

Chapter VII

Summary and Conclusion

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Chapter I

In chapter 1, a general introduction covering the description of different types of surfactants, their properties and their molecular assemblies, viz., micelles are presented. Self-assemble surfactants or surfactant aggregates become popular to the researchers in recent years due to a huge benefit achieved in many industries producing detergents, cosmetics and pharmaceuticals which have surfactants as one of their constituents. Added electrolyte has great influence on the shape of ionic micelles and also as the counterion concentration is increased, the shape of ionic micelles changes in the sequence spherical - cylindrical - hexagonal - lamellar.

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Chapter II

The scope and object of the present investigation has been incorporated in chapter II. Recently the role of the counterion binding has been recognized in the evaluation of the energetics of micellization process. The study of the effect of counterions eliminates some of the complications by leaving the properties of the amphiphilic ion as a constant factor and thus simplifies some of the interpretation of the experimental results. But, it often leads to complications connected with limited stability and preparative difficulties of the surfactant containing different counterions. Further, the literature of dodecyl benzene sulfonate moiety with different counterions is very rare.

The micellar structure of sodium dodecyl benzene sulfonate changes to bilayers in presence of added electrolyte. Compounds with polar groups such as alcohols can be expected to solubilize in the hydrophilic regions. Addition of alcohol can strongly influence the behaviour of the micelle and changes the micellar size depending on the hydrophilic/hydrophobic character of the alcohol.

Dye-micelle interaction is effective to determine the cmc of the surfactant. On the other hand self aggregation of the dyes is important to understand the self-quenching phenomena occurring in the different instruments and also the phenomena of energy transfer in biological systems. Surfactant mixtures are commonly preferred in medicinal and pharmaceutical formulations and industrial preparations due to the purpose of suspension, solubilization and dispersion as compared to single surfactant. The mixed surfactant exhibits superior interfacial properties such as higher surface activity and lower critical micelle concentration (cmc). Generally, it has been observed that with anions that associate strongly with the surfactant cations, worm-like micellar growth occurs rapidly at low surfactant and salt concentrations. The rheological behaviour exhibited by these system is viscoelastic and analogous to that observed in solution of flexible polymers. These surfactant solutions undergo similar rheological behaviour whether they are prepared directly from surfactant salts with a strongly associating anion or by addition of strongly associating anions to solutions prepared from surfactant salts with weakly associating anions. The rheological behaviour observed for wormlike micelles in the surfactant solution is similar to that for flexible polymers, and therefore, aqueous solutions of entangled wormlike micelles are often called "living polymer systems". The research of wormlike micelles has drawn considerable interest owing to their superior properties and wide applications.

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Chapter III

Surfactants with different counterions were prepared from purified SDBS by ion-exchange techniques using a strong ion-exchange resin. The cmc and other thermodynamic parameters were determined from the temperature dependence surface tension as well as specific conductance data.

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At a specific temperature, the cmc values of the surfactants follow the order $\text{Na}^+ > \text{Li}^+ > \text{NH}_4^+ > \text{K}^+ > \text{N}^+(\text{CH}_3)_4 > \text{N}^+(\text{C}_2\text{H}_5)_4 > \text{N}^+(\text{C}_3\text{H}_7)_4 > \text{N}^+(\text{C}_4\text{H}_9)_4$. Among tetraalkyl ammonium cations along with ammonium cations, the binding ability is highest for $\text{N}^+(\text{C}_4\text{H}_9)_4$ and decreases in the following order $\text{N}^+(\text{C}_4\text{H}_9)_4 > \text{N}^+(\text{C}_3\text{H}_7)_4 > \text{N}^+(\text{C}_2\text{H}_5)_4 > \text{N}^+(\text{CH}_3)_4 > \text{NH}_4^+$. As a result, the reduction of the electrostatic

intermicellar repulsive force occurs which leads to the formation of the micelle in the lower concentration range.

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The maximum surface excess concentrations (Γ_{\max}) is a useful measure of the effectiveness of adsorption of the surfactant at air-solution interface, since it is the maximum value that adsorption can attain. For dodecyl benzene moiety with varying counterions, a slight increase may be due to the lower hydration effect of the dodecyl benzene sulfonate surfactants at higher temperature and hence increasing tendency to move the molecules to the air-liquid interface. The benzene ring in the surfactants may also be partially responsible for this result via steric inhibition during adsorption process. With increase in temperature, amphiphilic molecule tend to form a closely packed monolayer film of the hydrocarbon chain at the air / solution interface owing to the decreased repulsion between the oriented head groups indicated by the value of A_{\min} .

