Effect of temperature on the viscosities of mixed micellar solutions

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Abstract. The effect of addition of Triton X-100 (TX-100) on the viscosities of Sodium dodecyl sulphate (SDS) micellar solution containing NaCl and Cetyltrimethylammonium bromide (CTAB) micellar solution containing KBr at various temperatures are presented. The viscosity of SDS micellar solution is found to increase on addition of TX-100 at all temperatures (25 to 45°C). However the increase in viscosity is large up to certain % of TX-100, after that the increase in viscosity is found to be small. Where as in CTAB micelles, at lower temperatures, the viscosity of micellar solution decreased up to certain composition of TX-100 and with further addition of TX-100 the viscosity got increased. At higher temperatures viscosity of CTAB micellar solution increased on addition of TX-100. Depending on the nature of surfactant system and temperature, the viscosity of micellar solution may increase or decrease on addition of TX-100. The thermodynamic parameters for the viscous flow of micellar solutions in the presence of TX-100 are also determined. The effect of TX-100 on the viscosity and the activation enthalpy for viscous flow of anionic micelles is tremendously large as compared to cationic micelles. This is due to transition of micellar shape from rod to elongated rod or to sphere in the presence of added TX-100.

INTRODUCTION

The main property of surfactant in solution is formation of micelles. Applications of such micellar solutions are in washing, cleaning, wetting, emulsifying, dispersion, and foaming. In all these cases the molecules accumulate at interface between the solution and the adjacent gaseous, liquid or solid phases. Surfactants, surface active agents or detergents are amphiphilic, organic, or organometallic compounds that tend to form association colloids or micelles in solution. Amphiphilic substances or amphiphiles are molecules possessing distinct region of hydrophobic and hydrophilic character. The balance between lyophobic and lyophilic properties is responsible for good surface activity. In different regions of these substances the polarity varies largely. Hence these substances are called as amphipathic, heteropolar or polar-nonpolar molecules.

Basing on the chemical structure of the hydrophilic part bound to the hydrophobic portion, the surfactant may be classified as cationic, anionic, noninoic or ampholytic (zwitterionic). The most characteristic and thoroughly studied property of surfactant solution is the co-operative self-association of solute within a fairly narrow concentration range in dilute solution to form high-molecular weight aggregates known as micelles. The solute concentration at which micelle formation first occurs is known as the critical micelle concentration (CMC).

The reason why do micelles form may be explained by taking into account the changes occurring when a monomer is transferred from its aqueous environment into the micelle. On transferring the monomer into the micelle, high energy of the hydrocarbon/water interface is lost, as the chain is now in contact with others of a like nature. Transfer of monomer into the micelle also means that the structure of water around the hydrocarbon part of the monomer is lost, therefore, an ordered state has become a disordered one with regard to the water, implying a positive entropy change and a decrease in free energy. The factor opposing the micelle formation in ionized surfactants is rise in free energy due to electrical work and translational freedom losses due to incorporation of
monomer into a micelle. This disordered to order transition gives a negative entropy change which will oppose the positive entropy changes occurring from loss of water structure. The overall decrease in free energy due to loss of hydrocarbon/water interfacial energy and water structure outweighs the free energy rise due to electrical work and translational freedom losses, giving a remarkable tendency to micellise.

Depending upon the nature of the hydrophilic head group, micelles can have either cationic, anionic, zwitterionic, or noninoic surfaces. Aqueous solutions of surfactant molecules, at CMC, associate dynamically to form normal micelles. Such micelles are roughly spherical. Surfactants in nonpolar solvents, in the presence of traces of water, associate to form the so called “reversed” or “inverted” micelles. The structure of the micelle is reversed, the polar head groups of the monomer being present in the centre of the micelle, and the hydrocarbon chains extending outwards into the solvent. Such micelles could be formed in presence of traces of water which forms a water pool in the interior of the micellar aggregate. The formation of micelle from more than one chemical species gives rise to what are known as mixed micelles.

