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## Interactions Between Sodium Dodecylsulphate and Triton X-100: Molecular Properties and Kinetics Investigations

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**Abstract:** Synergistic effects in the mixed micelle of Sodium Dodecylsulphate (SDS) anionic and Triton X-100 (polyoxyethylene (9.5) p-1, 1, 3, 3-tetramethylbutylphenol) nonionic surfactant mixtures were investigated. The critical micelle concentrations of the mixtures were determined by ultraviolet/visible (UV) spectroscopic method at 25°C. The mixed micellar compositions and the estimation of the extent of interaction were determined on the basis of the regular solution model. The critical micelle concentration (cmc) values were lower than predicted from ideal mixture theory. Micellization is enhanced by the mixing of the two surfactants, that is synergistic interaction of the SDS and Triton X-100 in the mixed micelles observed. The reduction in cmc resulting from the mixing is comparable to those in other anionic/nonionic surfactant systems. The regular solution model interaction parameter  $\beta$  of -2.19 was obtained, indicating an overall attractive interaction in the mixed micelle. Further evidence of molecular interaction in the mixed micelle was obtained from the kinetics of the aqutation of Iron (II) bipyridyl complex in the mixed surfactant systems where a marked dependence of the aqutation rate on medium compositions was observed.

**Key words:** Synergistic, micellization, interaction-parameter, mixed micelle, aqutation

### INTRODUCTION

In many applications, surfactant mixtures often give rise to enhanced performance over single component systems, consequently surfactant blends are employed in a wide variety of practical applications such as enhanced oil recovery, food and cosmetic production, detergency, textiles and paint production<sup>[1,2]</sup>. By tuning or engineering the interactions between different components, non ideal mixing effects can be exploited to raise or lower the critical micelles concentrations (cmc's) often referred to as synergism or anti-synergism<sup>[3]</sup>. These effects have stimulated research on the physical properties of mixed micellar aggregates in an attempt to interpret the nature and mechanism of interactions among surfactants<sup>[4]</sup>. However, some characteristics of these systems such as the dissimilar behaviour of anionic-nonionic and cationic-nonionic surfactants remain to be explained<sup>[4,5]</sup>. Despite the overt interest in elucidating these physical properties, little work has been done to characterize mixed micelles as reaction media<sup>[6-8]</sup>. The present study explores the synergistic interaction between Sodium Dodecyl Sulphate (SDS) and Triton X-100 as well as the effect of this mixed micellar system on chemical reactivity. The dependence of the critical micelles concentrations (cmc's) in composition, the extent of molecular interactions, the

free energy of mixing and the dependence of the rate of aqutation of Iron (II) bipyridyl ion  $[\text{Fe}(\text{bipy})_3]^{2+}$  on medium composition are also presented.

### MATERIALS AND METHODS

**Materials:** The anionic surfactants SDS (molecular biology grade) was purchased from Sigma and has a stated purity of approximately 99% and the nonionic surfactant Triton X-100 from Riedel-de-Hans of scintillation grade. All surfactants were used without further purification. The complex  $[\text{Fe}(\text{bipy})_3]^{2+}$  was synthesized by adapting the method described by Schick<sup>[9]</sup>. Water used was distilled and deionized.

**Critical micelle concentration determination:** The critical micelle concentrations (cmc's) of the pure ionic surfactants were determined by electrical conductometry, while those of the nonionic surfactant and ionic/nonionic mixtures were determined spectrophotometrically. For conductivity measurements, Metler Toledo conductivity meter model MC 126 coupled with an automatic temperature compensation probe was used.

A wavelength scan of Triton X-100 solution using an  $\alpha$ -Helios Pye-Unicam spectrometer, shows two absorbance peaks at 223 and 276 nm. The cmc of pure

Triton X-100 was obtained from absorbance-concentration profile at 276 nm. Similarly, the cmc's of the surfactant mixtures was obtained from absorbance-concentration profiles at various mole fractions of SDS in the total surfactant mixture at the same wavelength of 276 nm.

**Kinetic studies:** Kinetic studies designed for the investigation of aqueous rate profiles of the complex in surfactant solution was carried out at a fixed temperature of 25.0±0.1°C by monitoring the change in absorbance of the complex as a function of time at the wavelength of maximum absorption, 522 nm, of the complex. Constant temperature was maintained by using a combination of Grant thermostating unit immersed in a water bath and a fast Austen pump, which pumped water from the thermostatted water bath at 25°C around the cell compartment of the UV/Visible spectrophotometer.