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The temperature dependency of DBS micelles having different counterions also enables one to determine the thermodynamic parameters of micellization. Negative sign of ΔH_m^0 suggests that surfactant aggregation is an endothermic process. The tetraalkyl ammonium surfactants have their enthalpy of micellization relatively close to each other. The enthalpy value first decreases with increase in chain length, reaches a shallow minimum for tetrapropyl ammonium counterions and then increases. A close look on the thermodynamic parameters support the view that in order to form micelle the gain in entropy is the major factor leading to negative change in Gibb's free energy. But for the alkali metals counterions, the fact that though the free energy changes are not very different, the entropy change is significantly higher and the enthalpy changes are much lower for K^+ counterion containing DBS compared to all other systems. This suggests that the entropy contributes as a major driving force in micellization. With increasing temperature, ΔS_m^0 decreases systematically for a particular type of counterion, suggesting a disruption of ordered arrangement of water dipoles around the amphiphilic part of the surfactant molecules. Though the free energy change is not very different for all the systems, the enthalpy change is relatively higher.

The effective interactions associated with hydrocarbon chains may be expressed by standard heat capacity of micelle formation, $\Delta_{mic}C_p^0$. The calculated values of $\Delta_{mic}C_p^0$ for DBS with varying counterions fall between a wide range of value viz., -67 to -934 J mol⁻¹ K⁻¹, for the variation of temperature between 283 K and 313 K. For the tetraalkyl ammonium counterions, the order of $\Delta_{mic}C_p^0$ values at a particular temperature is as follows: (CH₃)₄N⁺ > (C₄H₉)₄N⁺ > (C₂H₅)₄N⁺ > (C₃H₇)₄N⁺. At high temperatures, $\Delta_{mic}C_p^0$'s give large negative values due to solvation of ions upon demicellization, and this is quite reasonable because as the temperature is increased cmc value also increases in all the present systems.

Enthalpy and entropy change in the micellization process show a linear relationship for all the surfactant systems at a particular temperature and this is known as the enthalpy-entropy compensation. The slope and intercept of the straight line has different meanings, slope interprets a measure of desolvation part of micellization which means a characteristic of solute-solute and solute-solvent interaction whereas the intercepts interprets solute-solute interactions. The intercepts (ΔH_m^*) has been found to be -32.6 kJ mol⁻¹ for DBS which correspond to the driving force of micellization where the entropy does not contribute the process at that particular temperature.

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The literature concerning DBS surfactant is not so huge as compared to SDS or AOT and this may be due to the presence of several isomeric forms of DBS moiety. The range of cmc values of the following three surfactants with varying counterions are 3.33 mM to 0.79 mM, 9.21 mM to 1.10 mM and 3.55 mM to 0.75 mM for DBS, DS and AOT respectively. For all the surfactant systems with tetraalkyl ammonium counterions, cmc decreases with increase in tetraalkyl ammonium chain length. The order of cmc for alkali metal counter ions and ammonium ion is not same for the three surfactants. The orders are: NH₄⁺ > Li⁺ > Na⁺ for dodecyl sulfate, NH₄⁺ > Na⁺ > Li⁺ > K⁺ for AOT and Na⁺ > Li⁺ > NH₄⁺ > K⁺ for DBS. This trend can be explained by the counterion binding to micelles. The general tendency of cmc change with temperature is parabolic in nature. However, the present DBS with different counterions show linear types of temperature dependency.

Among the Γ_{max} values of DS, DBS and AOT, only the DS follows the general trend with temperature. The order of Γ_{max} values is lower in the case of DBS as compared to DS and AOT suggesting effectiveness of adsorption of this surfactant at air-solution interface is low. The lower A_{min} values for DS and AOT suggest that these amphiphiles tend to form a closely packed monolayer film of the hydrocarbon chain at air / liquid interface as compared to DBS with same counterions.

In between the DS and DBS systems, the ΔG_m^0 value is higher for DS systems particularly more pronounced for the alkyl ammonium counterions. The enthalpy of micellization is negative for all the counterions in case of AOT and DBS. But for DS, there are both positive and negative value of enthalpy change of micellization suggests that both exothermic and endothermic process occurs at the micellization process. The less enthalpy values are shown by potassium counterions for both AOT and DBS surfactants with higher enthalpy values.

