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Studies on the interaction between polymer and surfactant in aqueous solutions

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The interaction between cationic cetyltrimethylammonium bromide (CTAB) and anionic sodium dodecyl sulphate (SDS) surfactants with polyethylene oxide (PEO) has been investigated using different techniques such as tensiometry, rheology and scanning electron microscopy (SEM). The driving force responsible for the interaction is supposed to be the minimization of interfacial force between the non-polar polymer parts and the solvent water by association. It is observed that the critical micelle concentration (cmc) increases with the increase in temperature and the cmc of CTAB is smaller as compared to SDS. Viscosity increases with the increase in polymer concentration and is higher in case of anionics. Dense micellar arrangement is seen for cationics. The result shows that the interaction of cationic surfactant is much higher than the anionic surfactant with PEO.

Keywords: Critical micelle concentration, Scanning Electron Microscopy, Polyethylene oxide

In recent years, investigations on the interaction between polymer and surfactant in solutions continues to draw the attention of many researchers because of their widespread (biological, pharmaceutical and many others) applications and play a significant role in the field of technological application and fundamental research. They influence solution and interfacial properties and are controlled by the state of their occurrence in aqueous solution. The interaction of water-soluble polymer and ionic surfactants in aqueous solutions are of great interest from the fundamental standpoint as special structure and dynamics of polymer–surfactant association can be used in the process of enhanced oil recovery[1-4].

The ability of surfactants to aggregate and form micelles adds the particular dimensions to their interaction with water soluble polymer. Surfactants are surface active agents that have the tendency to adsorb at the interfaces in the form of monolayer and to lower the free energy of the phase boundary; also these are used for emulsifying and solublizing the immiscible substances. Polymers are usually employed to control the rheology of solutions and suspensions, and when present together with the surfactant synergistic interaction between polymer and surfactants occur. Addition of polymers to micellar solution may modify micellar properties of the surfactants. Micellar solutions often act as emulsifiers and provide surface tension control. Stabilization of micelles upon binding to polymer results from the reduction of interfacial tension between hydrophobic core and water while their polymer additives modify rheological behavior and enhance micellar stability, and are superior in properties like binding, thickening and stabilizing agents[5-7]. The earlier investigations were mostly concerned with the experimental observations based on different techniques and analysis. Ansari *et al.*[8] studied the polymer-surfactant interactions and effect of tail size variation on micellisation process of cationic surfactant in aqueous medium. They used surface tension measurement and conductivity measurement to study the interaction between appositively charged surfactant-polymer systems. Few investigators studied the polymer surfactant interaction by using other techniques. Sardar *et al.*[9] investigated the polymer-surfactant interaction by using conventional/ gemini cationic surfactants. Ali *et al.*[10] used different techniques for studying the polymer- surfactant interaction. Mahajan and Nandini[11] studied the micellization and phase behavior of binary mixtures of anionic and non ionic surfactants in aqueous media by surface tension, fluorescence spectroscopy and cloud point measurement. Zhang and Lam[12] investigated the study of mixed micelles and interaction parameters for nonionic polymers with normal surfactants and used binary mixtures of nonionic surfactant and cationic surfactant by surface tension method and found weak influence on surface tension that decreases with increasing concentration at low polymeric surfactant concentration. Naorem and Devi[13] studied the conductometric and surface tension studies on the micellization of some cationic surfactants in water-organic mixed media. Zeno *et al.*[14] investigated interactions between polyethylene oxide and fatty acids sodium salts by surface tension measurements. They found that the interaction is dependent on fatty acid solubility and increase in the solubility of fatty acid seems to lead a less pronounced interaction while, in contrast, increase in the polymer chain length enhance the phenomenon, hence it is used to maintain good retention. Dupas *et al.*[15] studied mechanical degradation of polyethylene oxide used as a hydrosoluble model polymer for Enhanced Oil Recovery and investigated the onset of mechanical degradation in both laminar and turbulent flows and for both dilute and semi dilute polyethylene oxide aqueous solutions. Mirgorodskaya *et al.*[16] studied the gemini surfactant-nonionic polymer mixed micellar system and employed tensiometry, dynamic light scattering, and optical spectrophotometry to characterize the aggregation behavior of a gemini (dicationic) surfactant in aqueous solutions in the presence of poly(ethylene glycol).

