Journal of Chemical Technology and Metallurgy, 56, 6, 2021, 1219-1224

KINETICS OF BASE HYDROLYSIS OF TRIS(1,10-PHENANTHROLINE) IRON (II) COMPLEX IN THE PRESENCE OF MIXED SURFACTANTS OF SODIUM DODECYL SULPHATE AND TRITON X- 100: SYNERGISM AND CATALYTIC PROPERTY OF MIXED MICELLES

R S S Srikanth Vemuri[1], Shyamala Pulipaka[2],
Venkata Naga Lakshmi Kilana[3], Krishna Murthy Mannam[4]

[1]*Department of Basic Sciences & Humanities,*
Vignan's Institute of Engineering for Women,
Kapujaggarajupeta, Visakhapatnam, Andhra Pradesh, India
[2]*Department of Physical and Nuclear Chemistry & Chemical Oceanography*
School of Chemistry, Andhra University, Visakhapatnam, Andhra Pradesh, India
E-mail: shyamalapulipaka06@gmail.com
[3]*Department of Chemistry, Gayatri Vidya parishad*
College of Engineering (Autonomous)
Visakhapatnam-530048, Andhra Pradesh, India.
[4]*Department of Chemistry (PG), S V R M College*
Nagaram, Andhra Pradesh, India

Received 28 September 2020
Accepted 10 January 2021

ABSTRACT

To explore the catalytic property of mixed micelles, the kinetic study of the base hydrolysis of $[Fe(phen)_3]^{2+}$ was carried out in the presence of mixed micelles formed by surfactants of sodium dodecyl sulphate (SDS) and TritonX-100 over a wide range of mol fractions (α) of Triton X-100 and total surfactant concentrations (C_t). As a prerequisite to the kinetic study, micellization behavior of the mixed surfactants of SDS and Triton X-100 has been studied. The critical micellar concentrations (C_{exp}) of the mixtures of the two surfactants were determined experimentally using surface tension measurements. Using the C_{exp} values the average interaction parameter was calculated which indicates a synergistic behavior of the mixed micellar system. In the kinetic study, it was found that, at fixed value of C_t , the pseudo rate constant (k_2) of reaction increases with increasing the value of α and decreases with increasing total surfactant concentration, C_t at constant α. The pseudo phase model was applied to interpret the kinetic data in terms of binding constants.

Keywords: kinetics, mixed micelles, synergism.

INTRODUCTION

Mixed micellar aggregates are systems composed of two or more different surfactants in equilibrium with monomers. These systems are important because of the synergism shown by the surfactant mixtures in their properties which results in better performance compared to pure surfactants [1 - 4]. The structural and physicochemical aspects of these micelles have been well studied [2, 5 - 8] but studies involving kinetics of reactions influenced by mixed micelles are very few [9 - 13]. In the few reactions reported in literature so far, simple pseudo phase model was applied to account for the kinetic behavior. We have earlier reported kinetics of alkaline hydrolysis of isatin in presence of CTAB/Triton X-100 mixed micelles [12]. In order to explore the catalytic behavior of mixed micelles further, we have taken up the kinetic study of the base hydrolysis of tris(1,10-phenanthroline)iron(II) complex, in the presence of SDS and Triton X-100 mixed micellar systems which was well studied in aqueous and other media [14 - 19]. It is essential to investigate the synergistic property of the micellar system before kinetic study to understand the catalytic property of the system. The synergistic behavior and the kinetic results are reported in this paper.

EXPERIMENTAL

All solutions were prepared in doubly distilled water and chemicals used were of analytical reagent grade. SDS and Triton X-100 were obtained from Merck, India and used without purification.

Determination of CMC of mixed micelles {Cexp}

The CMC's of pure SDS, pure Triton X-100 and the mixtures of SDS - Triton X-100 were determined from surface tension measurements using a stalagmometer at an ionic strength, $\mu = 0.08$ mol dm^{-3}. CMC's were determined at different total surfactant concentrations and at different mole fractions of SDS surfactant[α].