The effective interaction associated with hydrocarbon chains may be expressed by standard heat capacity of micelle formation, $\Delta_{mic}C_p^0$. The $\Delta_{mic}C_p^0$ values for comparison are calculated for only SDBS and SDS systems due to their very similar molecular formula and also contain a dodecyl moiety in hydrocarbon chains. The calculated values of $\Delta_{mic}C_p^0$ for SDBS fall between a wide range of value viz., -381.8 to -933.8 J mol⁻¹ K⁻¹ for the temperature range 283-293 K. On the other hand, SDS which also yields $\Delta_{mic}C_p^0$ values between -607 and -644 J mol⁻¹ K⁻¹ in the same temperature range.

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Chapter IV

Added electrolytes are known to affect the aggregation behaviour of ionic surfactants. In the present study, the surfactant chosen is again dodecyl benzene sulfonate (DBS) with different counterions, viz., Na⁺, Li⁺, K⁺, NH₄⁺, (CH₃)₄N⁺, (C₂H₅)₄N⁺, (C₃H₇)₄N⁺ and (C₄H₉)₄N⁺ and the electrolytes are the symmetrical tetraalkyl bromides. The critical micellization concentrations of DBS with different counter ions in presence of corresponding aqueous bromide salt solutions in the concentration range of (5-0.5) mM were determined mainly by surface tension and partly also by the electrical conductivity method. Increasing the concentration of a particular electrolyte causes a substantial decrease in the cmc. This can be accounted for by the fact that in

solutions of high ionic strength, the forces of electrostatic repulsion between head groups in a micelle are considerably reduced due to charge screening. Such reduction in the cmc values of anionic surfactants is also observed in presence of all systems with corresponding bromide electrolytes. TMA⁺ ions with smallest ionic size are the most hydrated in aqueous solution compared to that of the others in the group, viz., TEA⁺, TPA⁺ and TBA⁺. The higher homologues of the series, TPA⁺ and TBA⁺, have long hydrocarbon chains and some of these chains are supposed to penetrate in the micellar core due to hydrophobic interaction. Hence, at a given temperature, the formation of micelles of DBS in these electrolyte media favours a cmc lowering in the order TMAB > TEAB > TPAB > TBAB.

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The increase in the β values on moving from TEA⁺ to TBA⁺ is due mainly to the increased hydrophobic interaction between the alkyl parts of both the surfactant and the added electrolyte. For inorganic ions including ammonium ions, similar result is observed due to the increase in size of the cations. Here, the order of β values is K⁺ > Na⁺ > NH₄⁺ > Li⁺. In the present case, slight increase in the values of Γ_{\max} is observed which may be due to the effectiveness of adsorption. With increase in temperature, the A_{\min} value shows the inverse trend as that of Γ_{\max} .

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The values of ΔG_{mic}^0 , ΔH_{mic}^0 and ΔS_{mic}^0 in the presence of 0.0005 M corresponding bromide salts have been calculated. The variation of ΔG_{mic}^0 with temperature is small for all the systems investigated. The values of ΔH_{mic}^0 increase with the increase in temperatures in all case. The higher negative values of enthalpy at higher temperatures probably suggest the importance of London-dispersion interactions as an attractive force contribution for micellization. The entropy of micellization for different systems are all large and positive except potassium dodecyl benzene sulfonate, indicating that the micellization process is entropy dominated. Presence of salt may screen electrostatic repulsion between head groups and decrease the thickness of the interfacial water layer. The thickness of the interfacial layer is decreased when salts are added into surfactant systems. The reason is that the positive ions of the salt can enter into the interfacial region and destroy the hydrated layer.

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The most interesting aspects of these microheterogeneous entities are their ability to accommodate organic molecules. In this respect ethylene glycol (EG) showed the reverse effect compared to the other alcohols and this may be explained by its higher dielectric constant, small hydrophobic surface and greater capability of hydrogen bond formation. Influence of very common short chain alcohols, viz. ethylene glycol on the micellization of DBS with different counterions in aqueous medium are studied in the present investigation within the temperature range of 293-313K. For SDBS-ethylene glycol-water system [10%, 20% and 30% ethylene glycol (w/w)], the cmc was determined conductometrically. The cmc values increase considerably upon addition of ethylene glycol. The larger cmc at higher ethylene glycol content is a result of the presence of a structure-breaking solute which in the aqueous phase adversely influences the hydrophobic group causing the micellization process unfavourable. The increase in cmc values with temperature at a given concentration of ethylene glycol is attributed to the disruption of the solvent structure with the increase in temperature.