### RESULTS AND DISCUSSION

**Micellisation in surfactant mixtures:** The behaviour of surfactant mixtures is usually described theoretically by a pseudo phase separation model. Mixtures of surfactant may be treated as ideal in which the cmc of the mixture  $C_{mix}$  is related to the cmc's of pure component  $C_i$ 's and the mole fraction ( $\alpha_i$ 's) of the component in the total mixed solute by Eq. 1<sup>[10]</sup>

$$\frac{1}{C_{mix}} = \sum_{i=1}^n \frac{\alpha_i}{C_i} \quad (1)$$

Although few micellar systems behave ideally, this model is useful as a reference system in the description of non-ideality. Mixtures of surfactants which do not obey equation 1 are said to be non-ideal. To account for the non-ideality in the mixed surfactants studied, the simplified approach proposed by Holland and Rubingh<sup>[4,11]</sup>, have been used. According to this model the monomer concentration of each component in the micelle mixture  $c_i^m$  is given by:

$$c_i^m = f_i \chi_i C_i \quad (2)$$

The activity coefficients ( $f_i$ ) are given by:

$$f_i = \frac{\alpha_i C_{mix}}{\chi_i C_i} \quad (3)$$

where,  $\chi_i$  is the mole fraction of each component in the mixed micelle. Using a simple regular solution approximation, the activity coefficients can be expressed

as functions of  $\chi_i$  and an appropriate molecular interaction parameter,  $\beta$  (for binary non-ideal mixtures).

$$f_1 = \exp [\beta(1-x_1)^2] \quad (4)$$

$$f_2 = \exp [\beta\chi_1^2] \quad (5)$$

The interaction parameter  $\beta$  can be determined when  $C_{mix}$  is known, this requires solving for  $\chi_i$  iteratively from:

$$\chi_i^2 \ln \left( \frac{\alpha_i C_{mix}}{\chi_i C_i} \right) = (1-\chi_i)^2 \ln \left( \frac{\alpha_2 C_{mix}}{(1-\chi_i) C_2} \right) \quad (6)$$

obtained from Eq. 3-5 and calculating  $\beta$  from the combination of Eq. 3 with 4 or 5 gives:

$$\beta = \frac{\ln \left[ \frac{\alpha_i C_{mix}}{\chi_i C_i} \right]}{(1-\chi_i)^2} = \frac{\ln \left[ \frac{(1-\alpha_1) C_{mix}}{((1-\chi_1) C_1)} \right]}{\chi_1^2} \quad (7)$$

With these values of  $\chi_i$  and  $\beta$ , the  $C_{mix}$  is calculated from the combination of Eq. 8 and 9a or 9b.

$$\chi_1 (1-\alpha_1) C_1 \exp \left( \frac{\beta(1-\chi_1)^2}{(1-\chi_1)} \right) + \alpha_1 C_2 \exp(\beta\chi_1^2) = 1 \quad (8)$$

$$\alpha C_{mix} = \chi_i C_i \exp \left( \beta(1-\chi_i)^2 \right) \quad (9a)$$

$$(1-\alpha) C_{mix} = (1-\chi_i) C_2 \exp(\beta\chi_i^2) \quad (9b)$$

The excess enthalpy of mixing  $H^E$  is described by the regular solution theory as:

$$H^E = x_1 (1-x_1) \beta RT \quad (10)$$

With the assumption that the excess entropy of mixing is zero, the excess free energy of mixing is equally given in the Eq. 10. The activity coefficient of SDS and TX-100 are related to the excess free energy of mixing by:

$$\frac{G^E}{RT} = x_{(SDS)} \ln f_{(SDS)} + (1-x_1) \ln f_{(TX-100)} \quad (11)$$

The deviation of  $\beta$  from zero results from molecular interaction between the surfactant head groups. Thus a

Table 1: Values of  $C_{mix}$  and the thermodynamic parameters for micellization of SDS/TX-100 mixtures in aqueous medium at 25°C