Kinetic measurements

The kinetic measurements were carried out using a Shimadzu UV-1800 double beam spectrophotometer by measuring the decrease in absorbance of $[Fe(phen)_3]^{2+}$ at 510 nm. The reaction was carried out under pseudo first order conditions, $[OH^-] >> [[Fe(phen)_3]^{2+}]$. The kinetic data are the average from duplicate runs with reproducibility less than ± 3 %. All the experiments were performed at 30.0 ± 0.1ºC.

RESULTS AND DISCUSSION

Determination of interaction parameter β and CMC{C_{calc}}

The pseudo-phase models are quite successful in predicting the behaviour of both binary non-ionic and binary ionic mixtures of surfactants which but in the case of binary mixtures of nonionic and ionic surfactants or of surfactants with different hydrophilic groups deviations from the ideal pseudo-phase model were observed. A pseudo-phase model where non ideal mixing is treated using a regular solution approach was developed for non-ideal binary surfactant mixtures which takes into consideration the activity coefficients f_1 and f_2 of the surfactants 1 and 2 involved in micellzation [20, 21]. The CMC of the mixtures can be calculated as

$$\frac{1\alpha}{C_{cal}} = \frac{(1-\alpha)}{f_1C_1} + \frac{}{f_2C_2} \tag{1}$$

In this equation, α_1 is the stoichiometric mole fraction of surfactant1in the mixture. For ideal behaviour, $f_1 = f_2 = 1$. The nature and strength of the interactions between surfactants is determined by calculating β parameter. The first step in the determination of the β parameter is determination of CMC experimentally (C_{exp}) from the surface tension (γ) versus log concentration (log *C*) plots of aqueous solutions of the individual surfactants and their mixtures. The value of C_{exp} was substituted in equation (2) is derived by Rubingh [20].

$$\frac{X_1^2 \ln[\alpha C_{exp}/X_1C_1]}{(1-X_1)^2[\ln(1-\alpha)C_{exp}/(1-X_1)C_2]} = 1 \tag{2}$$

where X_1 is the mole fraction of surfactant 1 in the mixed micelle. Equation (2) was solved for X_1 using Gauss - Newton iterative method in FORTRAN developed by the authors to obtain the value of X_1. Substitution of the value of X_1 in Equation (3) gives the value of interaction parameter β for each mole fraction.

$$\beta = \frac{\ln[\alpha C_{exp}/X_1C_1]}{(1-X_1)^2} \tag{3}$$

The value of β is a measure of the extent of interaction between the surfactants, negative values indicating synergism and positive values antagonism. Once the values of X_1 and β are known, f_1 and $f_2$were calculated using the expression

$$f_1 = \exp(\beta(1-X_1)^2 \text{ and } f_2 = \exp(\beta X_1^2) \tag{4}$$

and then C_{calc} calculated using equation (1). From the values of f_1 and f_2,the total monomer concentration of the two surfactants (C_{mon}) above the mixture CMC for a given total surfactant concentration (C_t) is obtained from equation (5).

$$C_{mon} = X_1f_1C_1 + (1-X_1)f_2C_2 \tag{5}$$

The total concentration of the micellized surfactants, C_M (= C_t - C_{mon}) is then calculated and used in the analysis of kinetic data in this work. Table 1 shows the values of X_1, β, C_{calc}, C_{mon} obtained. The β values indicate that SDS-Triton X-100 mixtures show a negative deviation from ideal behavior implying attractive interactions between the two surfactants in the micelles.

Table 1. CMC_{12}, X_1, β and Average β for SDS-Triton X-100 System in 0.08 mol dm^{-3} Na_2SO_4 at 30°C.