With increase in temperature, the ΔG_m^0 value becomes more negative, which is a general trend. The other two thermodynamic parameters viz. ΔH_m^0 and ΔS_m^0 also show their necessary contribution in favour of micellization process. The entropy of micellization is positive in water and becomes less positive in the presence of increasing amounts of ethylene glycol. The overall exothermicity of the present system indicates that both the structure-breaking ability of ethylene glycol and its interaction with the hydrophilic groups of the surfactants are dominating factors. Depending upon the temperature and the proportion of ethylene glycol present, small negative ΔG_t^0 as observed are there in different surfactants, may be due to a reduction of the micelle solvation in the mixed solvent.

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Chapter V

One of the most fundamental and important structural parameters of micellar aggregates is the aggregation number, or the average aggregation number of detergent molecule in micelle unit. The value of the aggregation number contains information on the micellar size and shape, which may be important in determining stability and practical applications of the investigated systems. In the present study, the measurement of aggregation number is done by a simple process based on the

quenching of a luminescent probe by a hydrophobic quencher. In the present experiment, the static quenching is done to measure the aggregation number of the surfactant with different counterions by steady state fluorescence quenching (SSFQ) process.

In the case of pyrene, a quencher is used to measure the aggregation number, the ratio of intensity of the first (I_1 at 373nm) and third peaks (I_3 at 384 nm) is a sensitive parameter characterizing the polarity of the probe environment. In the present study, good experimental result for all the surfactants have been obtained suggesting constancy of both N and K_{SV} . At 298 K, the aggregation number become minimum in the case of NH_4^+ counter ion. But as the alkyl groups are substituted for hydrogens, the aggregation number increases because of the formation of larger aggregates which is the consequences of the increased charged screening at higher counter ion binding capacity via stronger hydrophobic interactions with the micelles. This increasing trend of aggregation number continues up to the tetraethylammonium ions. But for tetrapropyl and tetrabutyl ammonium ions, aggregation number progressively decreases. It seems apparent that in the present systems, as the hydrophobicity of the counter ions increases, the counter ion binding/condensation increases due to increased hydrophobic interactions and eventually the cmc decreases. However, enhanced electrostatic charge screening of the head groups is incapable of increasing the aggregation number of the micelles for tetrapropyl and tetrabutylammonium counter ions. For alkali metal counter ions, hydration plays an important role along with ionization degree and hydrophobic interactions. As the size of the counter ion increases, the degree of hydration decreases due to more hydrophobicity of the counter ions and also enhanced electrostatic charge screening of the head groups.

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In the chapter, we also use an oxazine dye with dodecyl benzene sulfonate with varying counterions to characterize qualitatively the dye-surfactant interactions. The oxazine dyes display surprising long-wavelength absorption and emission maxima in fluorescence which makes these groups of dye an important fluorescent probe. We have studied the steady-state spectra of surfactants by a typical oxazine dye, Cresyl fast violet. Due to these dye-surfactant interactions, the changes in spectral characteristics are observed qualitatively. At concentration below the normal cmc,

surfactants and dyes can interact to form a mixed micelle of the two species, lowering the resultant cmc. Above the cmc, a change in the molecular environment of the dye due to incorporation into the micelle interior is observed.

At concentrations of surfactants below the cmc, the fluorescence intensity decreases continuously with increase in surfactant concentration. When the surfactant concentration reaches cmc, the intensity starts increasing continuously with increase in surfactant concentration. The result suggests that the free monomer is tied up in ion pair or clusters at sub-micellar region.. The order of the ion pair formation or cluster formation for alkali metal counter ions is as follows: $\text{Li}^+ > \text{K}^+ > \text{Na}^+$ and for tetraalkyl ammonium counter ion and ammonium ion the trend is as follows: $\text{NH}_4^+ > (\text{C}_4\text{H}_9)_4\text{N}^+ > (\text{C}_3\text{H}_7)_4\text{N}^+ > (\text{C}_2\text{H}_5)_4\text{N}^+ > (\text{CH}_3)_4\text{N}^+$. These trends are probably observed as the consequences of the increased charged screening and higher counter ion binding capacity via stronger hydrophobic interactions with the micelles.

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Anisotropy measurement was done with the same dye in presence of surfactants. The data were analyzed with the software "Felix GX", supplied by the manufacturer with the fluorescence spectrophotometer instrument. The lower the anisotropy value, the faster is the rotational diffusion. The trend is normal for all the surfactant except lithium dodecyl benzene sulfonate and ammonium dodecyl benzene sulfonate due to high hydration enthalpy of lithium and intermediate size of the ammonium ion.