The interaction of cationic surfactants with water soluble polymers has been studied by a number of researchers using different techniques. Comparison of the surfactants having different charge and head group in the presence of water soluble polymer possessing high molecular weight has not been done earlier. Therefore, in the present work micellisation of surfactants having cationic head group CTAB and anionic SDS with aqueous solution of PEO has been studied using tensiometry, rheology and SEM analysis.

Experimental Section

Polyethylene oxide, PEO (molecular weight 100,000, Alfa Aessar), cetyltrimethylammonium bromide, CTAB (≥99.0%, Sigma) and sodium dodecyl sulphate, SDS (≥99.0%, Sigma), were used as received. Demineralized double distilled water was used for the surface tension and other measurements.

Surface tension measurements

Surface tension (γ) of the aqueous surfactant solution was measured by a Hardson tensiometer (Hardson & Co., Kolkata) at room temperature using a platinum ring. The tensiometer was calibrated against water. In an experimental run, γ at each mole fraction was measured by successive addition of concentrated solution of the mixture in pure water at room temperature and the surface tension was measured after proper and thorough mixing and equilibration. In order to determine the values of critical micelle concentration (cmc), two concentrations – characterized by the linear decrease of surface tension and the second one to the region of concentration with nearly constant surface tension were used. The cmc values were obtained from the break point of the surface tension versus log [surfactant] curves. The accuracy on the individual surface tension reading is approximately 0.5 mNm^{-1}.

Rheology

Viscosity measurements in the shear rate range from 0-100 s^{-1} were done with a controlled stress rheometer, Physica MCR 102 rheometer (Anton Paar, Graz, Austria) used gap width 0-5 mm. The obtained viscosity was plotted as function of surfactant concentration.

SEM

A drop of each sample was spin-coated on an aluminium stub and frozen with liquid nitrogen. Afterwards, the samples were dried and sputter-coated with gold in vacuum by a BAL-TEC-SCD 005 instrument (180 s/30 mA/50 mm distance) (BAL-TEC AG, Principality of Liechtenstein). Scanning electron microscopy (SEM) images were taken with the Jeol JSM 65100LV scanning electron microscope (Japan) with a 25-kV acceleration voltage.

Results and Discussion

Tensiometry

The surface tension was measured for CTAB and SDS solutions in presence and absence of different weight percentages of PEO at 298.15 K-318.15 K. Surface tension versus surfactant concentration plots in the presence of polymer shows two distinct zones as shown in Fig. 1. For surfactants in the presence of equal solutions of PEO, surface tension decreases as a function of log [surfactant] and the first plateau of slope is indicative of surfactant binding of polymer and is referred as critical aggregation concentration (cac). At the second critical concentration surface tension becomes almost constant, since at this point free surfactant micelles start to form in solution. This concentration is known as critical micellization concentration (cmc). From the figures, it is observed that with the increase in temperature there is less or no effect on cac but cmc increases in all the cases as we increase the surfactant or polymer concentration. Generally, the effect of temperature on the cmc of surfactants in aqueous solution is complex. On one hand, the temperature increase causes decreased hydration of the hydrophilic group which favours micellization. But on the other hand temperature increase also causes disruption of the structured water surrounding hydrophobic group which disfavours micellization. Thus, the relative magnitude of these two opposing effects determines whether the cmc value increases or decreases over a particular temperature range[8]. In the present investigation the cmc values increase with the increase in temperature indicating