The discontinuity in some physical property of the solution can be used to identify the CMC, and techniques such as light scattering, ultracentrifugation and viscosity are used to determine the size and shape of the micelle.

The critical micelle concentration and micelle size depends on the length of the hydrocarbon chain. Generally, the CMC decreases as the hydrocarbon chain length increases. For ionic detergents the CMC initially decreases with increasing temperature at low temperature and increases at high temperature. For nonionic detergents the CMC decreases with increasing temperature. The CMC has been found to increase up to a pressure of 1000 atmospheres and decrease with further increase of pressure.

Additional of polar and nonpolar additives to the solutions of surfactants may alter the aggregation behaviour such as CMC, aggregation number, size and shape of micelle. It is clear that, in addition to their function in areas of commercial interest, surfactants play a major role in the effective accomplishment of life process, such as adherence and food emulsification in micro-organisms and surfactant tension in the mammalian lung. Surface active agents are also used in pharmaceuticals and agricultural preparations. These surface active agents may influence the biological efficacy of the drug or pesticide. Many poorly soluble drugs and pesticides are administered in a solubilized form using micellar solutions for increasing the bioavailability and targeting to the site action. Certain surfaces have the ability to increase the permeability of some bacterial cell walls, and hence are synergistic with some antibacterial agents.

It is also clear from the literature that micellar media have attracted wider attention than other media in recent years, with specific and judicious choice of media, chemical transformations can be carried out more swiftly, under milder conditions with higher yields and fewer by-products and if necessary with good stereo and regio-chemical control.

As seen earlier that the structural changes in the organized media are sensitive to the condition under which they are prepared. A study of transition of one structural state to another is very important from their practical application point of view. However from the literature a little amount of work is done on the formation of mixed micelles with larger aggregates (worm like micelles). In order to study in detail we have selected two mixed micellar systems composing of anionic surfactant/non-ionic surfactant and cationic surfactant/non-ionic surfactant. Structural transition in these mixed micelles have been studied by viscosity measurements of aqueous solutions of 0.3M SDS + 0.5M NaCl and 0.1M CTAB + 0.1M KBr in presence of added Triton X-100 (TX-100). Addition of TX-100 form mixed micelles and change the micellar properties.

Additionally, the effect of temperature on the viscosities of aqueous micellar solutions of SDS/NaCl/TX-100 and CTAB/KBr/TX-100 has been studied. The activation free energies (ΔG*), enthalpies (ΔH*) and entropies (ΔS*) of viscous flow have been calculated. The range of variables covered in the present study has been compiled in Table.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum</th>
<th>Maximum</th>
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<tbody>
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<td>Temperature (°C)</td>
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<td>65</td>
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<tr>
<td>For SDS/NaCl System</td>
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<tr>
<td>Concentration of TX-100 (wt%)</td>
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<td>For CTAB/KBr System</td>
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<tr>
<td>Concentration of TX-100 (wt%)</td>
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<td>5.63</td>
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</table>
MATERIALS AND METHODS

Materials

Sodium dodecyl sulphate (SDS) and Cetyltrimethylammoniumbrimoide (CTAB) were obtained from Sigma-Aldrich of “AR grade” with ≥99% purity were recrystallised twice from ethanol-water mixture and acetone respectively. Both the surfactants were ascertained from the absence of minimum in the surface tension versus logarithm of concentration plots. The critical micellar concentration of SDS and CTAB were $8.2 \times 10^{-3}$M and $9.2 \times 10^{-4}$M respectively at 25°C.

Polyethylene glycol tert-octylphenyl ether known as Triton X-100 or TX-100, was obtained from Sigma-Aldrich of “BioXtra Grade” and was used as supplied. Both potassium bromide (KBr) and Sodium Chloride (NaCl) obtained from Rankem of “AR grade” were ignited on an evaporating dish for one hour and stored in a desiccator until use. Demineralized water redistilled from alkaline potassium permanganate was used.

