

Synergistic interaction of mixed micelles evidenced by kinetic investigation

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ABSTRACT: *The present study explores the synergistic interaction of anionic surfactant SDS with nonionic surfactants TX-100 and Tween 20 as well as the effect of these mixed micellar systems on chemical reactivity. The dependence of the CMC with the composition of the mixed micelle, the extent of micellar interactions and the dependence of the rate of electron transfer between PSAA and $[Fe(NN)_3]^{3+}$ with medium composition are all presented in this paper. The negative interaction parameter (β) for the SDS/TX-100 and SDS/Tween 20 binary mixtures, gives a direct evidence for the existence of synergism in the mixed micelles. The electron transfer reaction between PSAA and $[Fe(NN)_3]^{3+}$ was studied in binary micellar systems containing anionic surfactant and nonionic surfactant viz., SDS/ TX-100 and SDS/Tween 20 with various mole ratios. It has been observed that above the CMC all these binary mixed micellar systems have catalytic effect on the electron transfer reaction rate. This kinetic investigation is a direct evidence for the existence of synergistic interaction.*

Key Words: *Mixed micelles, Critical micellar concentration, Electron transfer reaction, Synergism*

1. INTRODUCTION

In fundamental and applied fields mixed surfactants are prevalent. In detergency, cleaning, emulsification, dispersion, chemical purification, targeted drug delivery, synthesis of advanced nonmaterial [1-4], cosmetics, wastewater treatment, food industries and oil recovery [5-8], the role of mixed surfactant systems has a vital role. The activity of mixed surfactants depends on their type, composition and concentration in addition to environmental factors. To compare the activities of the mixed surfactants with that of their individual components with regard to their applications, prior fundamental studies are essential. Like surfactants, the mixed surfactants also form micelles after a threshold concentration called the critical micelle concentration (CMC), whose determination is an essential physicochemical property normally adopted for exact and detailed understanding of the self-organizing behaviour of surfactants. In recent years, detailed studies on mixed surfactant systems have been made [9-14]. The binary mixtures of surfactants have been considered and the experimental results have been analyzed and compared in the light of the proposed solution and thermodynamic theories. The results have helped to reveal the synergistic and antagonistic behaviour of the binary combinations. Synergism is defined as a condition at which the properties of a mixed surfactants is better than those attainable with the individual components. Mixtures of different surfactant types often exhibit cooperative interactions or synergism on the properties of a system [15]. Synergism in mixed surfactants system can be related to surface tension, mixed micelle formation, foaming, wetting, solubilizing and emulsification power, detergency, etc. [16-18]. Synergism can be attributed to non-ideal mixing effects in the surface films and in the micelle aggregates, which result in interfacial tension and substantial lowering of CMC, than would be expected on the basis of the properties of constituent surfactants. Conventional anionic surfactant mixtures with other classical surfactants were widely investigated. However, the mostly used anionic compound was sodium dodecyl sulfate (SDS). In many applications, the anionic-nonionic surfactant mixture is often used because of the enhanced overall performance over single component system. For example, anionic-nonionic mixed micelles show advantageous solubilisation behaviour, exhibiting higher cloud points than those of the single nonionic micelle, along with lowering of Krafft point than those of the single anionic micelle. Furthermore, mixing anionic and nonionic micelles may raise or lower the CMC from that obtained by ideal mixing (CMC^d).

2. EXPERIMENTAL

2.1. Critical Micelle Concentration Determination

Knowledge of physicochemical parameters like experimental CMC values of individual micelles, the CMC of mixed micelle and mole fractions of the micelles in the binary mixture are necessary to study the extent of interaction between the components of a mixed micelle. The quantitative synergistic interactions in binary mixtures can be calculated using β interaction parameter [19, 20]. The deviation of β from zero results from molecular interaction between the micellar head groups. Thus a negative deviation from ideal behaviour of C_{mix} function as reflected by its negative β value, corresponds to a net attraction or cooperation between two different micellar molecules. If the β value is positive which shows anti-synergism or antagonism, corresponds to net repulsion between two micelle molecules in the binary mixture.