Mol fraction of TRITON X-100, α	$CMC_{12}x10^3$ (mol dm^{-3}) Experimental	$CMC_{12}x10^3$ (mol dm^{-3}) Calculated	X_1	β	f_1	f_2	$C_{mon}x10^3$ (mol dm^{-3})
0.0	1.0	-	-	-	-	-	-
0.1	0.8	0.83	0.759	-2.63	0.985	0.859	0.83
0.2	0.6	0.80	0.577	-1.03	0.832	0.709	0.60
0.4	0.4	0.40	0.434	-1.85	0.553	0.706	0.40
0.5	0.25	0.25	0.418	-3.56	0.299	0.537	0.25
0.8	0.25	0.25	0.301	-3.68	0.116	0.716	0.25
0.9	0.15	0.15	0.323	-6.69	0.046	0.498	0.15
1.0	0.4	-	-	-	-	-	-

Kinetic Study

The kinetic investigations have been carried out in the presence of mixed micelles of SDS and Triton X-100 under the conditions, $[OH^-] >>> [Fe\ (phen)_3]^{2+}$ thus isolating $[Fe(phen)_3]^{2+}$. A plot of $\log(A_t)$ versus time (where A_t is the absorbance at time t) has been found to be linear for at least 95 % of the reaction showing first order kinetics with respect to $[Fe\ (phen)_3]^{2+}$. The study was carried out at different initial concentrations of OH^- ion and the plots of pseudo first order rate constant k' versus $[OH^-]$ were found to be linear with a small positive intercept. The observed first order rate constant can be written as

$$k' = k_1 + k_2[OH^-] \tag{6}$$

where k_1 is the OH^- independent path and k_2 is the OH^- dependent path as is the case in aqueous medium.

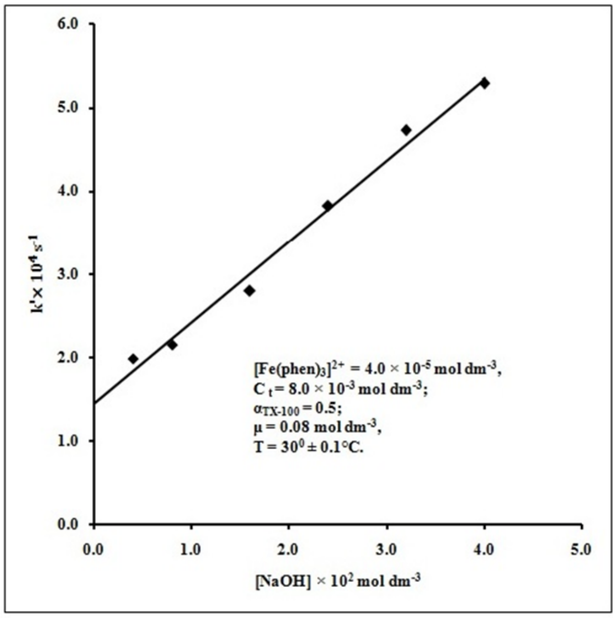

Fig. 1. k' vs. [NaOH] at $[Fe(phen)_3]^{2+} = 4.0x10^{-5}$ mol dm^{-3}; [SDS] = $4.0x10^{-3}$ mol dm^{-3} ; α = 0.5; μ = 0.08 mol dm^{-3}, T = 30°C.

Effect of pure SDS and Triton X-100 on the rate

Fig. 2 shows a plot of k' against different initial concentrations of SDS and Triton X-100. The plot shows that k' values fall sharply with increase in concentration of SDS till about $1x10^{-3}$ mol dm^{-3} and beyond this, the increase in SDS concentration shows saturation effect. The first order rate constant values decrease more than thirty times in SDS micellar media compared to aqueous medium. In contrast to the above observation, the reaction is marginally accelerated in the presence of Triton X-100. The inhibition by SDS is attributed to the electrostatic repulsions between OH^- and the anionic surfactant that prevent OH^- ions from reaching $[Fe\ (phen)_3]^{2+}$ which are accumulated on the negative surfactant.