$\alpha_{SDS}$	$C_{mix}/10^4 M$	$\chi_{SDS}$	$\chi_{TX-100}$	$f_{SDS}$	$f_{TX-100}$	$C_{SDS}^m / 10^4 M$	$C_{TX-100}^m / 10^4 M$	$H^E/RT$	$\beta$
0.00	2.28	0.000	1.000	-	-	-	-	-	-
0.25	2.79	0.071	0.929	0.120	0.988	0.697	2.092	-0.162	-2.459
0.33	3.00	0.097	0.903	0.125	0.976	0.990	2.100	-0.224	-2.555
0.50	3.92	0.116	0.884	0.206	0.973	1.960	1.960	-0.207	-2.021
0.63	4.80	0.170	0.830	0.217	0.938	3.022	1.775	-0.313	-2.219
0.75	6.76	0.201	0.799	0.308	0.928	5.070	1.690	-0.297	-1.847
0.83	8.49	0.266	0.734	0.323	0.862	7.043	1.443	-0.410	-2.098
0.90	12.00	0.334	0.666	0.394	0.791	10.800	1.200	-0.467	-2.098
1.00	82.00	1.000	0.000	-	-	-	-	-	-

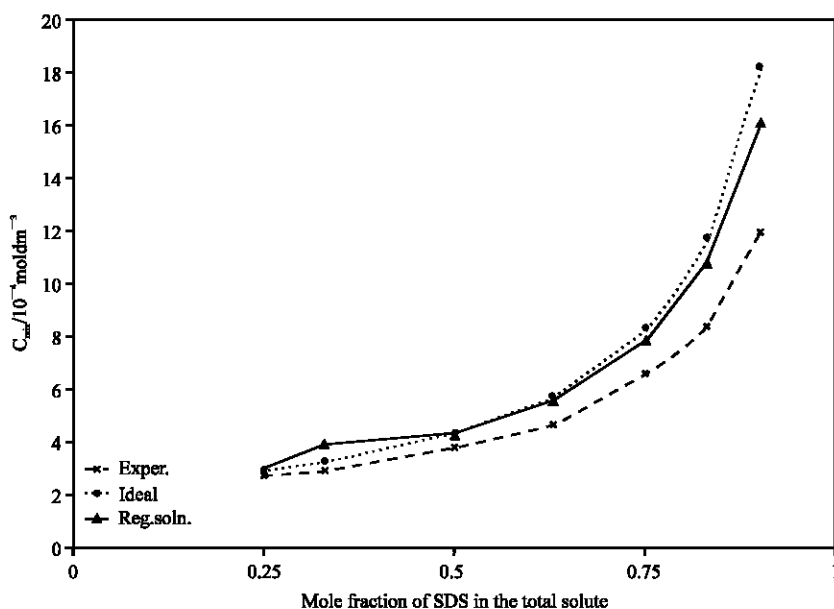


Fig. 1: Experimentally determined cmc( $c_{mix}$ ) of SDS/TX-100 mixed system compared with the ideal and the theoretically predicted cmc of the mixture for  $\beta = -2.19$

negative deviation from ideal behaviour of the  $C_{mix}$  function as reflected in negative  $\beta$  values, corresponds to a net attraction or cooperation between the two different surfactant molecules. For mixtures of monovalent and non-ionic surfactant,  $\beta$  values are, as a rule<sup>[11]</sup> considerably smaller and fall in the range  $-5 < \beta < -1$ . Table 1 lists the cmc's,  $\chi_{SDS}$ ,  $\beta$  and the free energy change of mixing for the SDS/TX-100 mixtures at different mole fraction of SDS.

Figure 1 shows plot of  $C_{mix}$  against mole fraction,  $\alpha_{SDS}$  of SDS in the total solute mixture for the ideal mixture theory, the regular solution model and observed data. Comparison with ideal mixture theory, shows that both regular solution theory and experimental data exhibit negative deviation. Observed average  $\beta$  value of -2.19 characterizes the experimental values, with the regular solution model been relatively closer to the experimental data than the ideal solution model. This negative value of  $\beta$  indicates synergistic behaviour of the components of

SDS and Triton X-100 in the mixed micelle, although this  $\beta$  value is less negative than the value of -3.4 obtained for mixed micelle of SDS and decaethylene glycol-nonylphenylether, another nonionic surfactant with similar structure as Triton X-100<sup>[12]</sup>, this may be as a consequence of the presence of branched isooctyl chain in Triton X-100 compared to the linear nonyl present in the latter.