Conductivity measurements were carried out in the aqueous solution of surfactants, SDS, Triton X-100 (TX-100), Tween 20 and four different binary mixtures of SDS with nonionic surfactants (TX-100 and Tween 20). The CMC of the binary mixtures of SDS/TX-100 (3:1 and 1:3) and SDS/Tween 20 (3:1 and 1:3) mixtures were determined by conductivity measurements. The data were acquired using digital conductivity meter. The solutions containing cell were immersed in a water bath and controlling the temperature variation at ± 0.1 K. The temperature was kept constant at 303 K. Surfactant solutions were prepared by dissolving the relevant surfactants in double distilled water at a higher concentration (0.04 M) in a 100 mL volumetric flask. The specific conductivity of 50.0 mL of double distilled water was measured. Then the conductivity of micellar solutions were measured by adding 2.0 mL increments into the 50.0 mL water. The specific conductivity values determined were plotted against the surfactant concentration for pure SDS, TX-100, Tween 20 as well as the binary mixtures of SDS/TX-100 and SDS/Tween 20. The break in the curve indicated the onset of the micellization process. Trials were repeated for reproducibility. The error in the CMC determination did not exceed 3%. The experimentally determined CMC^{ex} values of various binary mixtures and theoretically calculated values are tabulated in Table 1.

Table 1. CMC values of mixed anionic-nonionic micelles at different mole ratios, in aqueous medium.

Mole fraction of SDS X_{SDS}	10^3 CMC, M			
	TX-100		Tween 20	
	CMC ^{id}	CMC ^{ex}	CMC ^{id}	CMC ^{ex}
1	8	8.2	8	8.2
0.75	1.08	0.708	0.168	0.14
0.25	0.395	0.356	0.067	0.055
0	0.3	0.34	0.05	0.05

2.2. Kinetic measurements

The tris(pyridyl) complexes of Fe(III), $[Fe(bpy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$, $([Fe(NN)_3]^{3+})$ were obtained by known procedure[21,22]. Phenylsulfinylacetic acid (PSAA) was prepared from phenylthioacetic acid (PTAA) by the controlled oxidation with hydrogen peroxide[23-25]. The kinetic measurements were performed using ELICO BL 222 Double Beam Biospectrophotometer. The kinetics were followed under pseudo-first order conditions where $[PSAA] \gg [Fe(NN)_3]^{3+}$ at 303 K. The reaction was initiated by mixing $[Fe(NN)_3]^{3+}$ and PSAA solutions acidified using $HClO_4$. The ionic strength was maintained in all the runs using $NaClO_4$. The reactions were carried out at different micellar concentrations above the CMC value range from 0.8×10^{-2} M to 15×10^{-2} M. All the reactions were carried out in 97 % H_2O - 3 % CH_3CN (v/v). The progress of the reaction was followed spectrophotometrically by monitoring the increase in absorbance of $[Fe(bpy)_3]^{2+}$ at 522 nm and $[Fe(phen)_3]^{2+}$ at 510 nm for the complexes $[Fe(bpy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ respectively. The values of rate constants, in micellar medium (k_1) and aqueous medium (k_w) are calculated from the slope of $\log(A_\infty - A_t)$ versus time plots. The observed results were reported in Tables 2 to 5. The rate constants for the electron transfer reaction between PSAA and $[Fe(NN)_3]^{3+}$ in all the surfactant media and binary mixtures increases initially, reaches a maximum and then decreases gradually giving rise to sigmoid type of curve.

Table 2. Effect of composition of surfactant on the rate constant of $([Fe(bpy)_3]^{3+})$ system in SDS/TX-100 medium

$10^2 [M]$ M	$10^4 k_1$ (s^{-1})			
	SDS	TX-100	SDS/TX-100 3 : 1	SDS/TX-100 1 : 3
	0	7.14 ± 0.04	7.14 ± 0.04	7.14 ± 0.04

0.8	7.94 ± 0.01	7.54 ± 0.08	11.9 ± 0.02	7.76 ± 0.04
0.9	8.15 ± 0.02	7.66 ± 0.11	12.1 ± 0.06	7.81 ± 0.01
1.0	8.43 ± 0.04	8.25 ± 0.02	12.3 ± 0.01	8.41 ± 0.06
2.0	11.1 ± 0.06	8.46 ± 0.01	14.9 ± 0.03	9.69 ± 0.07
3.0	14.0 ± 0.05	8.66 ± 0.14	17.6 ± 0.05	9.92 ± 0.02
4.0	16.4 ± 0.01	11.4 ± 0.21	19.8 ± 0.02	12.7 ± 0.06
5.0	19.6 ± 0.02	15.8 ± 0.03	21.9 ± 0.04	16.6 ± 0.08
7.0	21.2 ± 0.01	14.6 ± 0.05	24.2 ± 0.07	15.1 ± 0.01
9.0	23.0 ± 0.12	14.2 ± 0.02	25.6 ± 0.06	15.2 ± 0.04
10	23.4 ± 0.08	13.5 ± 0.06	27.4 ± 0.08	14.9 ± 0.01
12	22.3 ± 0.04	12.2 ± 0.07	26.3 ± 0.04	14.0 ± 0.09
15	21.5 ± 0.05	11.6 ± 0.05	25.5 ± 0.02	13.7 ± 0.05

