

Investigating the Micellization Behavior of Cetyltrimethylammonium Bromide: As Affected by the Contents of Poly(ethylene oxide) and Temperature of the System

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ABSTRACT: The micellization behavior of cetyltrimethylammonium bromide (CTAB) is investigated in the absence and presence of poly(ethylene oxide) employing surface tension, light scattering, and viscosity and conductance measurement. It has been concluded that the critical micellization concentration (CMC) of CTAB in the presence of polymer increases with the increase in polymer concentration. The three ranges of interaction among the polymer and CTAB with respect to concentration of CTAB are identified at surface tension plot and noted to depend upon polymer concentration. The effect of temperature over these interactions and CMC of CTAB has been investigated. It is observed that the CMC, ΔH , and flow activation energy of the system increases with the increase in polymer concentration whereas CMC of CTAB

decreases with the temperature. R_H and R_g/R_H values determined by light scattering also indicate such type of behavior. The CMC values have also been obtained by viscosity and conductivity measurement. The results and conclusions drawn through all the techniques were consistent. New methodology has also been introduced to interpret the data obtained by surface tension, viscosity, and conductance measurement, and get information about the point of interaction and saturation of polymer with surfactant, which was noted to be very useful and informative. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2133–2142, 2010

Key words: CTAB; PEO; light scattering; surface tension; viscosity; CMC; polymer–surfactant interactions.

INTRODUCTION

Surfactants and polymers are used together in many formulations and industrial processes to boost their properties and it has greatly stimulated the interest of scientists in polymer/surfactant systems.^{1–28} However, the interactions between neutral polymers and surfactants are not well understood and needs further investigation. Moreover, the experimental work on polymer/surfactant mixtures has mainly concentrated on bulk solution properties, about which a substantial body of information and understanding is available whereas the interfacial properties of such solutions are considerably less accessible.^{29–37} In neutral polymer/surfactant systems, the electrostatic interactions are much weaker and other mechanisms like hydrophobic interactions between the polymers and the surfactant chains are always pres-

ent and can in some systems be the predominant interactive forces. It is generally observed that the surfactants self-associate cooperatively and form aggregates, at critical aggregation concentration (CAC). The CAC is usually lower than the critical micellization concentration (CMC) of the surfactant by a factor of 1–10 in contrast to polyelectrolyte/oppositely charged surfactant systems which is about 100–1000.^{38,39} The strength of the interaction between polymers and surfactants can be characterized by CAC/CMC ratio, though the quantity gives a semiquantitative idea of the interaction.⁴⁰

Surface tension has been the main tool for the study of the air/solution interface and the patterns of behavior though considered to be well established for weakly interacting systems,⁴¹ but no mechanism has been proposed to get quantitative information about these interactions, partly because the Gibb's equation cannot usually apply to determine the surface composition. Studies presented so far concern water-soluble homo-polymers, for instance poly(ethylene oxide) (PEO), or poly-(vinyl pyrrolidone), and surfactants such as sodium dodecylsulfate.^{42,43} However, not much is known about the interactions among the homo-polymers and anionic, or cationic, short-chain surfactants. As it is stated earlier polymer–surfactant interactions are controlled by a

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balance between hydrophobic and electrostatic interactions and are modulated by temperature and other parameters which affect the surface properties of either of the component of the system. The role of the above parameters in the stabilization of polymer-surfactant systems is not easy to quantify and very few information are available.⁴³ It has prompted us to investigate the role of temperature over cetyltrimethylammonium bromide (CTAB) and its interactions with quite a high molecular mass PEO using different techniques like surface tension, light scattering, conductance and viscosity and to propose some techniques for the interpretation of results and correlate these observations with the interactions.

EXPERIMENTAL

Material

The surfactant *N*-cetyl *N,N,N* trimethyl ammonium bromide, CTAB, and PEO having molecular mass 6 kg/mol was used for investigation. CTAB was obtained from Fluka (Buchs, Germany) whereas PEO was donated by Department of Physical Chemistry, University of Bayreuth, Germany which was originally obtained from Shell (Munich, Germany) and used as such. The de-ionized water whose conductance ranged from 1.2 to 2.5 $\mu\text{S}/\text{cm}$ was used as a solvent.

Surface tension

To investigate the amphiphilic character of the surfactant and polymer, the surface tension (γ) is considered to be the best conventional method used for the purpose. The du-Nouy ring detachment technique was used to measure the surface tension of polymer and CTAB and their mixture in de-ionized water. The instrument employed was digital TE3 tensiometer provided by Lauda (Lauda-Königshofen, Germany). All the measurements were made sufficiently slowly to ensure equilibrium conditions. To observe the effect of temperature on the surface tension, the measurements were made at different (30–55°C) temperatures. The temperature was maintained up to ± 0.1 using Ecoline circulation thermostat model E 015T (Lauda-Königshofen, Germany).

Laser light scattering measurement

The aggregation behavior of CTAB in the absence and presence of PEO in water was studied by static and dynamic laser light scattering techniques. The measurement was made at different concentrations while keeping the temperature constant. Prior to laser light scattering (LLS) measurements, all samples were filtered using a filter of 0.02 and 0.25 μm pore size for the solvent and solution, respectively.

Instrument used for the purpose was DAWN EOS/QELS supplied by Wyatt USA, with helium-neon laser of 632.8 nm wavelength as light source. A cylindrical cell (SV) of 2-cm diameter was used for the purpose.