Preparation of Solutions

0.3M SDS in 0.5M NaCl and 0.1M CTAB in 0.1M KBr solution were prepared by weighing required amount of surfactants and salts in two volumetric flasks with distilled water. The solutions thus obtained were used as stock solutions or as mixed solvents to study the effect of TX-100 on its properties. The concentrations of mixed solvents were fixed throughout the work. Different solutions of TX-100 were prepared in the mixed solvent (0.3M SDS + 0.5M NaCl or 0.1M CTAB in 0.1M KBr) and the concentrations of TX-100 were calculated as weight % of TX-100 in the mixed solvent.

Viscosity Measurements

The viscosities of the solutions were measured in Ubbelöhde viscometers thermostatted at a fixed temperature. Since the viscosities were highly dependent on the rate of flow, the method used was same as described by Gamboa and Sapulveda. For this purpose, a wide U-shaped tube containing water was connected to the branch of the viscometer which under normal operation conditions is open to the atmospheric pressure. This device allowed us to change the pressure, p under which the solution flows and thus to obtain viscosity values at different rates of flow, from the slopes of the straight lines p versus 1/t according to the well known Poiseuille equation

$$p = \eta \times A \times 1/t$$

Where t is the time of flow of the solution in a given viscometer. A is a characteristic constant of the viscometer (obtained by calibration with liquids or solutions of known viscosities), and η the specific viscosity. Relative viscosity of solution $\eta/\eta_o$ is given by $\eta/\eta_o = t/t_o$, where $t_o$ is the flow time for the solvent. Density corrections were not made since it was found that these were negligible. Micellar transition from larger aggregates to smaller ones were studied by the temperature dependence of the viscosities of the systems. Relative viscosities were measured at 25, 30, 35, 40 and 45°C. The temperature of the bath was controlled to an accuracy of ±0.1°C.

RESULTS AND DISCUSSION

In the present investigation, measured relative viscosities of aqueous micellar solutions with fixed salt concentration and in the presence of various weight percentages of Triton X-100 are obtained in for 0.3M SDS + 0.5M NaCl and 0.1M CTAB + 0.1M KBr systems respectively.

Plots of $\ln(\eta/\eta_o)$, where $\eta$ and $\eta_o$ are the viscosities of the solution and solvent water respectively, versus the % TX-100 are shown in Fig.1 for SDS and Fig.2 for CTAB. From Fig.1 it may be seen that on addition of TX-100 the increase in $\ln(\eta/\eta_o)$ is large up to certain % TX-100, after that the increase in $\ln(\eta/\eta_o)$ is small.

From Figs.1 and 2 it may be seen that the variation of $\ln(\eta/\eta_o)$ with added Triton X-100 for SDS and CTAB micellar systems are in different trends. These may be explained by considering the formation of mixed micelles with TX-100.
Mixed micelles are formed in mixed solutions of SDS and TX-100 or CTAB and TX-100. They are uniformly mixed in the mixed micelles. In the formation of SDS/TX-100 mixed micelle, TX-100 molecules are solubilized such that the α-methylene group of SDS is near to the phenoxy ring of TX-100 which are nearest to the polar head of SDS.

In the formation of CTAB/TX-100 mixed micelle, TX-100 molecules are solubilized such that the α-methylene group of CTAB is near to the phenoxy ring of TX-100. The trimethyl groups attached to the polar heads of CTAB molecules are located between the first oxyethylene groups next to the phenoxy rings of TX-100 molecules. The exterior part of the mixed micelles are closely packed (coiled) hydrophilic polyoxyethylene chains. They gradually extend with an increase in CTAB/TX-100 molar ratios in the mixed solutions.