Effect of α (mole fraction of Triton X-100) and C_t (total surfactant concentration) on the rate

A series of kinetic runs were carried out over a wide range of stochiometric mole fractions (α) and at different

Table 2. First-order rate constants, $k^{'}x10^4\ s^{-1}$ of reaction in SDS-Triton X-100 surfactant mixtures varying Triton X-100 mole fractions (T=30°C, $[Fe(phen)_3]^{2+} = 4.0x10^{-5}$ mol dm^{-3}; [NaOH] = 0.03 mol dm^{-3}; μ = 0.08 mol dm^{-3}). The First-order rate constant, k_W obtained in bulk water (in the absence of surfactant) is 15.14x10^{-4} s^{-1}.

[SDS]×10^3 (mol dm^{-3})	α			
	0.2	0.4	0.6	0.8
0.4	6.02	6.09	7.33	8.41
0.6	5.88	6.06	6.42	8.21
0.8	5.76	5.96	5.89	7.54
1.0	4.41	5.76	5.72	6.95
2.0	3.19	4.57	5.36	6.74
4.0	2.65	4.46	5.00	6.45
8.0	2.64	4.17	4.82	6.24
16.0	2.59	4.01	4.52	6.14
24.0	2.55	3.98	4.42	5.61
30.0	2.51	3.84	4.21	4.94

The First-order rate constant, kW obtained in bulk water (in the absence of surfactant) is 15.14x10-4 s^{-1}.

total surfactant concentrations (C_t). The observed rate constants are shown in Table 2. The results show that, at a fixed C_t, as the mole fraction of Triton X-100, i.e., α increases, the rate increases. The presence of nonionic surfactant molecules minimizes the electrostatic repulsions between the SDS head groups, thus facilitating micellar ionization (Counter ion binding decreases leading to increase in rate). Also, as the mole fraction of

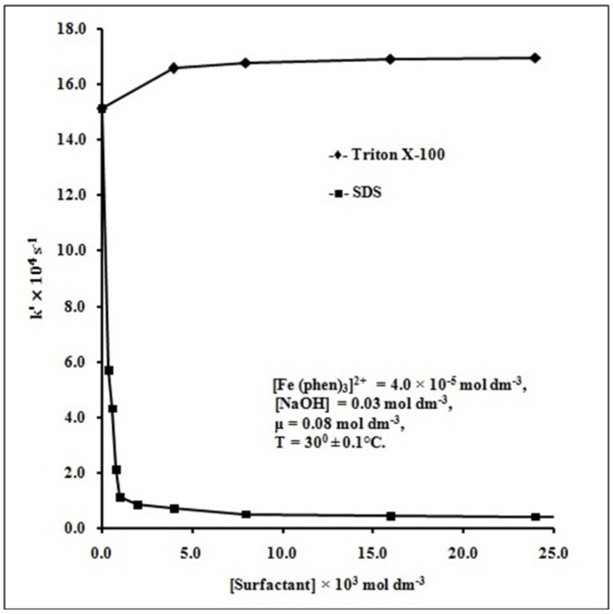

Fig. 2. k' vs.[surfactant] of SDS and Triton X-100 at $[Fe(phen)_3]^{2+} = 4.0x10^{-5}$ mol dm^{-3}; [NaOH] = 0.03 mol dm^{-3}; μ = 0.08 mol dm^{-3}; T = 30°C.