Viscosity measurement

The Ostwald-type viscometer was used to measure the viscosity of surfactant, polymer and their mixture in deionized water at different temperatures. The viscometer was first washed and dried properly and then the measurements were made. The required temperature of the viscometer was maintained by suspending it in the above stated water bath/thermostat, model E 015T (Lauda-Königshofen, Germany).

Conductance

The conductance of the solution of surfactant, polymer and their mixture was measured in de-ionized water using InoLab Cond. 720 conductivity meter (Buchs, Germany). The conductivity cell and the vessel used for the measurement were properly cleaned and the meter was standardized before use.

RESULTS AND DISCUSSION

Surface tension

The surface tension of *N*-cetyl *N,N,N*, trimethyl ammonium bromide (CTAB) measured with and without the addition of PEO (6 kg/mol) is plotted as a function of surfactant concentration. It can be noted that the variation in surface tension of surfactant and its mixture with respect to surfactant concentration is according to expectation (Fig. 1) and observed for other such systems.^{28,44} The plot of surface tension of pure surfactant or mixture can be divided into three parts. In the first part of the plot the surface tension decreases slowly till it reaches to a point which we call as critical concentration of the surfactant (CC), further increase in concentration decreases the surface tension sharply and ultimately leads to a minimum value of surface tension and becomes constant. The concentration at which the surface tension becomes constant/minimum is called CMC.^{12,28} Such behavior is due to the fact that at low concentration the surfactant molecules are present in solution in molecular state and coexist in equilibrium with a monolayer at the air water interface. Increasing the solution concentration leads to increase in adsorption of surfactant at the interface and concomitant reduction in surface tension. Further addition of surfactant leads to further accumulation of surfactant at the interface and hence the surface tension decreases drastically. As the system is saturated

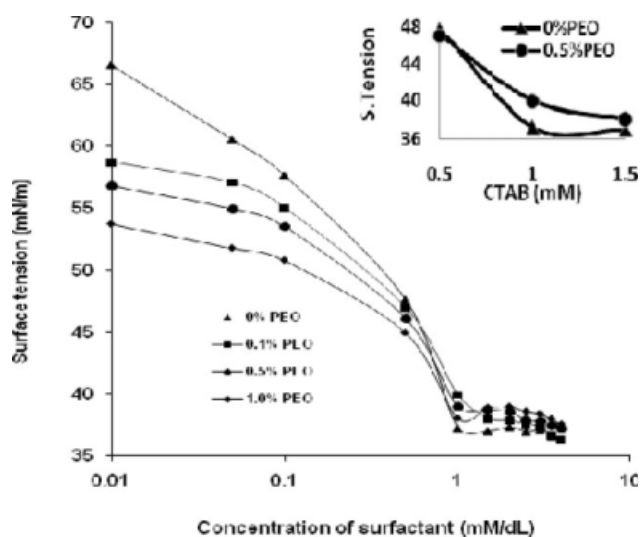


Figure 1 Surface tension of *N*-cetyl *N,N,N* trimethyl ammonium bromide (CTAB) with and without the addition of PEO (6K). The insertion is the same data plotted for 0% and 0.5% PEO for limited range of surfactant concentration.

with the surfactant molecules the micelles (aggregate) formation of surfactant takes place and hence no further change in the surface tension is observed. This concentration of surfactant is called the CMC.

The addition of polymer (PEO 6K) to surfactant solution changes the shape of surface tension plot and three identifiable points in the surface tension of the mixture which are conventionally designated T_1 , T_2 , and T_3 are observed as shown schematically in Figure 2. The first break (T_1), at the low concentration end of the approximate plateau, is the CAC for the system, i.e., the concentration at which micellization of the surfactant on to the polymer in the bulk phase begins. T_3 corresponds to the formation of another approximate plateau in the surface tension at high surfactant concentration and is the CMC for the onset of formation of free surfactant micelles in the bulk. T_2 is the point where the bulk polymer is more or less saturated with surfactant micelles and this point is generally less well defined than T_1 and T_3 . Any further addition of surfactant to the solution at T_2 is not bound to the polymer and therefore lowers the surface tension as T_3 is approached. In the region between T_1 and T_2 the activity of the surfactant is constant or slowly decreases as surfactant aggregates form on polymer in the bulk phase.^{12,22,37} However, the difference between the surface tension of pure surfactant and that of surfactant-polymer mixture decreases with the increase in CTAB concentration and ultimately the surface tension of the mixture becomes higher than the surfactant alone as depicted in Figure 1 and its insertion. This indicates that the interactions between the polymer and surfactant are low^{12,28,38} but the points where the inter-

actions begin (T_1) and the saturation point (T_3) can be identified over the surface tension versus concentration curve^{12,28,38,44} as shown schematically in Figure 2. Figure 1 also indicates that the span of T_2 increases with the addition of polymer as more surfactant is required to saturate the polymer due to interactions among polymer and surfactant.^{28,43} The plausible explanation for the above stated trend is that in dilute solutions of surfactants the polymer and surfactant can act individually and the effect of reducing surface tension is added up. However, with the increase in concentration of surfactant, it interacts with the polymer molecules. The surfactant molecules get adsorbed at polymer molecules or *vice versa* and the effect is lost or reduced.^{43,44} Further increase in surfactant concentration leads to availability of surfactant at the surface and the surface tension is further reduced till it has the same value as that of pure surfactant (the minimum value of surface tension). To quantify the trend of decrease in surface tension and find out the maximum amount of surfactant required to solubilize or interact with the added polymer, the decrease in surface tension of surfactant is plotted as a function of surfactant concentration in Figure 3. It can be noted that the difference in surface tension of surfactant and the surfactant-polymer mixture decreases with the increase in surfactant concentration and approaches to zero, the concentration of surfactant at which the difference becomes zero is taken as T_1 . Further increase in surfactant concentration decreases the difference in surface tension and reaches to a minimum value which is designated as T_2 . However, if more surfactant is added the difference increases and approaches to zero again. This concentration of surfactant is designated as T_3 . It can be concluded that the interaction parameters can be