Figure 2 shows plot of the mole fraction  $\chi_{SDS}$  of SDS in the mixed micelle against the mole fraction  $\alpha_{SDS}$  of SDS in the total solute mixture, showing a negative deviation from ideality. Table 1 show that the activity coefficients of the components in the mixed micelle were less than 1 and  $f_{SDS}$  was consistently smaller than  $f_{TX-100}$ . The non-ideality of the mixture results from a decrease in the activities of SDS in the mixed micelle. This is due to the insertion or incorporation of the non-ionic groups between the ionic groups decreasing the repulsive forces between the SDS groups, which invariably leads to decrease in the charge

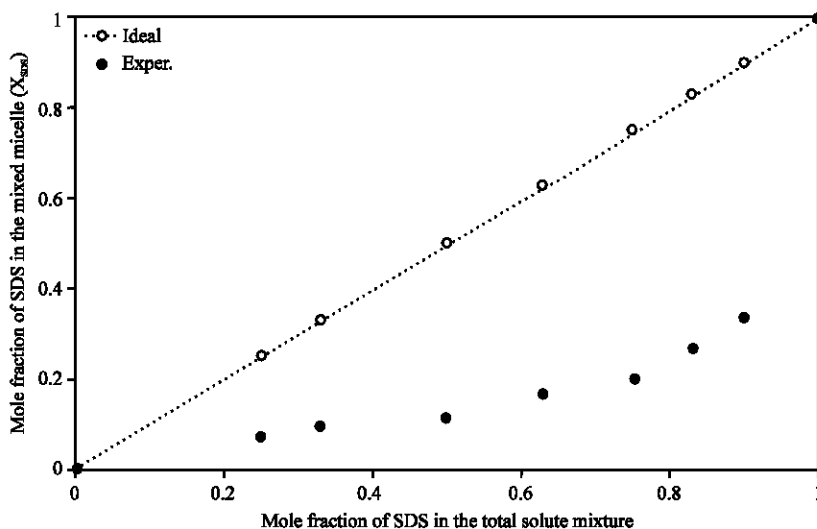


Fig. 2: Plot of the mole fraction of SDS ( $\chi_{\text{SDS}}$ ) in the mixed micelle against the mole fraction ( $\alpha_{\text{SDS}}$ ) in the total solute

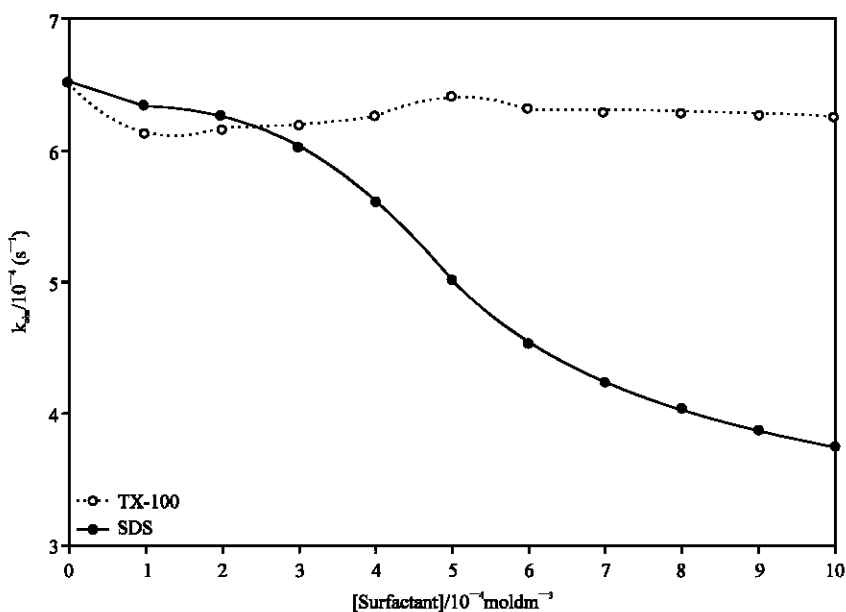


Fig. 3: Plot of the pseudo-first order rate constant against surfactant concentrations

density and thus the ionic-ionic repulsion are less than in pure SDS micelle. The above is constant with the mechanism proposed by Rathman and Scamehorn<sup>[13]</sup>.

**Kinetic measurement:** The influence of mixed micelles on reactivity was investigated by studying the aquation of Iron (II) bipyridyl complex in aqueous solution of the mixed micellar system indicated above. The reaction exhibits properties which make it an excellent candidate as a probe for micellar influence, since its rate is extremely sensitive to medium affects.