The polarity in the micro-environment of CTAB/Triton X-100 mixed micelles is found to be very small in comparison with SDS/Triton X-100 micelles well above CMC. The lower micropolarity shown by CTAB/Triton X-100 micelles infers the formation of more close micelles in which the water penetration is very much restricted, so that the incorporation of cosurfactant CTAB in the micelle of Triton X-100 causes a more dehydrated structure of the mixed micelles. Hence at lower temperatures the viscosity of CTAB/KBr/Triton X-100 micellar solutions decreases with added Triton X-100 up to certain % of Triton X-100 is due to the solubilization of dehydrated Triton X-100 in solution. Further addition of TX-100 increases the viscosity of mixed micellar solution is because of increased hydration of Triton X-100 molecules in the micelle. But at high temperatures (at 40°C and 45°C) viscosities of micellar solution increases from the beginning on addition of TX-100 infers the incorporation of hydrated TX-100 molecules in CTAB/KBr micelles in formation of swollen mixed micelles.

The temperature dependence of viscosities of micellar solution in the presence of TX-100 have also been studied for both SDS/TX-100 and CTAB/TX-100 micellar systems at fixed salt concentrations. The viscosity of the micellar solution was found to decrease with increasing temperature. Plots of ln(η/η₀) versus 1/T for micellar solutions in the presence of added TX-100 are shown in Fig.3 for SDS/NaCl and Fig.4 for CTAB/KBr systems. The observed linearity of the ln(η/η₀) versus 1/T plots can be interpreted in terms of the equation:

$$\ln(\eta/\eta_0) = \ln A + \Delta G^*/RT \quad \text{.................................(2)}$$
Here A is a constant and $\Delta G^*$ is the activation free energy for viscous flow. Since the densities of the solutions were very close to unity, hence by neglecting kinematic corrections, values of the activation free energy, $\Delta G^*$, were calculated from the slopes of straight lines obtained from plots of $\ln(\eta/\eta_0)$ versus $1/T$.

The temperature effect on viscosities of mixed micellar solutions may be explained by considering the effect of temperature on ionic micelles and nonionic micelles individually in aqueous solutions. Observation of high values for viscosities in cationic and anionic micellar solutions in the presence of added salts is due to micellar sphere-to-rod transition which occurs over a certain range of concentration of either surfactant or added salt. Temperature studies on concentrated ionic micellar systems with and without added electrolytes indicated that an increase in temperature favours the conversation of rod-like micelles into spherical ones. Where as in nonionic micellar system such as aqueous solutions of TX-100, the micelle is found to be in spherical or oblate ellipsoid shape, but the size of micelle and aggregation number increases with increasing % TX-100.

Increasing the temperature of TX-100 micellar solution, towards the cloud point, micelle radius and aggregation number increase, the increase in aggregation number being large above 40°C. And the degree of hydration at first increases but then tends to saturate with increasing temperature.

In SDS/NaCl/TX-100 micellar systems, relative viscosities are found to decrease with increased temperature and show linear variation of $\ln(\eta/\eta_0)$ versus $1/T$ for all compositions of added TX-100. Where as in CTAB/KBr/TX-100 micellar systems, the relative viscosities are found to decrease with increasing temperature up to 5.6% of TX-100 and follows linear variation of $\ln(\eta/\eta_0)$ with $1/T$.

Further addition of TX-100 to CTAB/KBr micellar system, relative viscosities are found to be more or less equal and will not follow linear relationship of $\ln(\eta/\eta_0)$ versus $1/T$. Hence we have not calculated $\Delta G^*$ values in this region.

The activation enthalpy, $\Delta H^*$ for viscous flow was calculated from the temperature dependence of $\Delta G^*$ by using the well known equation:

$$\frac{\partial (\Delta G^*/T)}{\partial (1/T)} = \Delta H^*$$ ..............................................(3)

The variation of $\Delta G^*/T$ with $1/T$ for micellar solutions in the presence of added TX-100 are shown in Fig.5 for CTAB/KBr and Fig.6 for SDS/NaCl systems. $\Delta H^*$ values were calculated from the slopes of straight lines obtained from the plots of $\Delta G^*/T$ versus $1/T$. Entropic contributions $\Delta S^*$ to the activation free energy was calculated from the obtained values of $\Delta G^*$ and $\Delta H^*$. $\Delta H^*$ and $\Delta S^*$ for SDS/NaCl/TX-100 and CTAB/KBr/TX-100 systems...
respectively. The variation of $\Delta H^*$ for viscous flow of micellar solutions as a function of added TX-100 are shown in Fig.7.