The interpretation of the results emerges from steady-state anisotropy of these dye-surfactant complex system is not straightforward; its value depends on various factors such as, the rotational motion and the possible dye - surfactant interactions. With decrease in surfactant concentration, the packing of amphiphiles at the interface is less compact which show a decrease in polarization value. Below the cmc, the increase in polarization value can also attributed to the higher dye-surfactant interactions. Upon addition of surfactant, the anisotropy initially increases fast, but this increase in a range of very low surfactant concentration and below the cmc. This is the evidence of interactions that reduce the dye's ability to rotate freely. A dye-surfactant ionic pair or cluster would result in such a decreased ability to rotate because of its larger size than an individual dye ion. The increase polarization value with increasing surfactant

concentration probably means that more surfactant molecule join the clusters as the surfactant concentration increases. Around the cmc, the increase of anisotropy value drops to an extent. This could be the result of the release some of the dye molecule from their ionic interactions with the surfactant monomers. Above the cmc, the anisotropy increases little before leveling off. This shows that the dye is less free to rotate in the micellar environment. The dye's lower ability to rotate above the cmc shows that it is within the micelle in a more rigid formation. The value of the cmc derived from polarization value is in good agreement with the value determined by surface tension and conductometrically for each of the surfactant. The slight difference in the cmc values observed in these two methods may be due to the fairly strong interaction of dye molecules with the surfactants.

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In the present experiments, time resolved fluorescence studies were also carried out to determine the emission decay parameters of all the surfactants with different surfactant concentrations. The concentration of the dye used was 5×10^{-6} (M). Thus, high dye concentrations could not be used, as at these concentrations lifetime values may be drastically decreased due to fluorescence quenching. So, only four set of concentrations for each dye have been taken for. The lifetime values did not change significantly in a regular manner with the change in surfactant concentration and indicates single exponential fluorescence decay characteristics in presence of all the surfactants.

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Chapter VI

Compared to single surfactant, the mixed surfactant exhibits superior interfacial properties such as higher surface activity and lower critical micelle concentration (cmc). Surfactant mixtures are commonly preferred in medicinal and pharmaceutical formulations and industrial preparations due to the purpose of suspension, solubilization and dispersion. Wormlike micelles are long, self-assembled, semi-flexible, breakable polymer-like materials with surfactant heads on the outside and tails in the core. They display a striking range of dynamical properties, including anomalous relaxation, shear banding, and rheological chaos. Above a threshold concentration c^* , wormlike micelles may entangle into a transient network, which

displays remarkable viscoelastic properties. Mixtures of cationic and anionic surfactants show not only synergistic effect of the aggregation properties but also triggered micellar grow in one dimension to form long worm-like micelles. In this chapter, the results of the study on their mixing behaviour, synergism, and one dimensional grow to worm-like micelles and rheological characteristics of this system are reported. Present study is divided in two major parts. In the first part, the synergistic effect of the mixing of cetyltrimethylammonium bromide (CTAB, a cationic surfactant) with SDBS (an anionic surfactant) is studied under Newtonian flow regime. In the second part, the formation of viscoelastic worm-like micelles is examined and the rheological behavior of the system is investigated under non Newtonian flow regime.

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Here the cmc's were determined for the mixed surfactant systems of various mole ratios at a particular temperature. Micellar aggregates are also formed in an aqueous solution containing SDBS and CTAB. But, the tendency of aggregation is different from that of the pure surfactants. Due to hydrophobic effect, the micellization process is a function of temperature, additive and solvent because the solvent property gets modified in the presence of an additive. The results indicate that the added cationic surfactant (CTAB in this experiment) is assisting in the micelle formation of the anionic surfactants.

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It is indeed interesting to note that the non-ideality of the CTAB and SDBS mixtures is not large. The charge neutralization between the head groups of the two components and the interaction of hydrophobic part of CTAB is the SDBS micelles improve the hydrophobic environment in the mixed state in comparison to the pure state. To analyse the synergistic effect of mixed surfactant, Rubingh's methods are applied.

The reason for the non-ideal behaviour among surfactant molecules upon mixing are then various types of molecular interactions. These interactions (either synergistic or antagonistic) can be analysed by RST which allows the evaluation of micelle mole fraction (x_1) and interaction parameter (β^m). A negative deviation from ideal behaviour, corresponding to negative β values is believed to result from a net

attraction between the two different surfactant molecules. In this system of CTAB and SDBS mixture, β values are also negative as found within the range of -2.45 to -0.364. Electrostatics yields a large contribution to the aggregate free energy for mixtures consisting of ionic surfactants. According to the Poisson-Boltzmann (mean field) description, this contributions mainly due to the entropically unfavourable organization of the counterions into a diffuse layer located outside the electrically charged surface of an aggregate, whereas the purely energetic effects usually are much smaller for surfactants mixtures like CTAB and SDBS which explains comparatively lower interactions parameter.