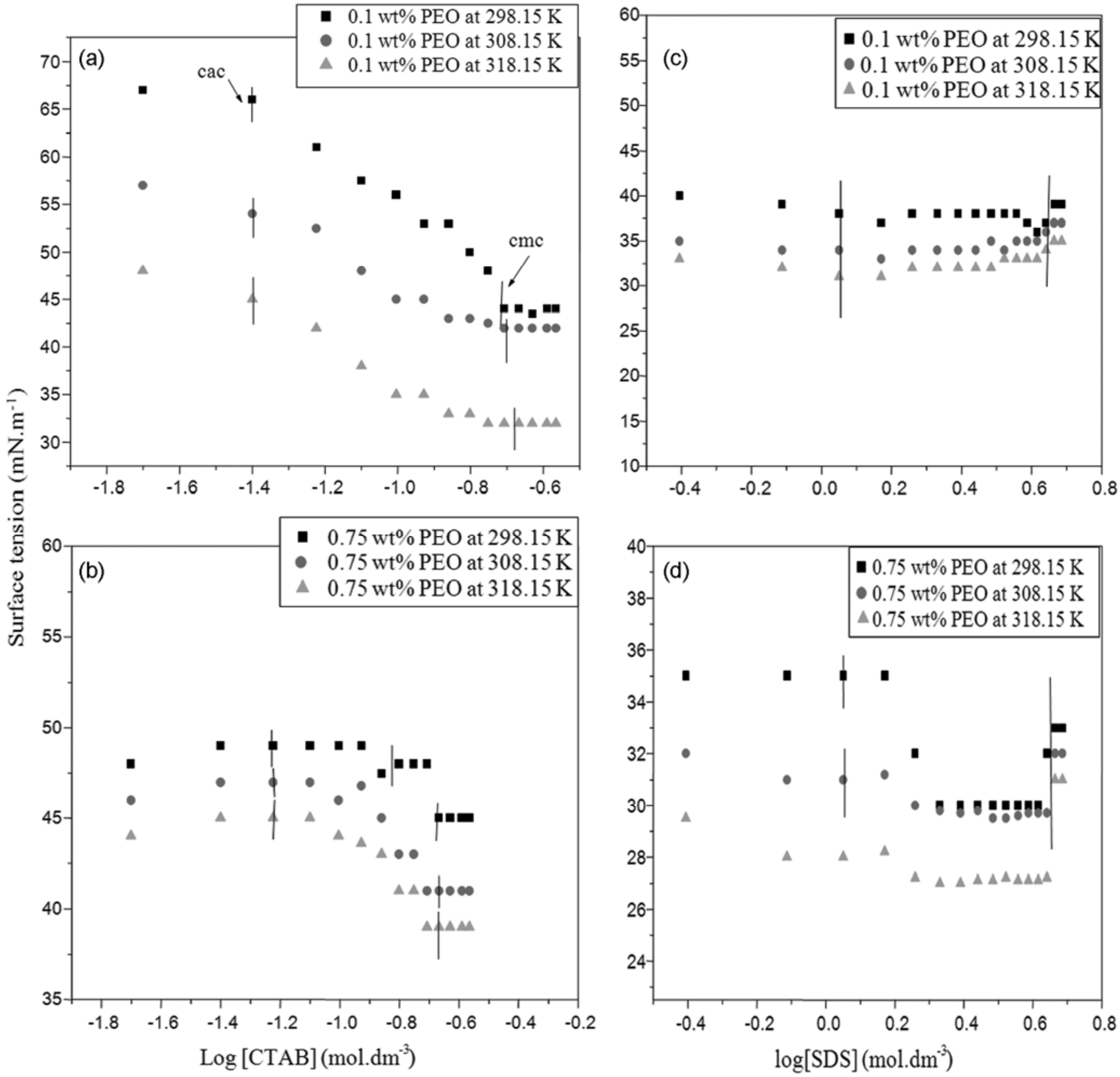

Fig. 1 — Representative plots of surface tension (γ) versus (a) log [CTAB] with 0.1 wt% PEO, (b) log [CTAB] with 0.75 wt% PEO, (c) log [SDS] with 0.1 wt% PEO & (d) log [SDS] with 0.75 wt% PEO at 298.15 K.

that the micellization is less favored in these system i.e. PEO/CTAB, PEO/SDS in water[7].There is small effect of temperature because of the ionic group present in surfactants and when interacted with the polymer micelles get stuck to polymer chain and aggregates are formed that offers lesser movement of micelles in the aggregate chain in the pool of polymer as the temperature is increased.

