CATALYTIC EFFECT OF TX-100/SDS MIXED MICELLES ON THE HYDROLYSIS OF [Fe (tpy)$_2$]$^{2+}$ COMPLEX- EVALUATION OF NON-IDEAL INTERACTION PARAMETERS USING GAUSS-NEWTON ITERATION TECHNIQUE.

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Abstract

A computational algorithm based on the Gauss-Newton iteration technique was developed to determine the composition of the mixed micelles of TritonX-100/SDS, the interaction between the two surfactants, β,and the activity coefficients of the surfactants in the micelle. Negative β values at different mole fractions of TritonX-100 were obtained which indicate synergism between the two surfactants.

The catalytic effect of mixed micelles of TritonX-100/SDS on the hydrolysis of $[Fe(tpy)_2]^{2+}$in the presence of base was studied over a number of mole fractions (α_a) of TritonX-100 and total surfactant concentrations(C_t). It was found thatthe rate of the reaction increases with α_a and decreases with increasing surfactant concentration, C_t. The analysis of kinetic data was carried out by applying the pseudo phase model. Binding constants, K_A, obtained from the kinetic data also indicate synergism between the two surfactants.

Keywords:kinetics, mixed micelles, pseudo phase separation model, base hydrolysis.

INTRODUCTION

Mixed micelles contain a mixture of two or more different surfactants. These mixed micelles are important because of the synergism exhibited to give a higher performancecompared to individual surfactants [1-4]. This is attributed to the interaction between the surfactants of different nature in the micelles. The physical properties of these micelles have been studied before [2,5-8] but kinetic study of reactions involvingmixed micelles are very few [9-12]. Therefore, to study the effect of mixed micelles on rates of reactions, a kinetic study of the base hydrolysis of bis(2,2';6',2"–terpyridyl)iron(II)

complex, in the presence of TritonX-100/SDS mixedmicelles has been carried out. A computational method for calculating the non-ideal mixing parameters using Gauss-Newton method was developed for use in understanding the synergetic behavior of the mixed micelles.

EXPERIMENTALSECTION

Double distilled-water was used for preparation of solutions and analytical reagent grade chemicals were used. SDS and TritonX-100 were obtained from Merck. Bis(2,2';6',2"-terpyridyl) iron(II), 0.02 mol dm^{-3}, was prepared by mixing ferrous ammonium sulphate (0.07842gm,Merck) and terpyridine(0.09334gm, sigma) in the ratio (1:2).

Experimental Determination of CMC of mixed micelles (C_{ex}):

Surface tension measurements were carried out to determine the CMC's of SDS, Triton X-100 and Triton X-100/SDS mixtures using a stalagmometer maintaining an ionic strength, μ, of 0.1 mol dm^{-3}[15].

Monitoring of the kinetics of the Reaction:

The reaction was followed by determining the absorbance of $[Fe(tpy)_2]^{2+}$ (λ_{max}= 556nm).A double beam spectrophotometer(Shimadzu UV-1800) was used for the purpose. Duplicate runs were performed and averages reported.

RESULTS AND DISCUSSION

The CMC's (C_{exp}) of the binary mixtures of Triton X-100 and SDS with varying compositions and total concentrations were found to deviate from the ideal values (C_{ideal}) that were calculated using the eq. (1), derived by Clint[13].

$$\frac{1}{c_{ideal}} = \frac{\alpha_a}{c_a} + \frac{1-\alpha_a}{c_b} \quad (1)$$

α_a, is the mole fraction of the surfactant 'a' and C_a, C_b are the CMCs of pure surfactants. Therefore, the treatment proposed by Rubing [14] that took into consideration of the interaction between the surfactant molecules of different head groups was applied. The mole fraction (x_a) of the surfactant 'a' in the mixed micelle (eq. 2) was determined iteratively by Gauss-Newton method.

$$f(x_a) = x_a^{\,2} ln\left(\frac{c_{\exp}\alpha_a}{c_a x_a}\right) - (1-x_a)^2 ln\left(\frac{c_{\exp}(1-\alpha_a)}{(1-x_a)c_b}\right) \quad (2)$$

Using the value of x_a, the interaction parameter β and the activity coefficients f_a and $f_b$of the surfactants 'a' and 'b' in the mixed micelle were determined using equations (3).

$$f_a = \exp\beta(1-x_a)^2$$
$$f_b = \exp\beta x_a^{\,2} \quad (3)$$

A computer program, 'MMC' developed by the authors with source code in FORTRAN-95 programming language, for calculating the values of the mole fraction x_a, the interaction parameter, β, activity coefficients f_a and f_b, and the concentrations of monomers above CMC is depicted in Fig. 1. The required input for the program is,

1. Total initial concentration of the surfactants 'a' and 'b'
2. CMCs of surfactants 'a' and 'b'
3. Initial mole fraction, α of the surfactant 'a' in the mixture, Experimental CMC (C_{exp}) of the mixed surfactant.