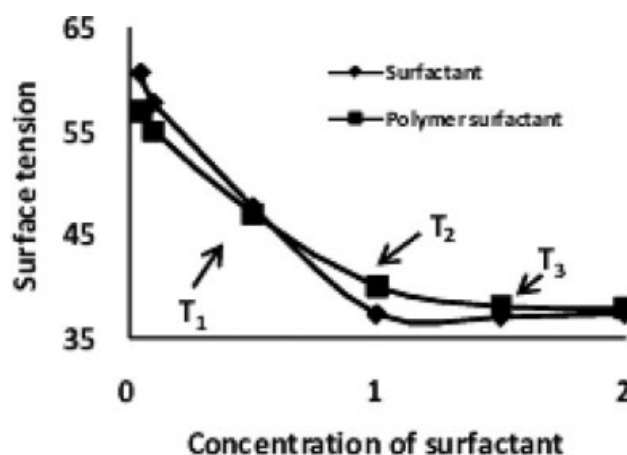


Figure 2 Schematic presentation of three ranges (T_1 , T_2 , and T_3) of polymer surfactant interactions and their effects over the surface tension of polymer-surfactant mixture.

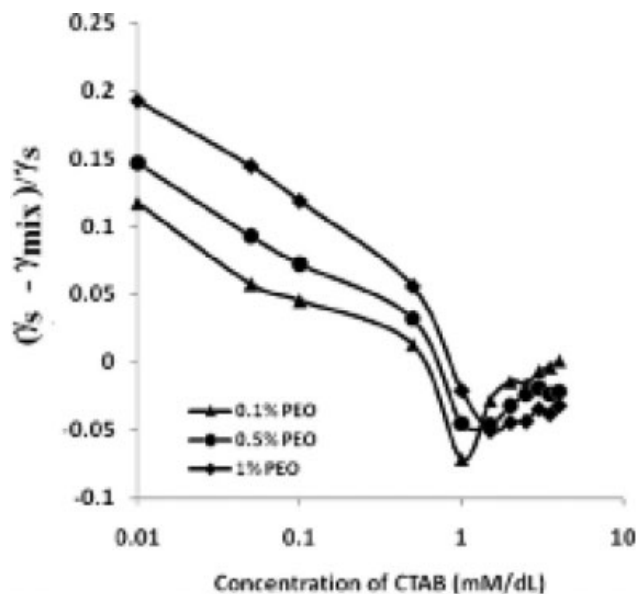


Figure 3 Dimensionless surface tension [= (Surface tension of surfactant (γ_s) – surface tension of polymer–surfactant mixture (γ_{mix}))/surface tension of surfactant] as a function of surfactant concentration.

very easily and accurately determined in this way. The concentration of surfactants at which the difference in surface tension becomes zero has been plotted against polymer concentration in Figure 4; it shows that with the increase in polymer concentration, the required surfactant concentration increases. Although the data can be fitted to linear regression but with logarithmic regression a better fit can be obtained with $R^2 = 0.943$, giving following regression.

Surfactant concentration (mM)

$$\ln 0.16(\text{polymer concentration (mM)}) + 1.483 \quad (1)$$

This equation states that the surfactant concentration approaches to zero when polymer concentration is equal or less than 10^{-5} mmol/L. It also tells that 1.483 is the concentration of surfactants corresponding to T_3 . Figure 4 also contains a plot of concentration of surfactant/polymer concentration versus concentration of polymer. This graph shows that the ratio goes down as the polymer concentration increases. For example when polymer concentration is increased from 2.86×10^{-3} to 2.86×10^{-2} the ratio reduces from 196 to 33.25. It can be noted that in low concentration of polymer almost one surfactant molecules is adsorbed at every monomer of polymer. However, with the increases in polymer concentration inter- and intramolecular molecular interactions among polymer molecules set in, resulting a change in conformation of polymer and reduces available sites to surfactants and hence the amount

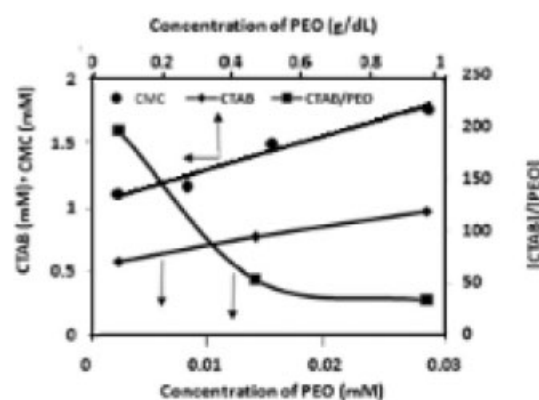


Figure 4 The concentration of surfactant (in terms of [CTAB] and [CTAB]/[PEO]) required to make the surface tension of mixture (polymer–surfactant) equal to pure surfactant and the CMC of surfactant as a function of polymer concentration.

of surfactant adsorbed at the polymer decreases.^{45–49} The CMC obtained from the dependence of surface tensions over surfactant concentration (Fig. 1) increases with the addition of polymer concentration (Fig. 4). It is due to the fact that the surfactant is solubilized by polymer; hence more surfactant is needed for micellization.^{28,43,50} These observations also support the idea given above.