In Fig. 2 variation of surface tension with increasing polymer concentration is shown at 298.15 K to see the effect of PEO concentration on cac and cmc. Both of these increase with the increase in polymer concentration due to the availability of more and more number of reactive binding sites to the surfactant monomer or micelle-like aggregates at polymer concentration thus more amount of surfactant is required. As the interaction of PEO with surfactants occur due to complex formation over a broad surfactant concentration range than the substantial amount of surfactant is required to form the aggregate

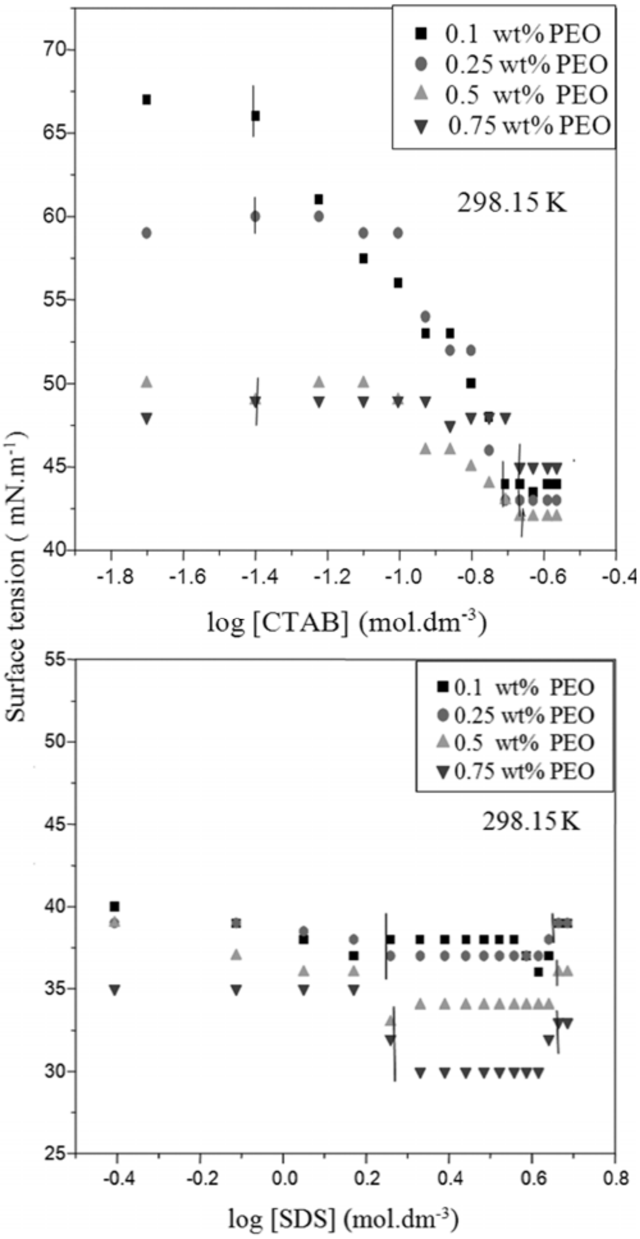

Fig. 2 — Representative plots of surface tension (γ) versus (a) log [CTAB] & (b) log [SDS] with various concentrations of PEO at 298.15 K

to the polymer chain which causes the increase in the cmc with increase in polymer concentration[8,17].

Figure 3 shows the plots of the variation of cmc at different temperatures with increase in PEO concentration for the surfactants CTAB and SDS. It is found that cmc of CTAB is less than SDS and with increase in temperature slight linear increase in cmc values is observed for all surfactants.

