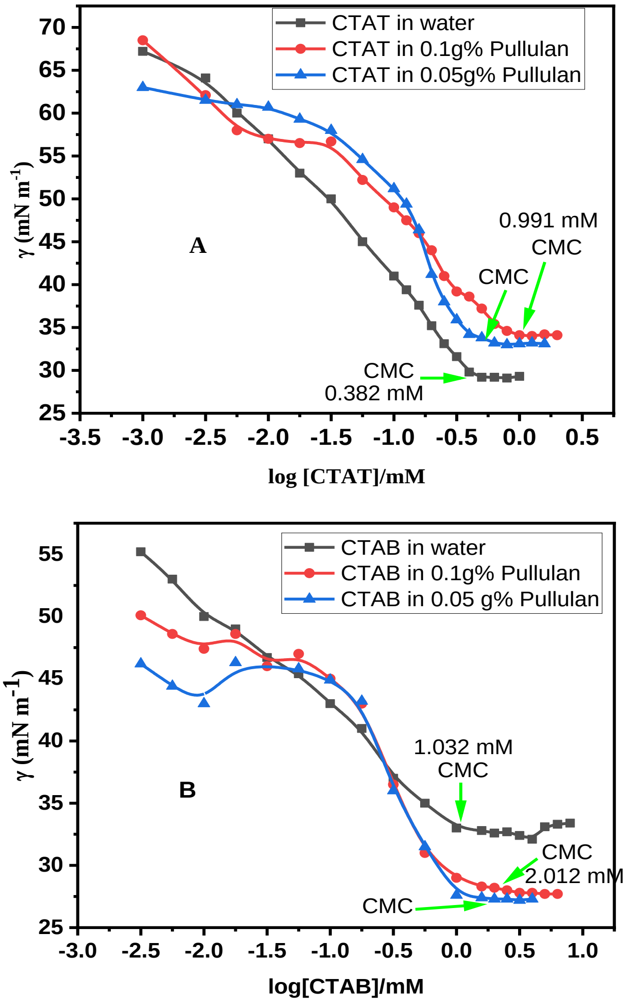

Fig. 1. Tensiometric profile of (A) CTAT and Pullulan and (B) CTAB and Pullulan in aqueous medium

concentration of pullulan (0.05g% to 0.10 g%) CMC values are increased in both surfactants supporting strong interaction which is stated earlier. Various surface parameters (Γ_{max}, A_{min}, Π etc) of surfactant s-polymer interaction could be calculated from tensiometry measurement.

3.2. Conductometry

The values of conductivity have been obtained as a function of surfactant concentration upon the addition of different concentrations of pullulan polymer in the aqueous solutions at the temperature of 298 K. The k values are quite helpful for describing the micelle assisted association system [21-22]. All the electrical conductance versus concentration profiles are shown in Fig. 2. There are two linear regimes present in each conductivity plot with different slopes. The slope of premicellar region is greater than post micellar region. The slope ratio of post to pre-micellar region provides the information about degree of dissociation (β) of counter-ions from the micellar surface. The meeting point of these two straight lines represents the CMC at which micellar aggregation occurs with counter ion association [23-26]. The motion of counter ion is restricted by the redissolution process and conductance increases more slowly in the second region (CMC). The measured values of CMC have been provided in the Table 1 and it was matched well with the values obtained from tensiometry.

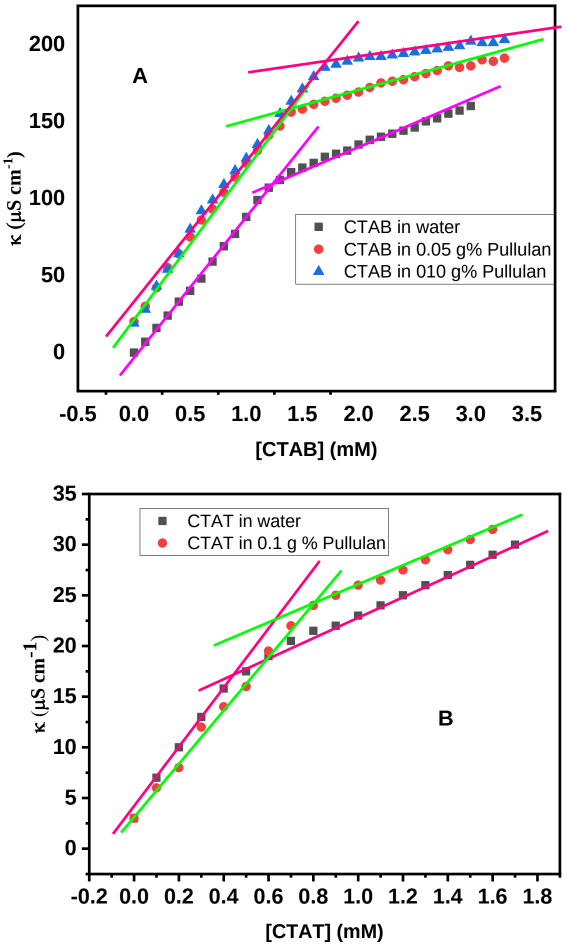

Fig. 2. Conductometry results of interaction between (A) Pullulan with CTAB and (B) Pullulan with CTAT in aqueous medium

