Studies on Polyethylene Oxide(PEO) and CTAB Interactions

Sunil Kumar[1] and Najam Sardar[2*]

[1]*D/o Petroleum Studies Aligarh Muslim University Aligarh*
[2]*D/o Petroleum Studies Aligarh Muslim University Aligarh*
E-mail: [1]sunilgautamgautam@ymail.com, [2]nsardar@rediffmail.com

Abstract—*The interaction of Polyethylene oxide (PEO) and cationic conventional surfactant (CTAB) in aqueous solutions is investigated by conductivity and viscosity techniques. Electrostatic and hydrophobic interactions play a dominant role in such systems. The conductivity study reveals that the interaction takes place between PEO and CTAB and the addition of PEO induces aggregation and instead of one break point, two break points appears in the conductivity curve being represented as Critical aggregation concentration (CAC) and Critical micelle concentration (CMC). The CMC of CTAB was increased by the addition of polymer. Viscosity study shows that the relative viscosity increases with surfactant concentration as well as polymer concentration.*

1. INTRODUCTION

Surfactants have received significant attention in the last decades due to their tremendous industrial and medicinal applications[1-6]. The addition of small quantity of polymer further enhances their potentials as their surface properties can be easily manipulated. Systems containing water, ionic or non-ionic surfactants and water-soluble polymers have been a subject of extensive investigations because they are vitally important to the success of product formulations aimed at a fundamental understanding of their properties as well as at evaluation of their use in various technical applications, e.g., in detergents and personal care products, chemical, pharmaceutical, mineral processing, biological applications, enhanced oil recovery, etc [7-12]. In the past, surfactants and polymers were used separately in many applications mainly for their individual function rather than for those arising out of their mutual interactions. When these two entities are present in systems, they generally provide better properties as compared to single entity. When present together, they can interact to provide beneficial properties or unusual and unwanted properties, such as hydrophobic aggregation, viscosity enhancement/untying, gel formation, solubilization and phase separation. Thus, surfactants and polymers in aqueous solutions attract attention in a wide field of practical applications as well as in academic circle.

Therefore, our objective was to investigate the surface behavior of cetyltrimethylammonium bromide (CTAB) surfactant and its interactions with nonionic polymer Polyethyleneoxide (PEO) at different weight percentages and different temperatures by using techniques like viscosity and conductance measurement. The results are quite interesting and could be of prolific use for selection of polymer-surfactant mixtures for use in the medicinal and pharmaceutical formulations, in industrial preparations, enhanced oil recovery processes, detergency, cleaning, emulsification, and dispersion.

2. MATERIALS AND METHODS

2.1 Materials

Polyethylene oxide, PEO (mol. wt 100,000, Alfa Aessar) and cetyltrimethylammonium bromide, CTAB (≥99.0%, Sigma), were used as received. Demineralised, double distilled water (DDW) of specific conductivity 1 to $2 \times 10-6$ S·cm^{-1} were used. The molecular structures of CTAB and PEO are shown in Fig. 1.
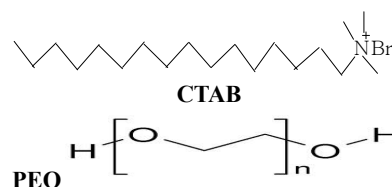

Fig. 1: Structures of CTAB and Polyethylene oxide

2.2 Preparation of Solutions

The water used to prepare solutions was double distilled twice over alkaline KMnO4 in glass (pyrex) distillation setup. Specific conductivity of pure double distilled water is 1.0-2.0 µS.cm-1. Special care was observed for cleaning the glass wares with chromic acid then with water and finally by rinsing with double distilled water and then dry them in oven.

The polymer stock solution was prepared by adding double distilled water under magnetic stirrer for 5 hours at room temperature and kept it for 24 hours to achieve complete

dissolution and equilibrium. Other concentration of 0.05, 0.25, 0.1, 0.5 wt % of PEO solution were prepared by diluting 1wt % of PEO with double distilled water. Surfactant solutions were prepared by adding the required amount of surfactants (C-TAB) in a specific polymer solution and stirred it for 1 hour and kept it for 3 hours.

2.3 Methods
2.3.1 Conductance Measurement
In the present investigation, the conductivity measurements were performed on a digital conductivity meter (Systronics Conductivity-TDS Meter 308, range 0.1 µS to 100 mS, accuracy ±1% of F.S. ± 1 digit, India). The conductivity runs were carried out by adding progressively concentrated surfactant stock solution into the system (demineralised double distilled water of specific conductivity 1 to 2 × 10−6 S·cm^{-1} or solution containing different weight percent PEO. The conductivity runs were carried out at different weight percent of PEO (0.05 to 1.0 wt %) and at four different temperatures 293.15 K, 303.15 K, 313.15, and 323.15 K. The temperature was maintained in a thermostated water bath with thermal stability of ±0.1 K.