The surface tension of the polymer–surfactant (PEO and CTAB) mixture is plotted against polymer concentration in Figure 5. It can be seen that the surface tension of solution containing less amount of surfactant decreases with the increase in polymer concentration and *vice versa*. This is due to the reason that if a solution contains small amount of surfactant and polymer is added to it the polymer being in big amount, some of its effect is lost in the interactions with surfactant while the rest of the polymer decreases the surface tension of the solution.

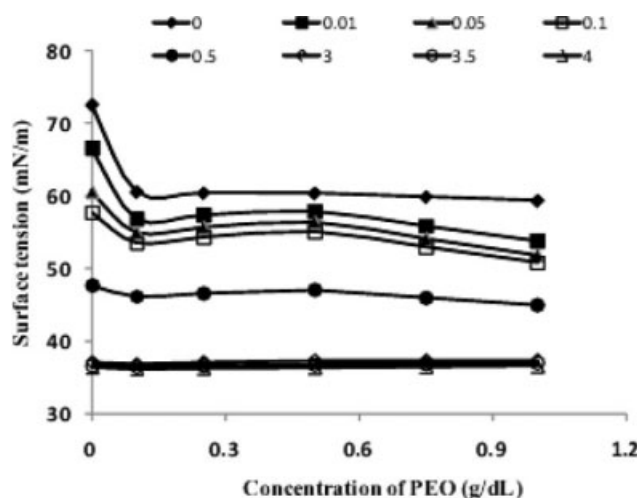


Figure 5 Surface tension of polymer–surfactant mixtures as a function of polymer concentration.

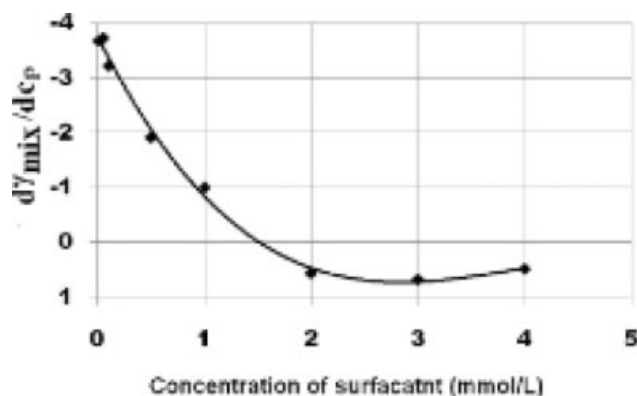


Figure 6 Variation in $d\gamma_{\text{mix}}/dc_p$ calculated from the plots shown in Figure 5 as a function of surfactant concentration. γ_{mix} and c_p are the surface tension of mixture and concentration of polymer, respectively.

However, if the surfactant concentration is comparable to polymer then almost all the polymer is solubilized in surfactant and shows no effect. If the amount of surfactant is much higher than polymer then due to polymer–surfactant interactions, the available surfactant at the interface decreases and surface tension of solution increases. It can be further confirmed from the slopes of surface tension plots versus polymer concentration which changes from negative to positive values when we move from lower surfactant concentration to higher ones (Fig. 5). The concentration at which the surface tension does not change by the addition of polymer was obtained from the slope of the plots of Figure 5 and displayed in Figure 6. It can be noted that the slope becomes zero when the surfactant concentration is about 1.48 which is the same as determined from Figure 4.

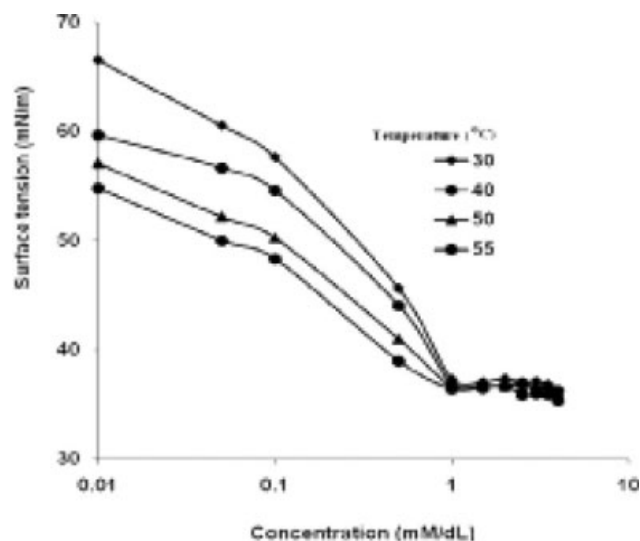


Figure 7 Surface tension of CTAB as a function of its concentration, measured at different temperatures.

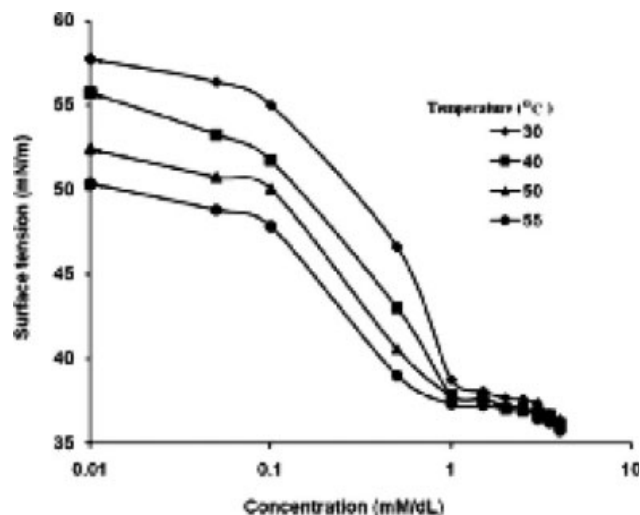


Figure 8 Surface tension of polymer (0.1% PEO)–surfactant (CTAB) mixture as a function of surfactant concentration measured, at different temperatures.