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Viscoelastic properties including dynamic rheology of the system at different temperature have been investigated to understand the microstructural pattern of the mixed micelles. The self-assembly of both CTAB and SDBS individually result in the formation of globular micelles near the respective cmc values. On the other hand, when the concentrations of the individual component of the mixtures are increased (e.g., CTAB = 100 mM and SDBS = 20 mM), a viscoelastic gel is formed and the flow becomes non-Newtonian in nature. The observed viscoelasticity is related to worm-like micelle (WLM) formation.

Therefore, in general, the experimental solutions exhibit three regions of rheological response. First, at low surfactant concentration, the solutions are Newtonian liquids with low viscosity and non-measurable elastic response. Second, with increasing surfactant concentration, they behave like polymer solutions in the semi-dilute regime, characterized by viscoelastic behaviour with a spectrum of relaxation times. Finally, with increase in the counter ion concentration, these materials enter a regime where their rheological response is similar to that of an entangled polymer or weak gel; however, unlike polymer systems, there relaxation after shear is dominated by a single relaxation time. In this chapter of the thesis rheology of viscoelastic worm-like micelles formed in the system of SDBS and CTAB mixtures have been studied.

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In our experiments, the rheological data are typical of viscoelastic wormlike micelles, with a plateau in G' at high frequencies and terminal behaviour of G' and G'' at low frequencies. Moreover, the sample is nearly a Maxwell fluid over a short range

of temperatures (303 K - 335 K). No cross over point is displayed beyond the temperature range of 303 K - 313 K, except at 281 K. We find that the Maxwell model fits the data well, especially at low and intermediate frequencies, as has been shown for normal worm in the above temperature ranges. When micelles are sufficiently long, they are converted into more flexible wormlike micelles which can flow comparatively easily. Which reflects by a level off in the G' . At further high concentration, a micro-structural change in micelle structure results the change in rheological parameter. The increase in viscosity to a very small extent can be attributed also by micro-structural change. It is expected that a sufficient amount of CTAB will be present which will be embedded between the head groups. Further with increase in temperature, the Br⁻ ion may be released and would show higher preference for the bulk phase. Such a release if occurs would increase the effective head group area, thereby driving micro-structural change of higher curvature resulting in an increase in viscosity.

At low frequencies the loss modulus (G'') is higher than the storage modulus (G'), indicating that the sample behaves as a liquid and also predominantly viscous whereas at high frequencies, G' is greater than G'' , which implies that the mixtures behave like a solid which is predominantly elastic in the temperature range 303 - 313 K. The dip of the G'' curve even at higher frequencies is due to the presence of further relaxation modes.

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The curve in the present system fits to good extent to a simple Maxwell model. The data points fit fairly well on a semicircle curve particularly at 303 K. A single exponential relaxation can be effectively explained in case of worm like micelles. In this case, the reptation mechanism is short circuited and the new relaxation process will be monoexponential with a new time scale. The deviations from the half circle occur at a circular frequency ω of the order of the inverse of the breaking time of the micelles. At higher frequencies the data deviate from the Maxwell model, which is typically the case when the systems can no longer be described by a single relaxation time. The large deviation from Cole - Cole plot with high angular viscosity is indicative that of a less structured system with poor viscoelastic behaviour.

The zero-shear viscosity of the surfactant mixtures was determined from controlled-stress measurements by extrapolating the viscosity-shear stress curve to zero

shear rates. In terms of stress relaxation, it is slowest at the viscosity peak and increases at both lower and higher temperatures. It is clear that with increase in temperature, η_0 increases indicating an increase in the curvature energy for surfactant aggregates which leads to an increase in micellar length and the formation of wormlike micelles. As the temperature further increased, the zero shear viscosity exhibits a flat maximum within 10°C to 26°C temperatures. Further increase in temperature decreases the zero shear viscosity and this can be explained due to the decrease of the micellar contour length or the formation of branched micelles. In summary, all these results support a fascinating and complex rheology to exist in the present system. This occurs due to structural evolution from a spherical micelle to a worm like micelle. Finally, the shift in cross over frequency ω to higher values indicate that the relaxation time τ decreases with temperature.

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