The critical micelle concentration of the pure surfactant used was obtained from the plots of specific conductivity (κ) as a function of the surfactant concentration. The CMC values were taken from the intersection of the two straight lines drawn before and after the intersection point in the κ versus surfactant concentration plots. In case of the polymer−surfactant mixtures the plots of κ versus [surfactant] showed two breaks, the CAC was determined by the intersection of first and second linear parts and the CMC in this case was the intersection point of the second and third linear parts.

2.3.2 Viscosity Measurement

The viscosities were measured using an Ubbelhode suspended level capillary viscometer. The viscometer was always suspended vertically in a thermostat with a temperature stability of ±0.1 K in the investigated region. The requisite amount of surfactant was added in PEO solution. These solutions were used as stock solutions to see the effect of surfactant concentration and further lower concentrations were made by dilution from the above stock. Viscosities of such solutions under Newtonian flow conditions were obtained as described elsewhere [13].

The viscosity runs were carried out at PEO concentrations of 0.1, 0.25 and 0.5 wt % with different CTAB concentrations used (0-50mM) at 293.15 K, 303.15K and 313.15K. The relative viscosity was calculated from the equation as shown equation (1)

$$\eta_r = t / t_0 \tag{1}$$

Where η_r, t and t_0 are the relative viscosity, flow time of solution and water, respectively. Density corrections were not made since these were found negligible [14].

3. RESULTS AND DISCUSSIONS

3.1 Conductivity Results

The conductance was measured for CTAB solutions in the presence and absence of different weight percentages of PEO at 293.15 K, 303.15 K, 313.15, and 323.15 K, respectively, to calculate CAC and CMC values.

The specific conductivity (κ) profiles as a function of concentration of pure CTAB in water at four different temperatures in pure water is as shown in Fig. 2. The intersection point of the two straight lines represents the usual CMC of surfactants. We can see that the critical micelle concentration (CMC) increases with temperature as reported earlier [15]. We can also observed that the conductance of surfactant solutions increases with the increase in concentration of surfactants. Such behavior is explained in a way that by increasing concentration of surfactant, the number of charged molecules as well as ions (the conducting species) increases which resulted in a linear increase in conductance with concentration. However, after CMC, the number of independent charged molecules of surfactant does not increase linearly with its concentration due to micelles formation.
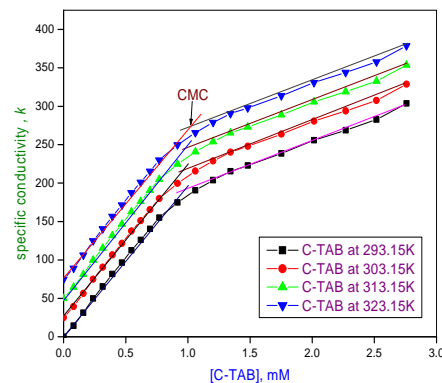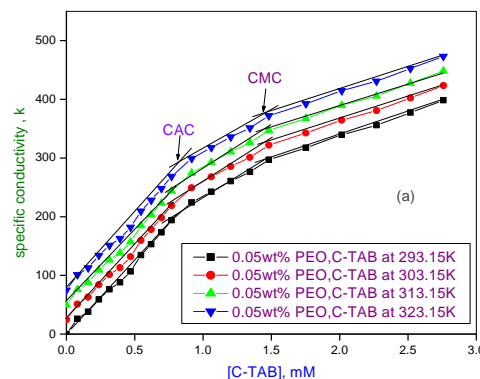