The output of the program which runs under a 32- or 64-bit Windows-10/11 environment. includes,

1. CMCs of mixed micelle, CMC experimental, CMC calculated, CMC under ideal conditions
2. The interaction parameter, β,
3. Mole fractions, $x_a$and $x_b$of surfactants 'a' and 'b' in the mixed micelle
4. The activity coefficients f_a and f_b. and
5. Concentrations of monomers of surfactants along with the concentration of mixed micelle at a given total concentration of surfactants.

The program can be compiled and executed using any Fortran compiler. The executable module of the program is available from the corresponding author on request. Sample results of the program, using the data from the literature are shown in Table 1. The values of the interaction parameter, mole fraction of the surfactant 'a' in the micelle, activity coefficients along with the monomer concentrations for the Triton X-100/ SDS systems studied by the authors obtained using the program MMC were tabulated in Table 2. These β values (Table 2) were found to be negative which indicate synergistic behaviour. Therefore, further kinetic studies were carried out.

Kinetic Study:

The kinetic study has been carried out under the conditions, $[OH^-] >>> [Fe(tpy)_2]^{2+}$in the presence of mixed micelles of Triton X-100/SDS and a plot of log(Abs) versus time (where Abs is the absorbance at time t) has been found to be linearshowing first order with respect to the metal complex. The study of the effect of OH^- ion on the rate of the reaction shows that the plots of pseudo first order rate constant k versus $[OH^-]$ arelinear with no intercept.

Catalytic effect of single surfactants (SDS and Triton X-100):

When the reaction was carried out in aqueous medium and SDS, the reaction was found to be slower in SDS micelles by thirty timesand the rate constants decrease with increase in concentration of SDS. Beyond $1x10^{-3}$ mol dm^{-3} there is no further increase in rate. In contrast to the effect of SDS, the reaction is accelerated(around six times) in the presence of Triton X-100 (fig2). The slow rate in SDS is due to the electrostatic repulsions between

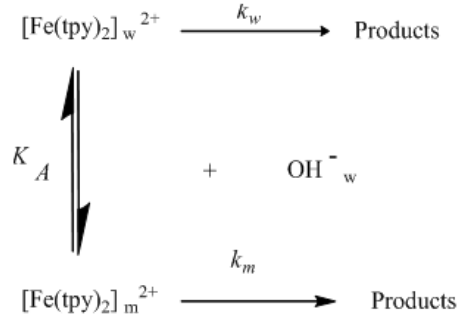
OH^- and the anionic SDS that prevent proximity of OH^- ions and $[Fe(tpy)_2]^{2+}$ while the $[Fe(tpy)_2]^{2+}$ions are present on the negative surfactant.

Catalytic effect of mixed micelles on the rate:

Kinetic runs were carried out at different stoichiometric mole fractions (α_a) and at different total surfactant concentrations(C_t)(Table 3). It can be seen that, at constant C_t, as the mole fraction of TritonX-100, α_a, increases, the rate increases. The presence of TritonX-100 reduces the repulsions between the SDS head groups which leads to increase in rate. Binding between $[Fe(tpy)_2]^{2+}$and SDS decreases as the mole fraction ofTritonX-100 increases, this increases the proximity between $[Fe(tpy)_2]^{2+}$and $[OH^-]$. Additionally, the impact of mixed micelles of TritonX-100/SDS was investigated while maintaining a constant mole fraction at various total surfactant concentrations. As the total surfactant concentration (C_t) increases, the rate constantsdecreases. The obtained results are a combination of two factors which act in opposite direction, negative catalytic effect by SDS which is more significant and marginal positive effect by TritonX-100.

Mechanism:

The reaction is first order with respect to both the metal complex and the base and therefore the mechanism given below was considered for the kinetics.



(4)

where k_w and k_m are the rate constants in aqueous and micellar phases respectively, K_A representsthe binding constant of the complex. Quantitative analysis for the kinetic data has been carried out using the pseudo phase model[1] given below.

$$\frac{1}{(k - k_w)} = \frac{1}{(k_m - k_w)} + \frac{1}{(K_A C_m (k_m - k_w))} \quad (5)$$

Based on equation (5), a plot of 1/ (k -k_w) versus 1/C_m gives the values of k_m and K_A from the slope and intercept (Fig.3,Table 4). And it was found that the binding constant, K_A of $[Fe(tpy)_2]^{2+}$decreases with increase in mole fraction of TritonX-100.