The surface tension of CTAB measured at different temperatures exhibited a similar trend for all temperatures and the surface tension was decreased with the increase in temperature (Fig. 7) as observed for other systems.^{49,50} With the increase in temperature the solvent–solute interactions changed and resulted a decrease in surface tension. It can be noted that the extent of decrease in surface tension with temperature decreases with the increase in surfactant concentration, which is due to the reason that in high concentration region ($C > \text{CMC}$) the surface tension is not much sensitive (or almost independent) to surfactant concentration. The surface tension of polymer (0.1%) surfactant mixture is also measured and displayed in Figure 8. It can be noted that the effect of temperature over the surface tension and CMC of polymer–surfactant system is comparatively more pronounced than surfactant alone. The rate of change in surface tension with temperature ($d\gamma/dt$) is display in Figure 9. The results show that the impact of temperature over the surface tension decreases with the increase in concentration of surfactants and ultimately approaches to zero. It has been noted that the CMC decreases with the temperature and this becomes more pronounced if polymer is added to the system (Fig. 10). Such a fashion can be explained in terms of that an increase in temperature results a decrease in polymer surfactant interaction and the concentration of surfactant required to reach to saturation point decreases and hence the CMC. As the properties of mixed system can vary from system to system hence it is difficult to compare with other systems in spite of working at similar conditions.^{48,51,52} To obtain the value of ΔH from CMC dependence over temperature, $\log \text{CMC}$ is plotted against $1/T$ and the values obtained in this

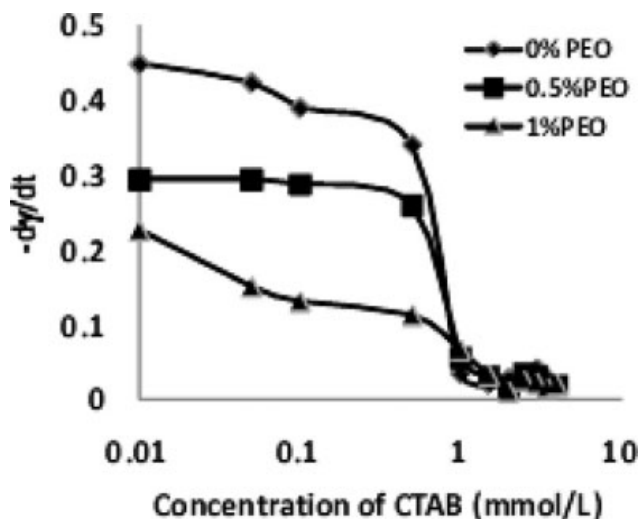


Figure 9 Change in surface tension of polymer–surfactant mixture with temperature as a function of surfactant concentration.

way are plotted as a function of polymer concentration (Fig. 10).⁵² It can be seen that ΔH increases linearly with the polymer concentration which is an indication of degree of polymer–surfactant interactions with the increase in polymer concentration.

Light scattering

The data obtained through dynamic light scattering (DLS) experiments was fitted to the correlation curve according to the following equation^{53,54} and shown in Figure 11

$$G(\tau) = \frac{I(t_0)I(t_0 + \tau)}{I(t_0)^2} = B + Ae^{-2q^2Dt} \quad (2)$$

Here $G(\tau)$, $I(t_0)$, and $I(t_0 + \tau)$ are the correlation factor, the scattered intensity at t_0 and scattered intensity for delayed time ($t + t_0$), respectively. B and A are constants and D is the diffusion coefficient. q is the scattering vector given as

$$q = 4\pi n/\lambda_0 \sin(\theta/2). \quad (3)$$

Here n , λ_0 , and θ are the solvent refractive index, wavelength of light in vacuum, and the scattering angle, respectively.

Further, the hydrodynamic radius (R_H) can be obtained using the Stokes–Einstein equation,⁵⁵

$$D = \frac{kT}{f} = \frac{kT}{6\pi\eta R_H} \quad (4)$$

Here k is the Boltzmann constant, T is the temperature, η is the medium viscosity, and $f (=6\pi\eta R_H)$ is the

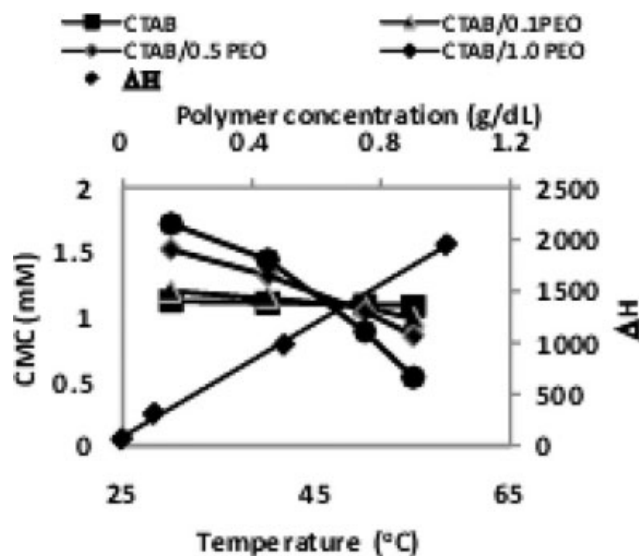


Figure 10 CMC and ΔH of polymer–surfactant mixture as a function of temperature and polymer concentration, respectively.