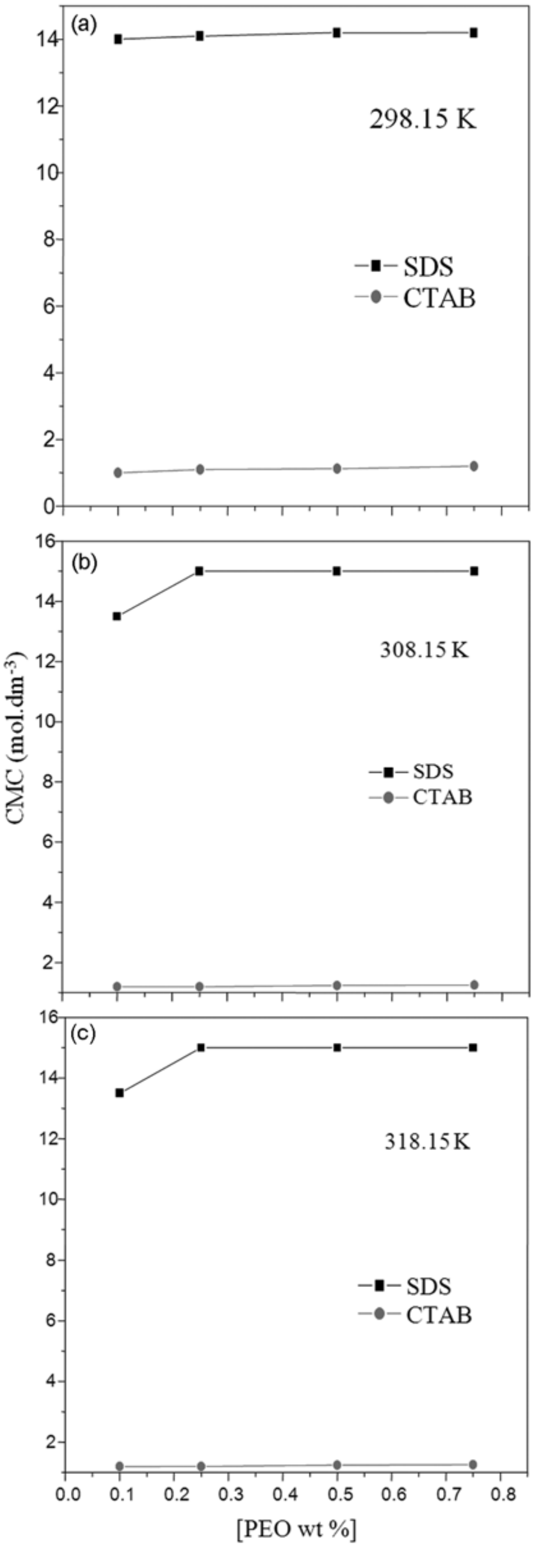

Fig. 3 — Plots of cmc versus [PEO] wt% at (a) 298.15 K, (b) 308.15 K and (c) 318.15 K

The slope of tensiometric profile near the cmc is the measure of interfacial adsorption efficiency of the surfactant and is quantified as Gibbs surface excess. The Gibbs surface excess, indicating the effectiveness of surfactants to be adsorbed at interface as compared to the bulk phase, has been calculated from the slope of tensiometric isotherm using the following equation:

$$\Gamma_{max} = -(1/2.303nRT)\lim_{[\,surfactant]\rightarrow cmc}(d\gamma/d\log[surfactant]) \quad \dots (1)$$

where Γ_{max} is in mol.m^{-2}, n is the number of species per surfactant molecule at the air solution interface and R is the gas constant. Surface excess values for ionic surfactant is 2. Table 1 shows that the Γ_{max} values decrease with the increase in PEO concentration as addition of PEO to water leads to decease the dielectric constant of the medium. Surfactant molecules become less active and capability of surfactant inactivation increases with increase in PEO concentration.