Synergism in mixed micelles is considered to be exhibited when a given property of the mixture can reach a more/less desirable value than that attained by either surfactant

component. Synergismin the present study is exhibited by the kinetic parameter, K_A, the binding constants of the reactants with micellar surface (Table 3). The value of K_A is 168.39,when $\alpha_{TX\text{-}100}$ is 0 while it is 0.729 at $\alpha_{TX\text{-}100}$ equal to 1. The values of K_A decreases from $\alpha_{TX\text{-}100}$ 0 to 1. However the trend in the values of K_A at $\alpha_{TX\text{-}100}$ = 0.6, 0.8 are closer to pure SDS i.e., $\alpha_{TX\text{-}100}$ = 0. If there was no synergism the values at $\alpha_{TX\text{-}100}$ = 0.6,0.8 should have been much lower than 10.492, 7.53 and closer to Triton X-100.

CONCLUSION

- Gauss-Newton iteration technique developed on FORTRAN was used to determine the interaction parameter β between the two surfactants.The negative values of β parameter obtained exhibit synergistic behavior.
- The binding constant valuesK_A, as a function of α_a, obtained from kinetic studies also showa synergistic behavior.
- The rate of the reaction in the presence of mixed micelle largely depends on the composition of mixed micelle and thereforereactions can be tailored for desired rates.

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Table 1.

S.No	System	Interaction parameter, β: Calculated by the Investigators	Interaction parameter, β: Calculated using the Program MMC	Reference
1.	TritonX-100/Cu(DS)$_2$	-1.60	-1.577	16
2.	Hpycl/TTAB	-1.72	-1.681	18
3.	SDS/TritonX-100	-4.12	-4.130	17
4.	TritonX-100/LiDS	-4.06	-3.830	16

Table 2. .CMC$_{12}$, x_a, β and Average β for TritonX-100/ SDS System in 0.1 mol dm^{-3} at 293K

Mol fraction of Triton X-100 α_a	CMCx10^3 mol dm^{-3} Experimental	CMCx10^3 mol dm^{-3} Ideal	x_a	β	f_a	f_b	[Monomer] x 10^3 moldm^{-3}
0.0	2.2	-	-	-	-	-	-
0.1	1.0	1.64	0.413	-2.11	0.484	0.697	0.388
0.2	0.8	1.31	0.512	-1.97	0.625	0.596	0.237
0.4	0.6	0.93	0.632	-2.03	0.760	0.445	0.174
0.6	0.4	0.72	0.676	-3.27	0.710	0.225	0.126
0.8	0.2	0.59	0.666	-6.56	0.481	0.054	0.058
1.0	0.5	__-	-	-	-	-	-

Table 3. First-order rate constants, k x10^5 s^{-1} of reaction in Triton X-100/SDS surfactant mixtures varying Triton X-100 mole fractions (T=293K, [Fe(tpy)$_2$]$^{2+}$ = 2.4x10^{-5} mol dm^{-3}; [NaOH] = 0.1 mol dm^{-3}; μ = 0.1 mol dm^{-3}).

[SDS]×10^3 (moldm^{-3})	α_a 0.2	0.4	0.6	0.8
0.4	40.30	44.52	68.70	80.22
0.6	26.48	42.21	61.41	68.70
0.8	23.41	38.38	57.19	66.01
1.0	13.05	25.71	52.20	57.19
2.0	10.05	18.04	50.64	54.88
4.0	7.67	15.73	49.13	54.12
8.0	5.37	13.05	48.74	50.28

The First-order rate constant, K_w obtained in bulk water (in the absence of surfactant) is 8.2x10^{-4} s^{-1}.

Table 4. Binding constants, $K_A$and rate constant,k_m obtained at varying Triton X-100 mol fractions (T=293K, μ=0.1mol dm^{-3}).