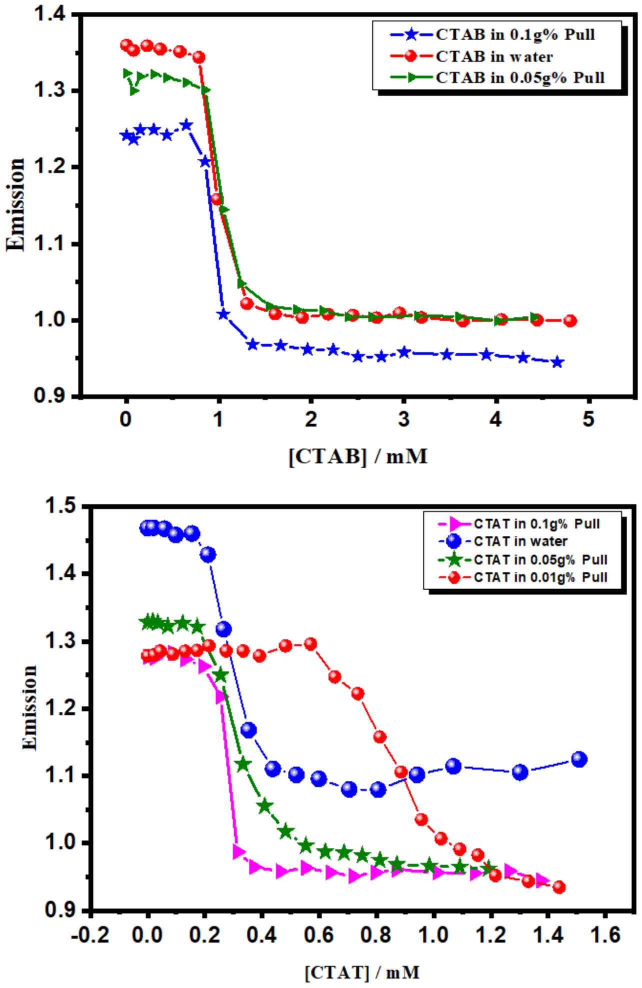

Fig.3. Fluorimetric profile of interaction of Pullulan with CTAT and CTAB in aqueous medium

Various thermodynamic parameters for micellization such as standard Gibb's free energy change (ΔG^0_{micell}), standard entropy change (ΔS^0_{micell}) and standard enthalpy change (ΔH^0_{micell}) could be determined from conductivity measurement.

From the table, it is seen that in the presence of polymer, the counter ion dissociation of surfactants increases this is due to interaction between polymer and charged surfactant a result counter ion of the surfactant becomes loss and β increase. On the other hand, this is may be due to electrostatic interaction between oppositely charged polymer (instantaneously developed charge) and surfactant molecules the complex formation favoured rather than micelle formation among the surfactant.

3.3. Spectrometry

Pyrene, already well established in literatures as a spectroscopic probe [27, 28] is employed in this study to detect the micellization. The emission spectra of the pyrene shows a marked dependence on medium polarity in its vibrational fine structure. The ratio, of the first (I_1) to third (I_3) vibronic peaks of pyrene, or 'micropolarity index' [29] is an important parameter that provides the details of the change in microstructural properties during the assembly of micelles and is therefore used for qualitative measurement of micropolarity experienced by the probe molecules surrounding it. decreases with increase in the hydrophobicity of immediate environment of pyrene. The micropolarity index (I_1/I_3) having values greater and less than unity accounts for the polar and non-polar environments respectively surrounding pyrene molecules [30]. In polymer- surfactant system, the early plateau region in the sigmoidal type plot at very low [surfactant] is an indication of nearly constant value of (I_1/I_3) pointing non-micellization of surfactant (Fig. 3). The ongoing saturation of surfactant micelles on polymeric chain gives rise to further constant nature of micropolarity CMC at higher amphiphile concentration. After CMC no change of polarity is observed by further addition of surfactant. The sharp decrease of I_1/I_3 provides strong proof of polymer-surfactant association. These type of interaction in case of conventional surfactants was presented in the literature [31, 26].

Table 1: Evaluation of different critical concentrations (mM) of surfactant in aqueous solution using Tensiometry and Conductometry at 298 K.

Conc of pullulan (g%)	Tensiometry CMC		Conductometry CMC		β (degree of counter ion dissociation)	
	CTAT	CTAB	CTAT	CTAB	CTAT	CTAB
Pure	0.382	1.032	0.426	1.181	0.302	0.312
0.05	0.548	1.608	-	1.462	-	0.304
0.10	0.991	2.012	0.845	1.510	0.380	0.402

4. Conclusion

The interaction of conventional surfactant with polymer shows that pullulan strongly interact with two surfactants. CTAT undergoes better association with pullulan than CTAB. Binding of the small aggregates maximizes at CMC with formation of free micelles. Therefore, this type of interaction provides a new dimension to the modern field of colloid chemistry with potential application.

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