Figure 3 shows the experimental results of the observed pseudo-first order rate constant  $k_{\text{obs}}$  as a function of the concentration of pure surfactants; that is SDS and Triton X-100 individually. The influence of the mixed micellar systems on the aquation reaction can be seen in Fig. 4 where values of observed pseudo first order rate constant  $k_{\text{obs}}$  obtained at fixed SDS are plotted against TX-100%. In each case,  $k_{\text{obs}}$  increase sharply with increase in TX-100%, approaching saturation at higher TX-100. Of all TX-100 concentration of 0.001 to 5.00% covered,  $k_{\text{obs}}$  decrease with increase in SDS, indicating an overall inhibition as SDS increases.

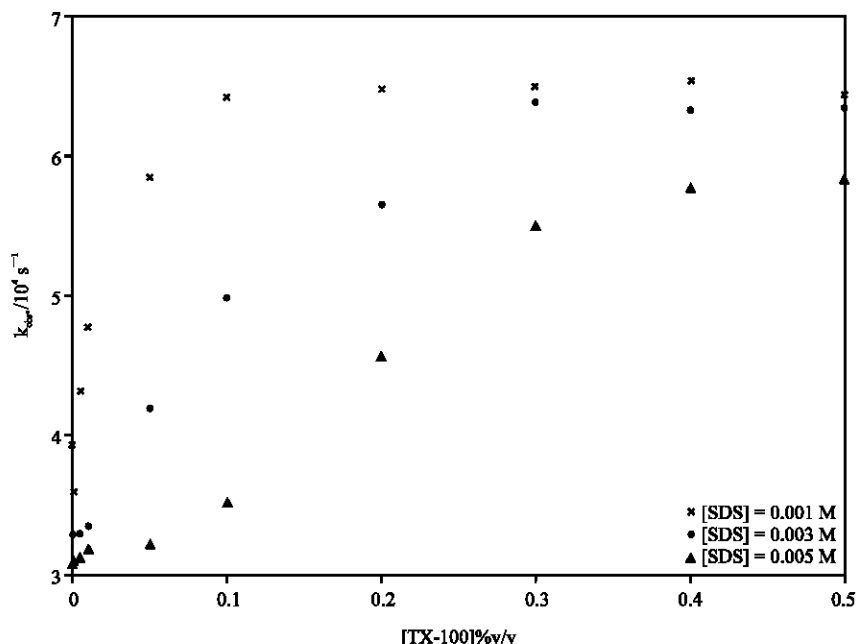


Fig. 4: Variation of the pseudo-first order rate constant against TX-100% v/v at constant SDS

In this system, increase in SDS gives rise to an increase in the stabilization of the complex ion through electrostatic attraction between the positively charged complex ion and the electron density of the SDS anionic head-groups in the micellar pseudo phase giving rise to inhibition of the aquation reaction.

It is important to note that TX-100 homomicelles exhibit little effect on the aquation of the complex ion even at concentration more than four times the cmc (Fig. 3); hence the observed rate enhancement by TX-100 at fixed SDS is significant (Fig. 4). Decrease in electrostatic attraction between the complex ion and the head group of anionic SDS resulting from decrease in electron density per surfactant monomer in the mixed micelle accounts for observed rate enhancement at fixed SDS. This is an important evidence for the formation of co-aggregates of SDS and TX-100 molecules in which the SDS molecules are inserted between the TX-100 molecules, at very low SDS concentration, the inhibition is very small and  $k_{obs}$  approaches that of bulk aqueous phase as TX-100 concentration increases up to saturation when further addition of TX-100 has no effect on the aquation rate.

### CONCLUSIONS

The mixed critical micelle concentrations of SDS/Triton X-100 mixtures at their different composition were measured using spectroscopic method. SDS and TX-100 mixtures exhibited synergistic behaviour in the mixed micelle comparable to other anionic/nonionic mixed

system. The average interaction parameter was estimated to be -2.19 on the basis of the regular solution theory. The excess enthalpy and free energy of mixing were negative, implying that the mixed micellization is exothermic and thermodynamically favourable.

Evidence of synergy in mixed micelle formation is confirmed in the kinetic studies of the aquation of Iron (II) bipyridyl complex ion in the present mixed surfactant system, where it was shown that the observed rate constant showed a marked dependence on the mixed surfactant medium compositions.

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