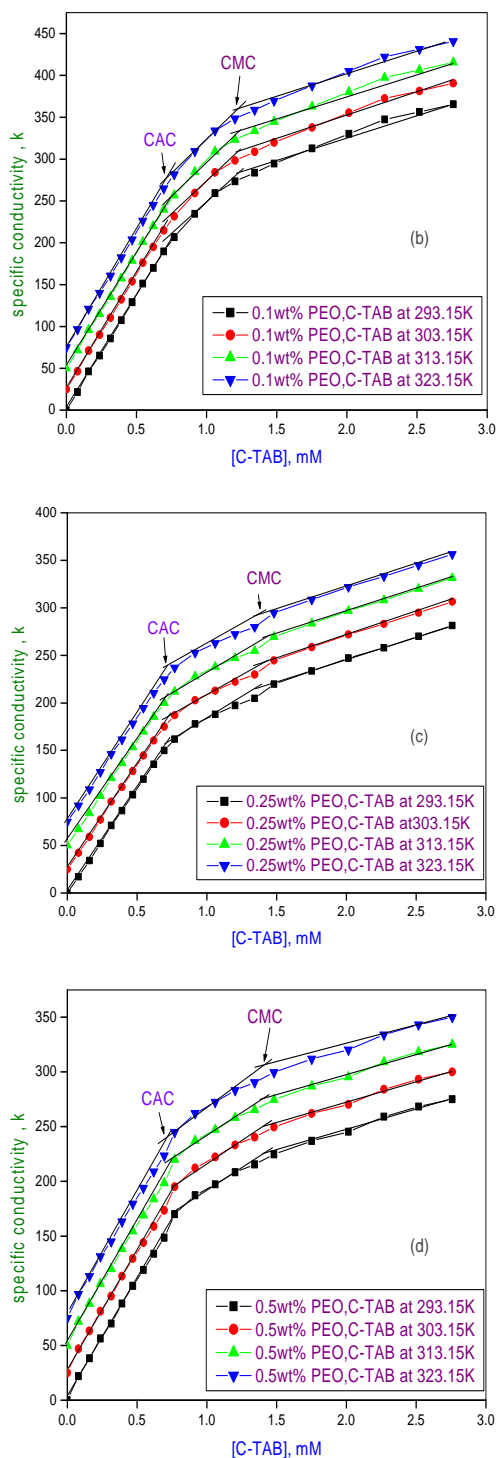**Fig. 2: Plots of specific conductivity (κ) versus [C-TAB] at different temperatures in water.**

kinds of aggregation phenomena. The first break is called critical aggregation concentration (CAC), where the interaction of polymer chain with surfactant starts. The second break point is called critical micelle concentration (CMC), where the polymer chain with surfactant and/or micelle like aggregates gets saturated, followed by formation of normal micelles on adding a greater amount of surfactant [15].

From Fig. 3, we can observe that, as the temperature increases, both CAC and CMC values increase for all concentrations of polymers. In general, the effect of temperature on the CMC of surfactants in aqueous media is complex. On one hand, 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 the hydrophobic group, which disfavours micellization. The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range. In the present study, the CMC values increase with an increase in temperature indicating that the micellization is less favoured in these three systems, i.e., PEO/CTAB in water. We can also observe that as the PEO concentration increases both CAC and CMC values also increases for all surfactants as shown in Fig. 4. The increase in CAC and CMC values might be 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 the surfactant is required to bind to the polymer as explained by other investigators [15].
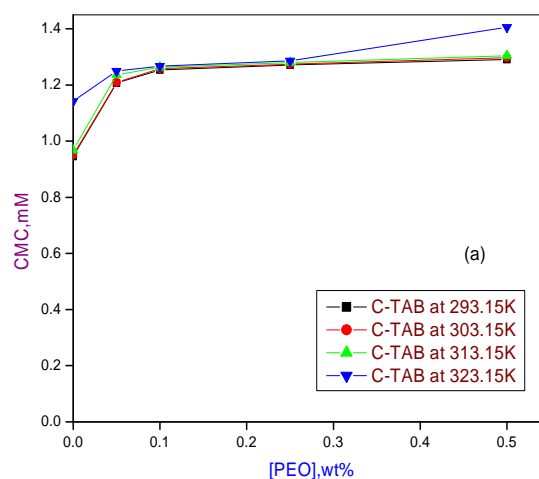
Fig. 4: Plots of CMC versus PEO wt% and CMC versus PEO wt% for C-TAB at various temperatures.

3.2 Viscosity Results

The relative viscosity of polymer solution in water as a function of polymer concentration, at three different temperature which it increases with the Polymer concentration is presented in Fig. 5. From Fig. 6 we can see that as the temperature increases the relative viscosity decreases. As the

Fig. 3: Plots of specific conductivity (κ) versus [C-TAB] at (a) 0.05, (b) 0.1, (c) 0.25 and (d) 0.5 wt% PEO at different temperature as 293.15K, 303.15K, 313.15K and 323.15K.