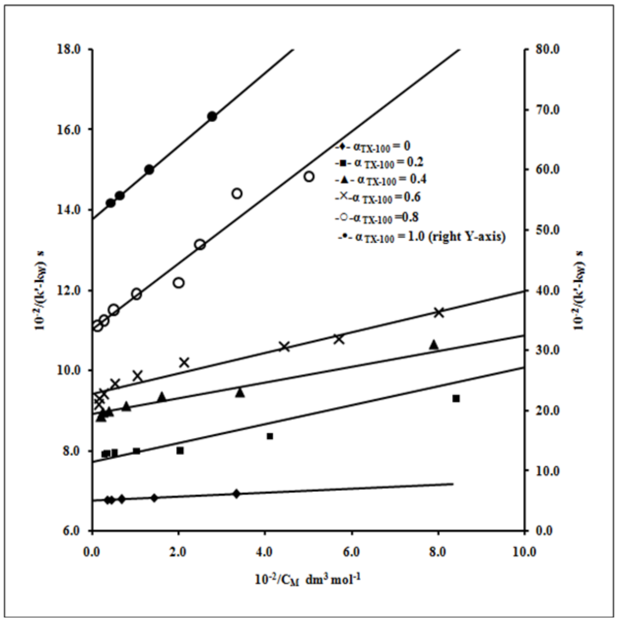

Fig. 3. $1/(k'-k_w)$ vs. $1/C_m$ at different mole fractions of Triton X-100 α = 0.2, α = 0.4, α = 0.6, α = 0.8, T = 30°C.

Table 3. Binding constants, K_A and rate constant, k_M obtained at varying Triton X-100 mol fractions (T=30°C, μ=0.08 mol dm^{-3}).

α	$K_A \times 10^{-2}$ ($dm^3\ mol^{-1}$)	$K_M \times 10^4$ (s^{-1})
0.2	73.36	27.88
0.4	41.34	26.39
0.6	36.80	25.75
0.8	11.06	24.85

Triton X-100 increases, binding between $[Fe(phen)_3]^{2+}$ and SDS decreases, decreasing the distance between $[Fe(phen)_3]^{2+}$and $[OH^-]$.

For a given mole ratio, the influence of mixed micelles of SDS/Triton X-100 was also determined at different total surfactant concentrations. The results show that the rate constants decrease with increase in SDS and hence total surfactant concentration C_t. Here there are two opposing factors, inhibition by SDS and marginal acceleration by Triton X-100. Since the inhibition by SDS is more significant, there is an overall decrease in the rate constants.

Mechanism

The values of $k_1 = 9.0 \times 10^{-5}\ s^{-1}$ and $k_2 = 1.043 \times 10^{-2}\ mol^{-1}\ L\ s^{-1}$. (Eq. 6, Fig. 1) indicate that $k_1 << k_2$. Therefore $k' \approx k_2\ [OH^-]$. Accordingly, the mechanism in Fig. 4 is considered for the kinetics in the presence of mixed micelles of SDS and Triton X-100. In this reaction scheme, k_W and k_M indicate the rate constants in aqueous and micellar pseudo-phases, respectively, and K_A represents the binding constant of the complex. The overall hydrolysis rate is the sum of the rates of the two pathways involving the hydroxide ion in bulk water and the cationic complex in each pseudo-phase. The decreasing trend of k' observed at a given Triton X-100 mole fraction, with increasing total surfactant concentration (or SDS concentration in the surfactant mixture) is explained by the equation of pseudo phase model [17] given below.

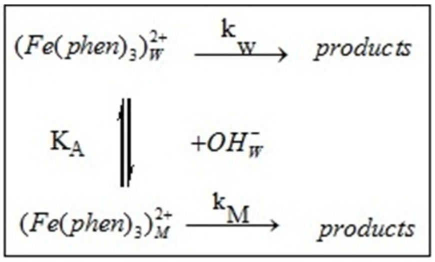

Fig. 4. The mechanism for the base hydrolysis of $(Fe(phen)_3)^{2+}$ in mixed micellar medium.

$$\frac{1}{(k'-k_w)} = \frac{1}{(k_M-k_w)} + \frac{1}{(K_A C_m (k_M-k_w))} \qquad (7)$$

According to equation (7), a plot of $1/(k'-k_w)$ versus $1/C_m$ should be linear with an intercept. Such a plot was obtained and the values of k_M and K_A are given in Table 3. k_M and K_A can be evaluated from the slope and intercept of the plot. The values show that as the mole fraction of Triton X-100 increases (i.e., as mole fraction of SDS decreases) the binding constant of the complex decreases and favours the approach of OH^- ion towards the complex. This is in agreement with the observed rate constant k' increasing with increase in the mole fraction of Triton X-100 (Table2).

CONCLUSIONS

The mixed critical micelle concentrations of SDS/Triton X-100 at different mole fractions determined experimentally were used to calculate interaction parameter β. The negative values of β parameter shows that SDS and Triton X-100 mixtures exhibit synergistic behavior.