[PSAA] = 1×10^{-2} M; [[Fe(bpy)₃]³⁺] = 4×10^{-4} M; [H⁺] = 0.5 M; μ = 0.6 M; Solvent = 97 % H₂O - 3 % CH₃CN (v/v);

[M] = Concentration of SDS/TX-100.

Table 3. Effect of composition of surfactant on the rate constant of ([Fe(phen)₃]³⁺) system in SDS/TX-100 medium.

10 ² [M] M	10 ⁴ k ₁ (s ⁻¹)			
	SDS	TX-100	SDS/TX-100 3 : 1	SDS/TX-100 1 : 3
0	8.33 ± 0.02	8.33 ± 0.02	8.33 ± 0.02	8.33 ± 0.02
0.8	9.80 ± 0.12	8.34 ± 0.08	11.3 ± 0.05	9.31 ± 0.07
0.9	10.1 ± 0.01	8.45 ± 0.04	13.8 ± 0.02	9.43 ± 0.04
1.0	11.3 ± 0.02	8.56 ± 0.06	14.4 ± 0.07	10.9 ± 0.01
2.0	12.3 ± 0.11	9.40 ± 0.02	15.4 ± 0.04	11.5 ± 0.04
3.0	13.7 ± 0.05	10.3 ± 0.05	18.2 ± 0.03	12.4 ± 0.06
4.0	14.8 ± 0.07	11.2 ± 0.07	19.6 ± 0.01	13.8 ± 0.08
5.0	15.6 ± 0.02	12.6 ± 0.02	22.1 ± 0.05	14.6 ± 0.02
7.0	18.9 ± 0.06	13.5 ± 0.01	24.8 ± 0.04	16.6 ± 0.05
9.0	21.7 ± 0.03	14.9 ± 0.06	29.1 ± 0.07	16.9 ± 0.06
10	20.2 ± 0.02	17.5 ± 0.03	28.3 ± 0.09	18.8 ± 0.04
12	18.0 ± 0.01	16.3 ± 0.01	27.4 ± 0.03	17.2 ± 0.01
15	17.8 ± 0.07	15.1 ± 0.03	25.9 ± 0.01	16.8 ± 0.09

[PSAA] = 1×10^{-2} M; [[Fe(phen)₃]³⁺] = 4×10^{-4} M; [H⁺] = 0.5 M; μ = 0.6 M; Solvent = 97 % H₂O - 3 % CH₃CN (v/v);

[M] = Concentration of SDS/TX-100.

Table 4. Effect of composition of surfactant on the rate constant ([Fe(bpy)₃]³⁺) system in SDS/Tween 20 medium.

10 ² [M] M	10 ⁴ k ₁ (s ⁻¹)			
	SDS	Tween-20	SDS/Tween 20 3 : 1	SDS/Tween 20 1 : 3
0	7.14 ± 0.04	7.14 ± 0.04	7.14 ± 0.04	7.14 ± 0.04
0.8	7.94 ± 0.01	7.19 ± 0.07	14.8 ± 0.01	7.51 ± 0.03
0.9	8.15 ± 0.02	7.21 ± 0.03	15.6 ± 0.03	7.92 ± 0.01
1.0	8.43 ± 0.04	7.86 ± 0.05	16.3 ± 0.07	8.03 ± 0.04
2.0	11.1 ± 0.06	8.02 ± 0.06	18.2 ± 0.06	9.45 ± 0.08
3.0	14.0 ± 0.05	8.23 ± 0.04	21.3 ± 0.01	11.2 ± 0.05
4.0	16.4 ± 0.01	10.5 ± 0.09	23.5 ± 0.04	14.6 ± 0.04
5.0	19.6 ± 0.02	14.7 ± 0.02	26.5 ± 0.09	16.3 ± 0.02
7.0	21.2 ± 0.01	14.2 ± 0.08	28.7 ± 0.02	18.6 ± 0.09
9.0	23.0 ± 0.12	14.1 ± 0.04	30.4 ± 0.04	20.4 ± 0.01
10	23.4 ± 0.08	13.2 ± 0.07	30.9 ± 0.05	21.7 ± 0.07
12	22.3 ± 0.04	11.7 ± 0.03	28.7 ± 0.06	19.1 ± 0.03
15	21.5 ± 0.05	11.1 ± 0.07	26.5 ± 0.07	18.5 ± 0.05