The plot shows two breaks in the presence of PEO in comparison to a single break observed in the absence of polymer as represented in Fig. 3. The two breaks in the presence of polymer are ascribed to the occurrence of two

solubility of the complex (and therefore the viscosity of the solution) is determined by an interplay between electrostatic repulsion and attraction due to hydrophobic effect. Hence, as the system becomes micro heterogeneous, close to the phase separation limit, the viscosity decreases. Table 1 shows the relative viscosity as a function of surfactant concentration for CTAB in pure water at 293.15K, 303.15K and 313.15K. Here also we observe a decrease in relative viscosity with temperature.
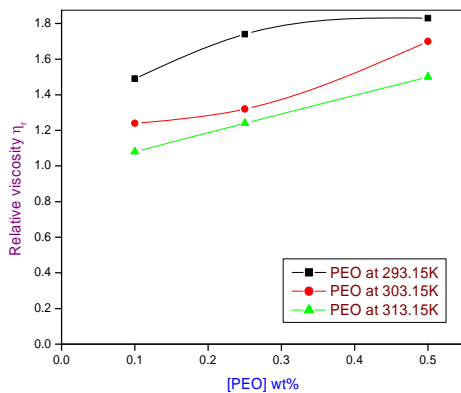

Fig. 5: Plot of relative viscosity versus [PEO] on different wt% in water at 293.15 K, 303.15 K, and 313.15 K.
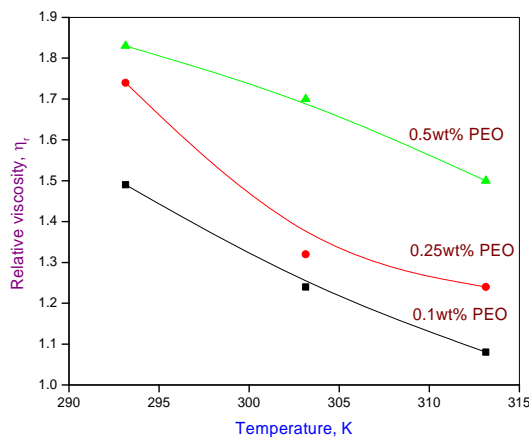

Fig. 6: Plots relative viscosity versus temperature for different polymer weight percentages.

Table 1: Relative viscosities of polymer and surfactants.

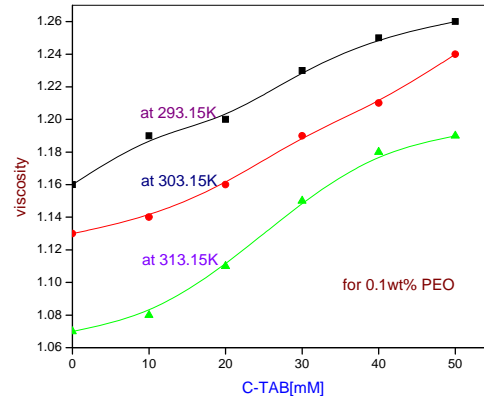| Surfactant concentration (mM)	Relative viscosity (η_r)								
	0.1wt% PEO			0.25wt% PEO			0.5wt% PEO		
	293.15K	303.15K	313.15K	293.15K	303.15K	313.15K	293.15K	303.15K	313.15K
C-TAB									
0	1.16	1.13	1.07	1.29	1.19	1.14	1.43	1.41	1.3
10	1.19	1.14	1.08	1.31	1.23	1.17	1.46	1.43	1.33
20	1.20	1.16	1.11	1.33	1.28	1.19	1.52	1.47	1.36
30	1.23	1.19	1.15	1.37	1.29	1.22	1.58	1.50	1.41
40	1.25	1.21	1.18	1.38	1.32	1.25	1.61	1.52	1.44
50	1.26	1.24	1.19	1.4	1.35	1.27	1.65	1.55	1.47

Fig. 7: Plots of relative viscosity versus [CTAB] at 293.15 K for different polymer weight percentages in C-TAB.