frictional coefficient for a hard sphere in a viscous medium. The R_H values obtained in this way for pure CTAB and PEO–CTAB mixture are plotted in Figure 12. The results indicate that R_H values increase slowly till the concentration approaches to CMC. However, as the concentration becomes higher than CMC it increases sharply, showing initiation of micellization. In case of mixture the value of R_H is higher and increasing rate is lower as compared to pure CTAB. Further to it the value of R_H is less than pure CTAB when its concentration is higher than CMC in PEO. Reason behind it is that the surfactant gets adsorbed over the polymer and hence the micelles size decreases as compared to pure CTAB.⁵⁶ The increase in polymer concentration makes the above stated impact more pronounced which prove the existence of interactions between polymer and surfactant molecules.

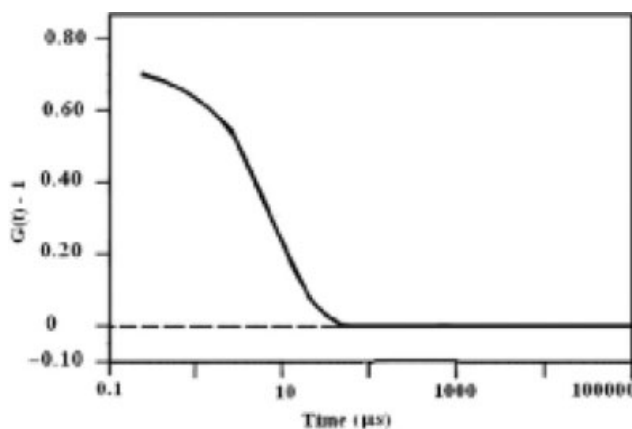


Figure 11 Schematic representation of correlation function can be obtained by dynamic light scattering measurement.

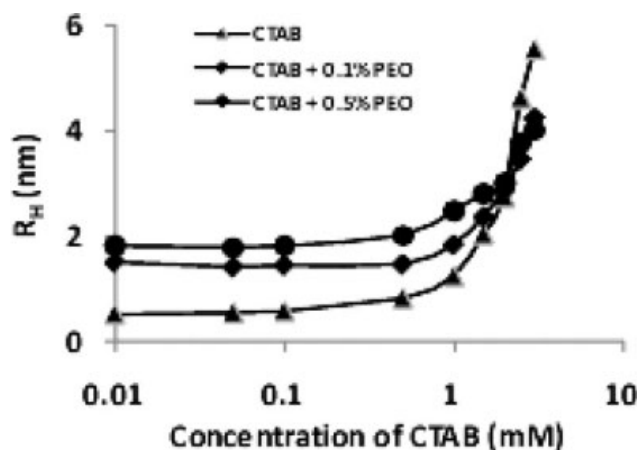


Figure 12 R_H of CTAB and its mixture with PEO as a function of its concentration.

According to laser light scattering theory for a dilute macromolecule solution or colloidal suspensions, Rayleigh ratio $[KC/R(\theta)]$ is related to polymer concentration C (g/mL) and the scattering angle θ by the following equation^{55,57,58}:

$$\frac{KC}{R(\theta)} = \frac{1}{M_w} \left(1 + \frac{1}{3} \langle R_g^2 \rangle q^2 \right) + 2A_2C + \dots \quad (5)$$

Here

$$K = \left(\frac{dn}{dc} \right)^2 \frac{4\pi^2 n^2}{N_A \lambda_0^4} \quad (6)$$

with M_w and, N_A , being weight-average molar mass and Avogadro's number, respectively.

The values of $KC/R(\theta)$ obtained for a set of concentration (C) and scattering angles (θ) are plotted against C and θ according to eq. (5) and are known as Zimm plots. From such plots the weight-average molar mass (M_w), the z-average radius of gyration (R_g), and the second virial coefficient (A_2) can be obtained. Further to it R_g is equal to R_H , if the particles are spherical; otherwise its value is less than R_H .⁵⁹ Moreover, the value of R_g varies from system to system and even depends upon conformation of the polymer molecules.^{59,60} For example, in case of spherical particles

$$R_g = \sqrt{2/5}R = 0.632R \quad (7)$$

for coil-like polymer molecules

$$R_g = 1/6 \langle \bar{R}^2 \rangle^{1/2} \quad (8)$$

and for rod-like polymer molecules

$$R_g = L^{1/2}/12 \quad (9)$$

Here, R is the radius of the sphere or root mean square end-to-end distance for spherical- or coil-like polymer molecules, respectively, and L is end-to-end distance of rod-like molecules.