[PSAA] = 1×10^{-2} M; $[[\text{Fe}(\text{bpy})_3]^{3+}] = 4 \times 10^{-4}$ M; $[\text{H}^+] = 0.5$ M; $\mu = 0.6$ M; Solvent = 97 % H_2O - 3 % CH_3CN (v/v);

[M] = Concentration of SDS/Tween 20.

Table 5. Effect of composition of surfactant on the rate constant of $[[\text{Fe}(\text{phen})_3]^{3+}]$ system in SDS/Tween 20 medium.

10^2 [M] M	$10^4 k_1$ (s^{-1})			
	SDS	Tween-20	SDS/Tween 20 3 : 1	SDS/Tween 20 1 : 3
0	8.33 ± 0.02	8.33 ± 0.02	8.33 ± 0.02	8.33 ± 0.02
0.8	9.80 ± 0.12	8.52 ± 0.05	15.2 ± 0.03	8.81 ± 0.07
0.9	10.1 ± 0.01	9.25 ± 0.04	16.3 ± 0.04	9.62 ± 0.05
1.0	11.3 ± 0.02	9.87 ± 0.02	17.4 ± 0.01	10.3 ± 0.09
2.0	12.3 ± 0.11	10.2 ± 0.08	18.1 ± 0.07	11.9 ± 0.06
3.0	13.7 ± 0.05	11.6 ± 0.03	18.6 ± 0.01	12.6 ± 0.01
4.0	14.8 ± 0.07	12.8 ± 0.05	19.4 ± 0.09	13.8 ± 0.04
5.0	15.6 ± 0.02	15.3 ± 0.07	20.4 ± 0.04	15.4 ± 0.07
7.0	18.9 ± 0.06	15.9 ± 0.09	21.4 ± 0.03	16.4 ± 0.08
9.0	21.7 ± 0.03	15.2 ± 0.05	22.9 ± 0.06	19.1 ± 0.06
10	20.2 ± 0.02	14.7 ± 0.04	23.5 ± 0.07	18.8 ± 0.04
12	18.0 ± 0.01	14.1 ± 0.01	22.1 ± 0.05	16.5 ± 0.03
15	17.8 ± 0.07	13.9 ± 0.06	21.5 ± 0.09	14.3 ± 0.02

[PSAA] = 1×10^{-2} M; $[[\text{Fe}(\text{phen})_3]^{3+}] = 4 \times 10^{-4}$ M; $[\text{H}^+] = 0.5$ M; $\mu = 0.6$ M; Solvent = 97 % H_2O - 3 % CH_3CN (v/v);

[M] = Concentration of SDS/Tween 20.

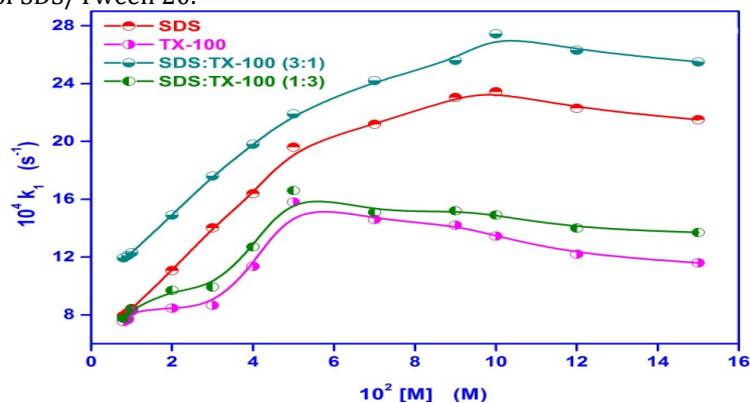


Figure 1. Effect of [SDS/TX-100] on the rate of electron transfer reaction between PSAA and complex $[[\text{Fe}(\text{bpy})_3]^{3+}]$.