Table 1 shows that the relative viscosity values as a function of [surfactant] concentration for CTAB at different weight percentages of polyethylene oxide (PEO) at 293.15K, 303.15K and 313.15K. Fig. 7 shows the effect of CTAB concentration and temperature for 0.1 wt % PEO. Here, we can see that for CTAB the increases in relative viscosity is slight and linear. Fig. 8 depicts the effect of surfactant concentration as well as PEO concentration on the relative viscosity of PEO+CTAB system at 293.15 K, similar plots were obtained at 303.15 K and 313.15 K, we can see that as the polymer concentration increases, relative viscosity also increases due to entanglement in polymer chains, the relative viscosity is highest at 0.5 wt% PEO+50mM surfactant (at 293.15K, η_r = 1.65 (CTAB), η_r =1.1.70 (16-6-16), η_r = 1.75 (16-5-16)) and lowest at 0.1 wt% + 50 mM surfactant(at 293.15K η_r =1.26 (CTAB). Table 1 and Fig. 7 shows the effect of temperature on relative viscosity of PEO+CTAB mixture. The relative viscosity decreases with increases in temperature as explained earlier.
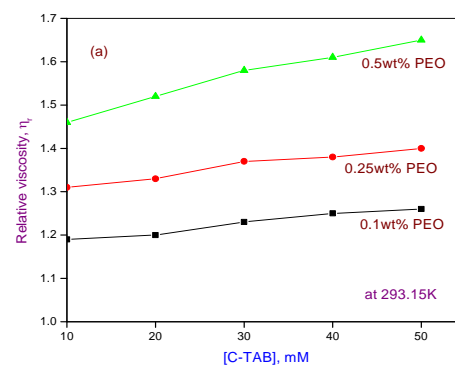

Fig. 8: Plots of relative viscosity versus [CTAB] at 293.15 K for different polymer weight percentages in C-TAB.

4. CONCLUSIONS

1) From the conductivity study, we can conclude that-
(a) The interaction takes placed between polyethylene oxide and C-TAB. Two points occurs in presence of polymer

called as CAC and CMC indicating polymer surfactant interaction.

(b) Both CAC and CMC values increases as the polymer concentration increases.

(c) As temperature increases both CAC and CMC values increases.

2) From the Viscosity study we can conclude that-

(a) Relative viscosity is a function of polymer concentration, surfactant concentration and Temperature.

(b) As polymer concentration increases relative viscosity increases.

(c) As surfactant concentration increases relative viscosity increases.

(d) Relative viscosity decreases with increase in temperature.

REFERENCES

[1] Hansson, P., Lindman, B., "Surfactant–Polymer Interactions'' *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 604.

[2] Goddard, E. D., Ananthapadamanabhan, K. P. "Interactions of Surfactants with Polymers and Proteins'' CRC Press, Boca Raton, 1993.

[3] Robb, I. D. In " Anionic Surfactants–Physical Chemistry of Surfactant Action" E. H. Lucassen–Reynders (Ed.), Surfactant Sci. Ser., vol 11, Marcel Dekker, New York, 1981.

[4] Goddard, E. D. "Polymer–Surfactant Interaction Part I. Uncharged Water-Soluble Polymers and Charged Surfactants" *Colloids Surf.*, **1986** *19*, 255.

[5] Saito, S. In "Nonionic Surfactants: Physical Chemistry" M. J. Schick (Ed.), Surfactant Sci. Ser., vol 23; Marcel Dekker, New York, 1987.

[6] Hayakawa, K.; Kwak, J. C. T. In "Cationic Surfactants: Physical Chemistry" Rubingh, D. N.; Holland P. M. (Eds.), Surfactant Sci. Ser., vol 37; Marcel Dekker, New York, 1991.

[7] Lindman, B., Thalberg, K. In "Interactions of Surfactants with Polymers and Proteins" Goddard, E.; Ananthapadmanabhan, K. P. (Eds.); CRC Press: Boca Raton, FL, 1993.

[8] Suurkuusk, J., Wadso, I. "A Multichannel Microcalorimetry system" *Chem. Scr.*, **1982**, 20, 155

[9] Kwak, J. C. T. "Polymer-Surfactant Systems" *Surfactant Science Series* vol. 77; Marcel Dekker: New York, 1998.

[10] B. Jonsson, B. Lindman, K. Holmberg, B. Kronberg, "Surfactants and Polymers in Aqueous Solution" John Wiley & Sons: London, 1998.

[11] Shah, D. O. "Surface Phenomena in Enhanced Oil Recovery" Plenum Press: New York, 1981.

[12] Cahn, A.; Lynn, J. "*Encyclopedia of Technical Technology*" Wiley–Interscience: New York, 1983.

[13] M. L. Zhang, "Cellulosic Associative Thickners" *Carbohydr. Polym.* 45 (2001) 1

[14] J. H. Guo, G. W. Kinner, W. W. Harcum, P. E. Barnum, "Pharmaceutical Applications of Naturally Occurring Water-Soluble Polymers" *Pharm. Sci. Tech. Today*, (1998) 1.

[15] A. P. Romani, M. H. Gehlen, R. Itri, "Surfactant-Polymer Aggregates Formed by Sodium Dodecyl Sulfate, Poly(*N*–vinyl–2–pyrrolidone), and Poly(ethylene glycol)" *Langmuir*, 21 (2005) 127.