Kinetic studies of the basic hydrolysis in these mixed micelles (SDS and Triton-X) show that there is a marked dependence of rate on the composition of mixed micelles.

Acknowledgements

PS is thankful to Ministry of Earth Sciences (MOES), National Centre for Coastal Research (NCCR) and Government of India for financial support under major project No MOES/ICMAM – PD/Supply, Order/81/2017 .

REFERENCES

1. P.M. Holland, D.N. Rubingh in: Mixed Surfactant Systems, (ACS Symp. Series.), P.M. Holland, D.N. Rubingh (Eds.), American Chemical Society, 1992, p.1.
2. J.F. Scamehorn, in: Phenomena in Mixed Surfactant Systems, (ACS Symp. Ser. 311), J.F. Scamehorn (Eds.), American Chemical Society, 1986, p. 25.
3. K. Ogino, M. Abe, in: Mixed Surfactant Systems, (ACS Symp. Ser. 311), J.F. Scamehorn (Eds.),

American Chemical Society, 1986, p. 68.

4. M.J. Rosen, in: Mixed Surfactant Systems, (ACS Symp. Ser. 311), J.F. Scamehorn (Eds.), American Chemical Society, 1986, p. 144.
5. H. Hoffmann, G. Possnecker, Langmuir, 10, 2, 1994, 381-389.
6. K.L. Herrington, E.W. Kaler, D. Miller, J.A. Zasadzinski, J.Chiruvolu, J. Phys. Chem., 97, 51, 1993,13792-13802.
7. J.B. Huang, G.X. Zhao, Colloid. Polymer. Sci., 273, 2, 1995,156-164.
8. Y. Kondo, H. Uchiyama, N. Yoshino, K. Nishiyama, M. Abe, Langmuir, 11, 7, 1995, 2380-2384.
9. H.K. Mandal, T. Majundar, A. Mahapatra, Colloids Surf. A., 380, 1-3, 2011, 300-307.
10. H.K. Mandal, T. Majundar, A. Mahapatra, J. Disper. Sci. Technol, 37, 4, 2016, 555-564.
11. S. Wright, C.A. Bunton, P.M. Holland, in: Mixed Surfactant Systems, (ACS Symp. Series), P.M. Holland, D.N. Rubingh (Eds.), American Chemical Society, 1992, p. 13.
12. V. Srikanth, P. Shyamala, A. Satyanarayana, Indian. J. Chem. Sec A., 51A, 12, 2012, 1701-1705.
13. C.A. Bunton, S. Wright, P.M. Holland, F. Nome, Langmuir, 9, 1, 1993, 117-120.
14. A. Ezz-Eldin,.A. Gharib, N. Gosal, J. Burgess, Croat. Chem. Acta., 74, 3, 2001, 545-558.
15. F.M. Mengerr, C.E. Portnoy, J. Am. Chem. Soc., 89, 18, 1967, 4698-4703.
16. J. Burgess, M.J. Blandamer, P. Cookson, D.L. Roberts, P. Wellings, F.M. Mekhail, P. Askalani, J. Chem. Soc, Dalton Trans, 1978, 996-1000.
17. M.J. Blandamer, J. Burgess, D.L. Roberts, J. Chem. Soc., Dalton Trans., 1978, 1086-1090.
18. G. Venkateswarlu, P. Shyamala, P.V. Subba Rao, K. Ramakrishna, Ind. J. chem. Sec A, 41A, 7, 2002, 1410-1414.
19. Deepa Sarkar, K.C. Khilar, Gousia Begum, P.V. SubbaRao, Colloids.surf.A., 268, 1-3, 2005, 73-77.
20. P.M. Holland, D.N. Rubingh, J. Phys. Chem., 87, 11, 1983, 1984-1990.
21. D.N. Rubingh in: Solution Chemistry of Surfactants, K.L. Mittal (Eds.), v. 1, Plenum Press, New York, 1979, p. 337.