It may be seen from the results that $\Delta H^*$ values cover almost the total contribution to $\Delta G^*$ for both SDS/NaCl/TX-100 and CTAB/KBr/TX-100 micellar systems, and accordingly the entropic contributions are zero\(^{15}\). Further, the observed linearity in the $\ln(\eta/\eta_0)$ versus $1/T$ plots also implies that the enthalpic and entropic contributions to $\Delta G^*$ are independent of temperature. The energy involved in the transition from larger aggregation to smaller aggregates is reflected by the $\Delta H^*$ values, which seems to be the more important contribution, related to the rupture of cylindrical micelles to give smaller aggregates.

**FIGURE 5.** Gibbs-Helmholtz plots for 0.1M CTAB + 0.1M KBr solution in the presence of Triton X-100

**FIGURE 6.** Gibbs-Helmholtz plots for 0.3M SDS + 0.5M NaCl solution in the presence of Triton X-10

**FIGURE 7.** Variation of activation enthalpy ($\Delta H^*$) for the viscous flow of surfactant solution as a function of added Triton X-100.

From Fig.7, it may be seen that $\Delta G^*$ and $\Delta H^*$ values are highly dependent on the nature of micellar systems and added TX-100. Activation energies for viscous flow of micellar solutions below the micellar transition from sphere-
to-rod were reported to be in the range 3.8-4.2 kcal/mole. Which are characteristic of water, aqueous solutions of molecularly dissolved substances, and spherocolloids. The high values of $\Delta H^*$ ($\Delta H^* \geq 12$ kcal/mole) correspond to the formation of larger aggregates (elongated rods), and small values ($\Delta H^* \approx 4$ kcal/mole) correspond to smaller aggregates (spherical micelles).

From the magnitude of these thermodynamic parameters for aggregated systems, the initial increase in $\Delta H^*$ values of SDS/NaCl micellar systems with increasing % TX-100 infers the increasing size of rod shaped micelles (elongated rods) by addition of TX-100 molecules (Fig.7). Further increase in % TX-100, $\Delta H^*$ values decreases slightly indicates the breaking of cylindrical micelles into smaller size cylinders. But smaller increase in the viscosity of SDS/NaCl micellar solutions with increase in % TX-100 above 2.5% of Triton X-100 is due to increasing hydration of solubilized TX-100 molecules in the mixed micelle.

In CTAB/KBr micellar systems, it may be seen from Fig.7 that the values of $\Delta H^*$ decrease with the addition of TX-100 that infers the breaking of rod shaped micelles into spherical micelles. From the shape of curve, it may be concluded that the transition of larger aggregates to smaller ones can not be conceivable in one step but the transition may occur in infinite steps as Triton X-100 is added to CTAB/KBr micellar solutions.

**CONCLUSIONS**

Addition of TX-100 to SDS/NaCl micellar solutions increases the size of rod shaped micelles up to certain % TX-100 and further addition of TX-100 decreases the size of cylindrical micelles into smaller cylinders. From viscosity measurements and thermodynamic quantities, it is also concluded that the degree of hydration of TX-100 molecules increases at higher % of TX-100. In CTAB/KBr micellar systems, the decrease in $\Delta H^*$ values with the addition of TX-100 infers the breaking of rod shaped micelles into spherical micelles. It is also concluded that the transition of larger aggregates to smaller ones cannot be conceivable in one step but the transition may occur in infinite steps.

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