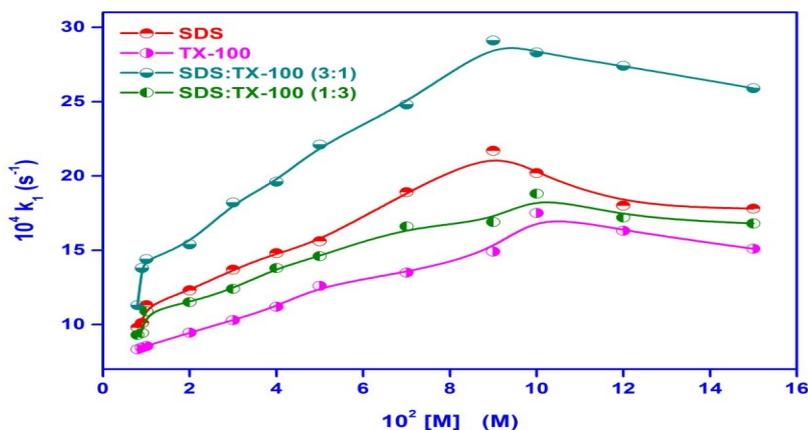


Figure 2. Effect of [SDS/TX-100] on the rate of electron transfer reaction between PSAA and complex $[[\text{Fe}(\text{phen})_3]^{3+}]$.

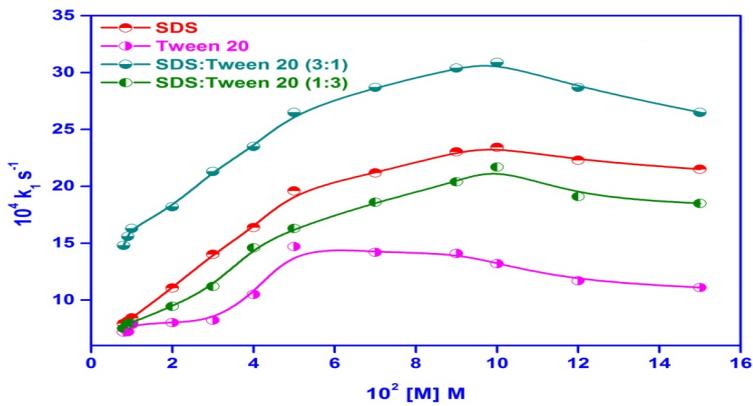


Figure 3. Effect of [SDS/Tween 20] on the rate of electron transfer reaction between PSAA and complex [Fe(bpy)₃]³⁺.

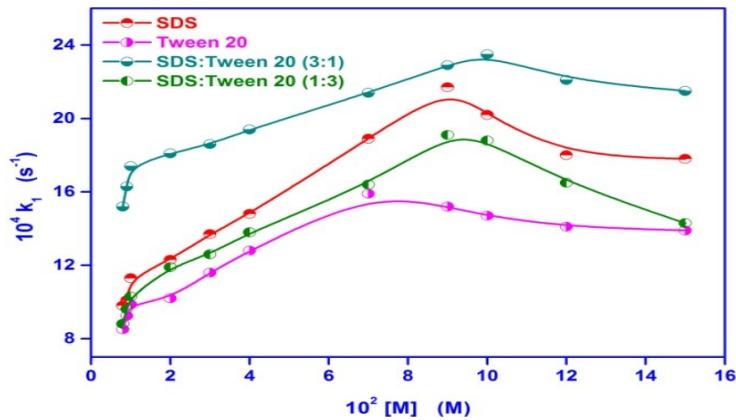


Figure 4. Effect of [SDS/Tween 20] on the rate of electron transfer reaction between PSAA and complex [Fe(phen)₃]³⁺.

3. DISCUSSION

3.1. Synergistic effects

Synergistic effects of binary mixtures viz., SDS/TX-100 and SDS/Tween 20 have been studied by determining their CMC values using conductometry. The anionic surfactants normally possess higher CMCs than nonionic surfactants. Aggregation or micellization of nonionic surfactants is mainly due to the hydrophobic interaction between hydrocarbon chains. This is more feasible because the hydrophobic groups are easily separated from the aqueous environment, whereas for ionic surfactants, high concentrations are necessary to overcome the electrostatic repulsion between ionic head groups during aggregation [26].