Assuming complete monolayer formation at cmc, the area of exclusion per surfactant monomer (A_{min}) at air-water interface can be calculated from the following relation:

$$A_{min} = 10^{18} / (N_A\Gamma_{max}) \quad \dots (2)$$

where A_{min} is in nm^2.molecule^{-1} and N_A is the Avogadro's number. Due to strong electrostatic repulsion and more steric factor between the surfactant and polymer, i.e., with the addition of PEO, lesser number of surfactant molecules are adsorbed at interface, leading to the availability of larger space per molecule at the interfacial region [8,17].

The values of surface parameters for CTAB and SDS at 298.15 K are given in Table 1. The highest value of A_{min} shows the close fitting of surfactants head on micelle. The closest fitting of surfactant heads increases with the concentration of the polymer. Similar trend is observed at other temperatures.

Table 1 — Surface parameters cac, cmc, Gibbs surface excess and minimum area per molecule (A_{min}) values of surfactants with various concentrations of PEO at 298.15 K.

Weight %	cac (mol.dm^{-3})	cmc (mol.dm^{-3})	Γ_{max} (10^{-4})	A_{min} (10^{-4})
CTAB				
0.1	0.6	0.9	49.54	3.35
0.25	0.7	1	8.33	19.94
0.5	0.71	1.1	1.94	85.6
0.75	0.8	1.2	1.26	130
SDS				
0.1	5	12	0.0875	330
0.25	5.1	14	0.036	4.60
0.5	6	15	1.29	128
0.75	6.2	15	0.09	180

Rheology

The viscosity was obtained from the rheometer at various polymer concentrations at fixed temperature 318.15 K and at constant shear rate of 100 m^{-1}. Figure 4 shows the variation of viscosity as a function of surfactant concentration (CTAB & SDS) for different weight % of PEO at a fixed temperature of 318.15 K. Here, we can see that for both the surfactants the viscosity increases as the concentration of polymer increases because large resistance to flow is attributed due to the entanglement in the polymer chain and it increases with the increase in polymer