The R_g/R_H of CTAB determined by using the above-mentioned equations and employing dynamic and static light scattering is reported in Figure 13. These values remain almost (~ 1 , indicating the shape of micelles as spherical) constant till CMC. However, if the concentration becomes higher than CMC it increases slowly concluding that the micelles are changing their conformation from spherical to nonspherical which may ultimately attain rod like configuration.⁶¹ It is further stated that the micelles of surfactants get adsorbed over the polymer chain and with the increase in surfactant concentration, the polymer chain configuration changes and more micelles are adsorbed over it which ultimately makes a beads necklace.^{46,47,62}

Viscometry

The viscosity of surfactant obtained at different temperatures is plotted versus surfactant concentration in Figure 14. It illustrates two sharp changes in viscosity which makes it possible to acquire CC and CMC. Therefore, we have calculated both the parameters for all the temperatures. We have also plotted reduced viscosity (=viscosity/concentration) versus concentration in Figure 15 for the whole range and for only semi dilute concentration of surfactant (insertion of Fig. 15). It can be noted that CC and CMC can be more easily and accurately determined in this way. The viscosity was also measured for polymer surfactant-mixture and the results obtained for CMC were consistent with the one obtained through surface tension and light scattering measurements. The flow activation energy can be obtained from viscosity data using the following equation⁶³:

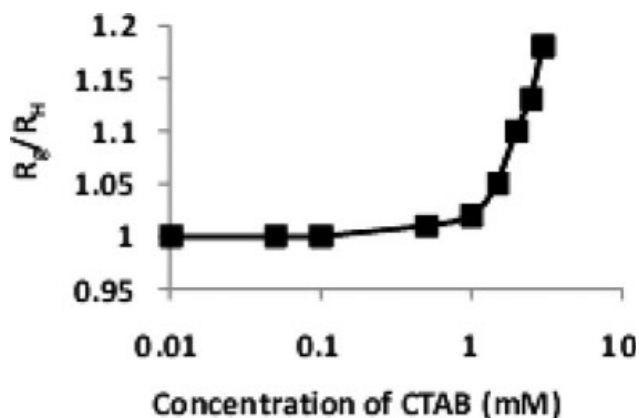


Figure 13 R_g/R_H values of CTAB as a function of its concentration.

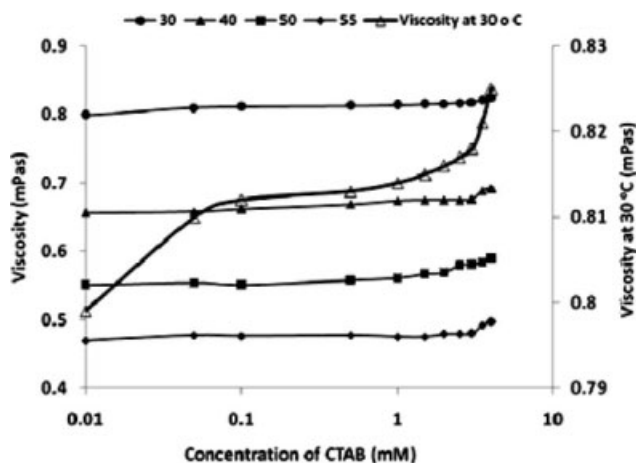


Figure 14 Viscosity of CTAB measured at different temperatures as a function of its concentration. The viscosity measured at 30°C is also plotted at extended scale to show the exact trend.

$$\eta = Ae^{-\frac{E_a}{RT}} \quad (10)$$

or

$$\ln \eta = \ln A - \frac{E_a}{RT} \quad (11)$$

Here A , E_a , and R are the pre-exponential factor, flow activation energy and gas constant, respectively. According to eq. (11), the flow activation energy can be obtained by plotting $\ln \eta$ versus $1/T$. The results so obtained are displayed in Figure 16. It can be seen that the flow activation energy increases with the addition of polymer, which indicates an increase in polymer–surfactant interactions with the increase in polymer concentration as concluded in

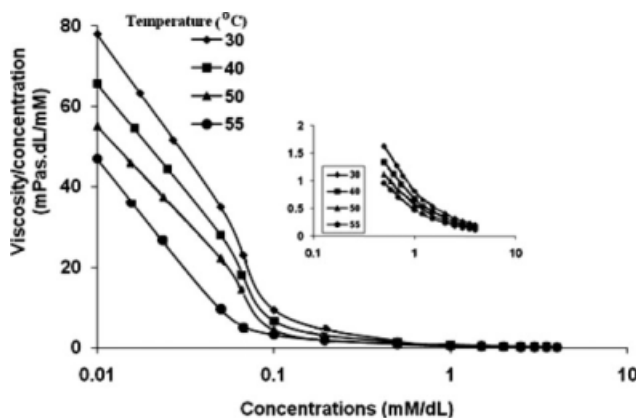


Figure 15 Viscosity/concentration of CTAB as a function of its concentration measured at different temperatures. The insertion shows the same data only for higher concentration of surfactant.

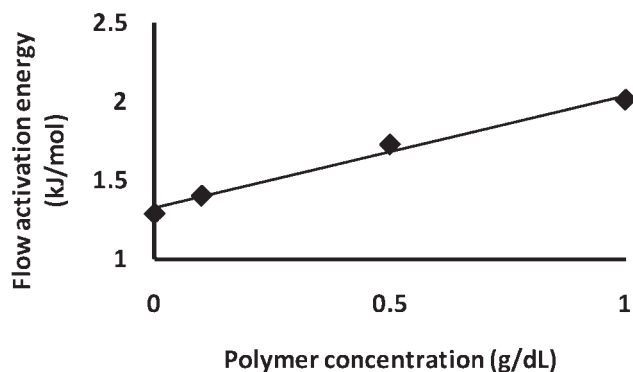


Figure 16 Flow activation energy (E_a/R) of 3 mM of CTAB as a function of polymer concentration.

case of both surface tension and light scattering data.