The CMCs of mixed surfactants are sharply decreased than that of pure SDS (Table 1). With the increase in mole fraction of non-ionic micelle, the CMCs decrease continuously from the CMC of pure SDS down to the CMC of pure non-ionic micelle. The experimental values of CMC and the mole fractions of the micelles in binary mixtures are used to calculate the interaction parameter, β. The ideal CMC of an ideal mixed micelle at any mole ratio of SDS to TX-100 or SDS to Tween 20 can be predicted with ideal solution theory.

$$\frac{1}{CMC^{id}} = \frac{\alpha}{CMC_1} + \frac{(1-\alpha)}{CMC_2} \tag{1}$$

where CMC₁ denotes CMC of TX-100 in SDS/TX-100 binary mixture and it is Tween 20 in SDS/Tween 20 binary mixture and CMC₂ is CMC of SDS. α is the mole fraction of the more hydrophobic (nonionic) micelle and (1 - α) is the mole fraction of SDS in the binary mixture of micelles. Due to the interaction between nonionic micelle (TX-100 (or) Tween 20) with SDS in mixed micelles, the experimental CMC of mixed micelle solution (CMC^{ex}) is always different from CMC^{id}. The CMC^{id} values are presented and compared with the experimentally observed values CMC^{ex}. The data in Table 1 clearly indicates that the CMC^{ex} are lower than that of CMC^{id}. Deviation of the experimentally obtained CMC values indicates that there is mutual interactions of the micelle molecules in mixed micelles.

According to nonideal theory of Holland and Rubingh [27], the deviation of CMC^{ex} from CMC^{id} can be represented by the parameter β , which also represents the interaction between nonionic micelle (TX-100 or Tween 20) and anionic micelle SDS in mixed solutions. The mole fraction of the more hydrophobic micelle in the mixed micelle (X_1^{id}) is calculated according to Motomura [28] using the relationship

$$X_1^{id} = \frac{CMC_2 \alpha}{CMC_2 \alpha + CMC_1 (1-\alpha)} \quad (2)$$

where CMC_1 is experimentally obtained CMC of the more hydrophobic (nonionic) micelle and CMC_2 is the CMC of SDS and α is the mole fraction of the more hydrophobic nonionic surfactant in the solution.

The X_1^{id} value is used to calculate the mole fraction of the more hydrophobic micelle in the real mixed micelle (X_1), according to Rubingh [27]. The X_1 value was obtained using the relation.

$$\frac{X_1^2 \ln(CMC^{ex} / CMC_1 X_1)}{X_1 \ln\left(\frac{CMC^{ex}}{CMC_2 X_1}\right)} = 1 \quad (3)$$

Eq. 3 was solved iteratively to obtain the value of X_1 from which the interaction parameter β , was evaluated using Eq. 4.

$$\beta = \frac{\ln(CMC^{ex} / CMC_1 X_1)}{X_1 \ln\left(\frac{CMC^{ex}}{CMC_2 X_1}\right)} \quad (4)$$

Synergism in mixed micelle formation exists when the CMC of the mixed micelles is less than that of individual micelles among the mixture. The conditions for synergism to exist in the mixture are [27, 29].

- (a) β must be negative,
- (b) $|\beta| > |\ln(CMC_1 / CMC_2)|$

A negative value of β indicates synergism in mixed micelle formation. A positive value indicates antagonism and if $\beta = 0$ then mixed micelle formation is ideal. The less negative value of β interaction means the weaker synergism. The value of β evaluated shows the deviation of CMC^{ex} with CMC^{id} . The values of the interaction parameter, β calculated for the binary mixtures of SDS/TX-100 and SDS/Tween 20 at different mole fractions are presented in Table 6.

Table 6. The interaction parameter (β) for the binary mixtures of SDS/TX-100 and SDS/Tween 20.

mole fraction X_{SDS}	β	
	SDS/TX-100	SDS/Tween 20
0.75	- 3.3	-3.9
0.25	-1.8	-2.4

The analysis of data (Table 6) indicates that, the interaction parameter (β) has negative value for both SDS/TX-100 and SDS/Tween 20 binary mixtures. This gives a direct evidence for the existence of synergism in the micelle mixtures. A negative deviation from the ideal behaviour of the binary mixture is reflected in negative β value. The negative β values correspond to a net attraction or cooperation between the two different surfactant molecules.