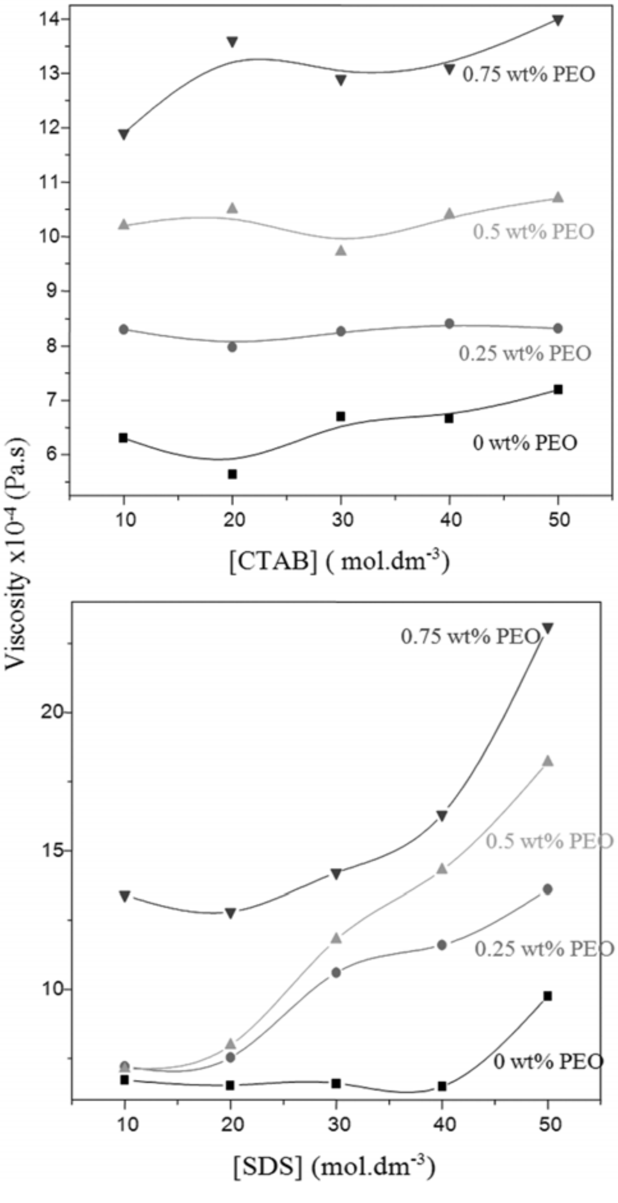

Fig. 4 — Plots of viscosity versus (a) [CTAB] and (b) [SDS] at 318.15 K

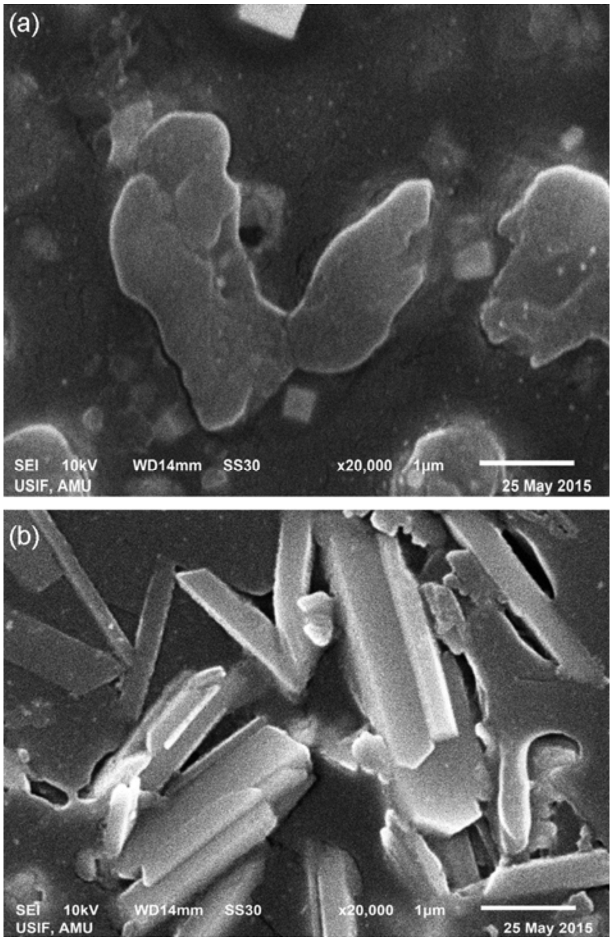

Fig. 5 — Scanning electron microscopy of (a) 10 mM CTAB, and (b) 20mM SDS surfactant with 0.75 wt% PEO

concentration and is seen higher in higher weight percentages due to presence of surfactant micelles. SDS exhibits higher increase in viscosity than CTAB.

SEM

SEM analysis of the surfactants CTAB and SDS is done to observe the micellar arrangements for their interaction with PEO. Spherical pool and ovular attachment is observed in case of CTAB and dense bundle like arrangement is seen in case of SDS with PEO that shows strong interaction of cationics due to low value of surface packing parameter than anionics (Fig 5).

Conclusion

The present study on micellisation of the cationic surfactant CTAB and anionic surfactant SDS in presence of the polymer PEO is investigated. The result shows that the cac and cmc values increase with the increase in polymer concentration and the cmc of CTAB is much lower than that of SDS. From the rheology studies it is observed that viscosity increases with the increase in polymer concentration and it is higher in case of the anionic surfactant SDS. Dense micellar arrangement in the polymer chain is observed by SEM analysis that shows its strong interaction than anionic SDS surfactant.

Acknowledgements

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Nomenclature

CTAB = Cetyltrimethylammonium bromide
CAC/ cac = Critical aggregation concentration
CMC/cmc = Critical micelle concentration
SDS = Sodium dodecyl sulphate
PEO = Polyethylene oxide
SEM= Scanning electron microscopy
Γ_{max} = Gibbs surface excess
A_{min}= Area per unit molecule

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