Conductometry

The conductance of surfactant and polymer–surfactant mixture measured shows a sharp increase with the surfactant concentration up to CMC (Fig. 17). However, further increase in concentration of surfactant reduces rate of increase in conductance (Fig. 17). This observation is very much similar to one observed by others.^{3,6,12,28,64} The data show a smooth increase in conductance with surfactant concentration and one can hardly find another hump in the data as pointed out by.^{12,65} To overcome this problem we calculated the percent difference in conductance of the mixture and plotted in as a function of surfactant concentration (Fig. 18). It can be noted that there are two surfactant concentration at which sharp variations in the curves takes place, pointing out the value of CC and CMC of the system clearly. Therefore this technique is more useful and can provide more accurate and price information about the required parameters. Certainly these results are

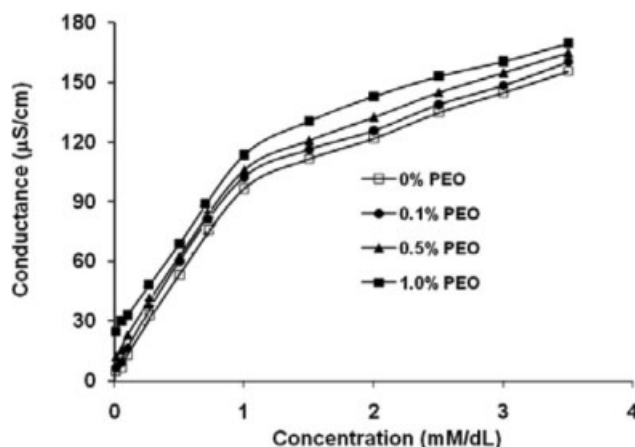


Figure 17 Conductance of CTAB measured with and without the addition of PEO.

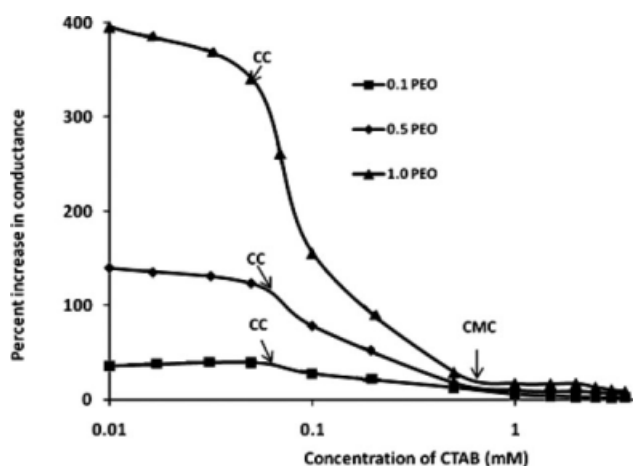


Figure 18 Percentage increase in conductance of CTAB by the addition of polymer as a function of surfactant concentration.

consistent with other techniques (Table I). We have also calculated the dissociation parameter of the surfactant from conductance data as stated in⁶⁶ which is the ratio of the slope of conductance versus concentration when $C > \text{CMC}$ and $\text{CMC} > C$. These results are plotted in Figure 19. It indicates that dissociation constant decreases with the increase in concentration of polymer. These variations also indicate that the polymer surfactant get adsorbed over each other and can not move independently.

CONCLUSIONS

The CMC of surfactant (CTAB) and polymer–surfactant mixture has been determined as a function of polymer concentration and temperature using surface tension, light scattering, viscosity, and conductance measurement. It has been observed that the CMC of the mixture of polymer and surfactant increases with the increase in polymer concentration and decreases with temperature. The ΔH values obtained from CMC data and flow activation energy from viscosity data increases with polymer concentration. The results and the conclusions drawn through various techniques are consistent. New

TABLE I
CMC (mmol/L) of CTAB and its Mixture with PEO at 30°C Using Different Techniques

Techniques employed	CTAB	CTAB + 0.1 %PEO
Surface tension	1.12	1.15
Light scattering	0.99	1.14
Conductometry	1.13	1.16
Viscometry	1.21	1.25
Average value	1.105	1.175
Standard deviation	0.087	0.088

CMC, critical micellization concentration; CTAB, cetyltrimethylammonium bromide; PEO, poly(ethylene oxide).

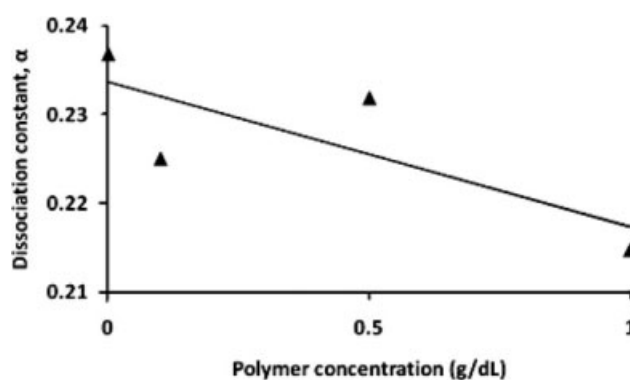


Figure 19 Dissociation constant of CTAB as a function of polymer concentration, determined from conductance data.

ways and techniques have also been introduced to interpret the data of surface tension, viscosity, and conductance to get the required information more accurately and precisely.

The funds provided by HEC to A. Rauf and F. Ahmad under different projects heading are gratefully acknowledged. The instruments, Digital TE3 Tensiometer, Lauda, and Ecoline Circulation Thermostat Model E 015T, Germany were kindly donated to M. K. Baloch by DAAD, Germany.

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