Although few micelles systems behave ideally, most of the mixed micellar systems reported behave non-ideally. The deviation of β from zero accounts for the non-ideality which results from molecular interaction between the surfactant head groups. Further, from the β values, in Table 6. it is proved that SDS/TX-100 mixed micelle show the weakest synergistic effect compared to SDS/Tween 20 mixture. The reason for weakest interaction is shorter hydrophobic tail of TX-100 compared to Tween 20. The oxyethylene part of TX-100 is shorter and less hydrophobic than the hydrocarbon tail of Tween 20. Furthermore, the repulsive force between the anionic heads of SDS are weaker at the surface of SDS/Tween 20 mixed micelle than at the surface of SDS/TX-100 mixed micelle. The head of Tween 20 molecule is larger than the head of TX-100 and captivate larger surface area of the mixed micelles. Larger head groups of Tween 20 molecule create greater distance between anionic heads of SDS, thus reducing repulsive forces, increasing synergistic effect and favouring mixed micelle formation.

The data also show that the β have lower negative values for the binary mixtures with higher nonionic mole ratio. Rubingh and Rosen [27,29] had indicated that for mixed micelles with lower TX-100 mole ratio showed higher synergism. This is in accordance with our results.

The CMC values of Tween 20 and its binary mixtures are low as compared with TX-100 and its mixtures. This is because the CMC values of pure components and mixed systems depend on hydrophobic chain length of the surfactants. With rise in alkyl chain length of Tween 20, CMC value of the surfactant decreases significantly. Micellization depends on the hydrophobicity of surfactants and polarity of the bulk medium. The hydrophobicity of the surfactants increases with the chain length, resulting in thermodynamic threshold required for the formation of the micelles to be reached at lower surfactant concentration in the case of higher alkyl chain length surfactants. The CMC of mixed micelles and the average β parameter calculated for SDS/ TX-100 and SDS/Tween 20 micellar systems are in good agreement with the values of β reported by other researchers [30,31].

3.2. Kinetic effect

The electron transfer reaction between PSAA and $[\text{Fe}(\text{NN})_3]^{3+}$ were studied in binary micellar systems containing anionic surfactant SDS and other nonionic surfactants such as SDS/ TX-100 and SDS/Tween 20 with various mole ratios. It has been observed that above the CMC all these binary mixed micellar systems have catalyzing effect on the electron transfer reaction rate.

In the case of SDS/TX-100 binary mixture (Table 2), at low concentration of TX-100 (3:1), enhancement of rate is observed for the reaction between PSAA and $[\text{Fe}(\text{bpy})_3]^{3+}$ while at higher concentration (1:3) rate retardation is observed compared to the reaction in SDS medium. The reason for the rate enhancement at low concentration of TX-100 can be explained by the reduction of repulsive forces between the head groups of SDS by TX-100. It is assumed that in the SDS/TX-100 mixture at low concentration of TX-100 the ethoxylated chain of the TX-100 coil around the negatively charged SDS, screening the electrostatic repulsion. Therefore the negative head of SDS micelle is readily available for the adhesion of the positively charged oxidizing species $[\text{Fe}(\text{NN})_3]^{3+}$. Thus more amount of $[\text{Fe}(\text{NN})_3]^{3+}$ ions are accumulated on the micellar surface. As the PSAA molecule with aryl moiety is also attached to the micellar phase by means of hydrophobic interaction, there is a close proximity between the reactants and thus rate of ET is enhanced than that of pure SDS.

It is also seen from the Table 6 that the interaction parameter β is a higher negative (-3.3) value for the higher ratio of SDS in SDS/TX-100 mixture micelle. The high value of β indicates high synergistic effect in the solution i.e. existence of more interaction between the micelles and reactants. Thus the observed rate enhancement in this composition (SDS/TX-100=3:1) is in accordance with the synergistic interaction.

At higher concentration of TX-100 in SDS/TX-100 mixture micelle (1:3 ratio), the observed rate retardation effect can be attributed by the occupation of more number of non-ionic TX-100 micelles in the surface and interface of the anionic micelle, SDS. This results in the dilution of negative charge density on the surface of the mixture micelle. Due to the reduction in negative charge, number of $[\text{Fe}(\text{NN})_3]^{3+}$ accommodated in the micellar phase is greatly reduced. At the same time number of PSAA molecules enter in to the micellar phase increases as a result of increase in hydrophobic attraction. This leads to retardation in the rate of reaction in SDS/TX-100 mixture (1:3) compared to the rate constant in pure SDS micelle. The less interaction between the components of micelle can also be seen from the low β value observed in this mixture (-1.8) (Table 6).

Interestingly when SDS micelle concentration is increased in SDS/TX-100 mixture micelle, increase in rate constant is observed throughout the concentration range. However, rate acceleration observed in low concentration of SDS is comparatively lesser than in higher concentrations of SDS. This can be explained by gradual increase in negative charge on the surface of the mixture micelle as the concentration of SDS increases. As the result of increase in negative charge on the mixed micelle, number of $[\text{Fe}(\text{NN})_3]^{3+}$ attached to the micellar phase also increases i.e, interaction between micelle and reactants increases. This explanation is supported by the observed less negative β value. The observed low negative (-1.8) (Table 6) β value for this mixture shows less synergistic interaction. This value correlates well with the lesser rate enhancement in this mixture compared to TX-100.

The higher rate acceleration in higher ratio of SDS in a binary mixture can be explained as follows. When a large amount of SDS is added to the TX-100, large amount of negative heads are available on the micellar phase for the adhesion of the positively charged reactant. Due to the accumulation of reactants on the micellar phase, the rate of reaction is accelerated more in the mixture compared to pure TX-100. The larger β interaction parameter (-3.3) (Table 6) for this mixture shows larger interaction among the micelle components. The enhanced kinetic effect observed in this mixture is a direct evidence for the larger synergistic effect shown by this higher anionic ratio mixed micelle. The same trend is also observed in the

rate of ET reaction between PSAA and $[\text{Fe}(\text{NN})_3]^{3+}$ in SDS/TX-100 and SDS/Tween 20 mixed micelles. (Table 3 to 5)

When the rate of the reaction in SDS/TX-100 and SDS/Tween 20 mixed micelle are compared, higher rate enhancement is observed in SDS/Tween 20 system. The head of Tween 20 micelle is larger than that of TX-100 and captures larger surface area of the binary mixture when mixed with SDS. The repulsive forces between the anionic heads of SDS are very much reduced in the presence of Tween 20. Because of the large head groups of Tween 20 molecules [32], distance between anionic heads of SDS increases. The reduction in repulsive forces leads to more interaction between the micelles. This higher interaction of mixed micelle makes the reactant $[\text{Fe}(\text{NN})_3]^{3+}$ strongly attached to the micellar phase. PSAA is also accumulated readily to the micellar phase due to the more hydrophobic nature of Tween 20. Tween 20 is more hydrophobic than TX-100 not only due to the larger size of the head group but also due to rise in alkyl chain length. With rise in the length of the tail, the hydrophobicity of the micelles increases. Therefore in SDS/Tween 20 mixture large amount of the reactants $[\text{Fe}(\text{NN})_3]^{3+}$ and PSAA are associated closely in micellar phase. This resulted in the enhancement of rate of reaction in SDS/Tween 20 mixture compared to SDS/TX-100 mixture.

This rate acceleration in SDS/Tween 20 can be further explained by its synergistic interaction parameter (Table 6). The experimentally determined higher β values for SDS/Tween 20 compared to SDS/TX-100 shows that SDS/Tween 20 is more synergistic than SDS/TX-100. When synergistic interaction is high the adsorption of reactants on the micellar phase is also high. Therefore the reaction between $[\text{Fe}(\text{NN})_3]^{3+}$ and PSAA takes place rapidly. This kinetic investigation is a direct evidence for the synergistic interaction.

4. Conclusion

It has been revealed that interaction parameter (β) has negative values for the SDS/TX-100 and SDS/Tween 20 binary systems indicating existence of synergism in the mixed micellar systems. SDS/TX-100 mixed micelles showed the weaker synergistic effect compared to SDS/Tween 20. The oxyethylene part of TX-100 is shorter and less hydrophobic than hydrocarbon tail of Tween 20, creating the weaker synergistic effect. Besides the repulsive forces between the anionic heads of SDS are weaker at the surface of SDS/Tween 20 mixed micelles than at the surface of SDS/TX-100 mixed micelles. The polar heads of Tween 20 molecule is larger in size than the head of TX-100 and occupies larger surface area of the mixed micelles. These results in the stabilisation of micellar phase by decreasing the surface charge density.

The observed kinetic results showed that the rate of electron transfer reaction enhanced more in mixed micelles. There is reduction in repulsive forces between the anionic head groups of mixed micelles through the insertion of non-ionic micelles. These led to the adsorption of reactants to the micellar surface and thereby increasing the electron transfer reaction. The CMC determination and kinetic results are the direct evidence for synergistic effect.

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