α_a	K_A×10^{-2}(dm^{3}mol^{-1})	k_m×10^4(s^{-1})
0.0	168.393	16.49
0.2	43.60	16.06
0.4	21.01	15.13
0.6	10.49	11.89
0.8	7.53	11.31
1.0	0.72	10.50

```
      implicit real*8(a-h,o-z)
      character ans
 5    write(*,*)
      write(*,*)'  Input total concentrations of surfactants a and b'
      read(*,*)ct
      write(*,*)'  Input CMCs of Surf-a and Surf-b'
      read(*,*)ca,cb
      write(*,*)"  Input the mole fraction of the surfactant 'a' and"
      write(*,*)"  the CMC of Mixed Surfactants"
      read(*,*)alpha,cexp
      cideal=1.0/(alpha/ca+(1.0-alpha)/cb)
      xa=alpha
10    p=log(cexp*alpha/(ca*xa))
      q=log(cexp*(1-alpha)/((1-xa)*cb))
      fx=xa**2*p-(1.0-xa)**2*q
      fdx=-1.0+2*xa*p+2*(1.0-xa)*q
      h=-fx/fdx
      xa=xa+h
      if(abs(h).ge.1.0e-12)go to 10
      beta=log(cexp*alpha/ca/xa)/(1.0-xa)**2
      fa=exp(beta*(1-xa)**2)
      fb=exp(beta*xa**2)
      ccal=1.0/(alpha/(fa*ca)+(1.0-alpha)/(fb*cb))
      xb=1.0-xa
      write(*,100)ct,ca,cb
      write(*,101)
      write(*,102)alpha,cexp,cideal,ccal,xa,xb,beta,fa,fb
c---------------------Free Monomers-above cmc
      delta=(fb*cb-fa*ca)
      cnum=-(ct-delta)+sqrt((ct-delta)**2+4*alpha*ct*delta)
      cdenom=2*((fb*cb-fa*ca)/(fa*ca))
      camon=cnum/cdenom
      cbmon=(1-camon/fa/ca)*fb*cb
      ctmon=camon+cbmon
      cmicell=ct-ctmon
      if(cmicell.lt.0.0)cmicell=0.0
      write(*,103)
      write(*,104)camon,cbmon,ctmon,cmicell
c-------------------------------------------------------
100   format(//3x,'Total conc. of Surf-a and Surf-b= ',e9.4
     1      //3x,'CMC-a= ',e9.4,2x,'CMC-b= ',e9.4)
101   format(//3x,'alpha-a',3x,'Mix CMC-Exp',4x,'Mix CMC-ideal',
     1  2x,'Mix CMC-Cal',3x,'Xa',4x,'Xb',8x,'Beta',6x,
     2  '  fa ',3x,'  fb '/)
102   format(3x,f5.3,3(5x,e10.3),2x,f5.3,2x,f5.3,5x,f6.3,
     1  4x, f6.2,2x,f6.2//)
103   format(/30x,'MONOMER CONCENTRATIONS',//15x,
     1  'Monomer-a',5x,'Monomer-b',5x,'Total monomer',6x,'[Micell]')
104   format(/3x,'Above CMC',2x,e10.3,4x,e10.3,6x,e10.3,7x,e10.3//)
      write(*,*)' Want to Input another set of data? Answer Y or N'
      read(*,*)ans
      if(ans.eq.'y'.or.ans.eq.'Y')go to 5
        stop
        end
```

Fig 1: Source Code of the Program 'MMC'

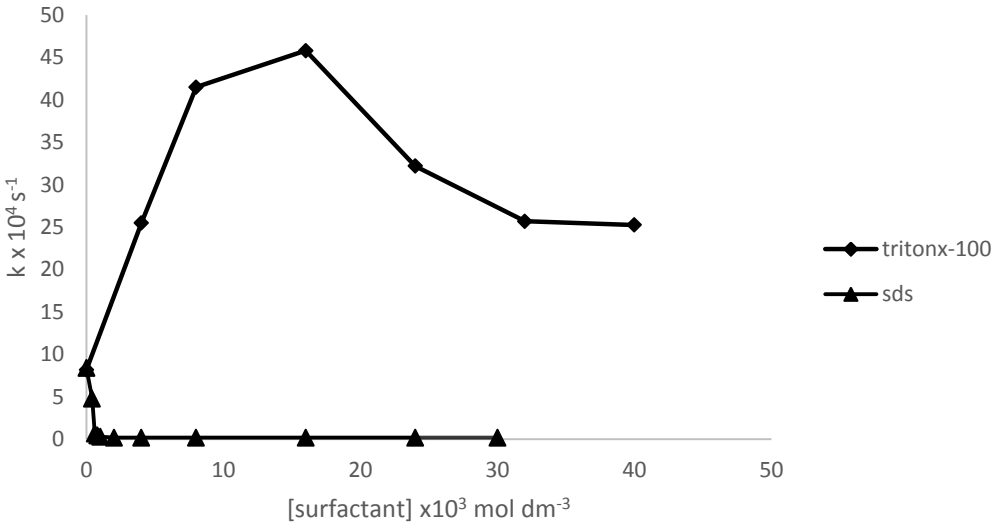

Fig.2. k vs [surfactant] of SDS and Triton X-100 at [Fe(tpy)$_2$]$^{2+}$ = 2.4 x10^{-5} moldm^{-3};

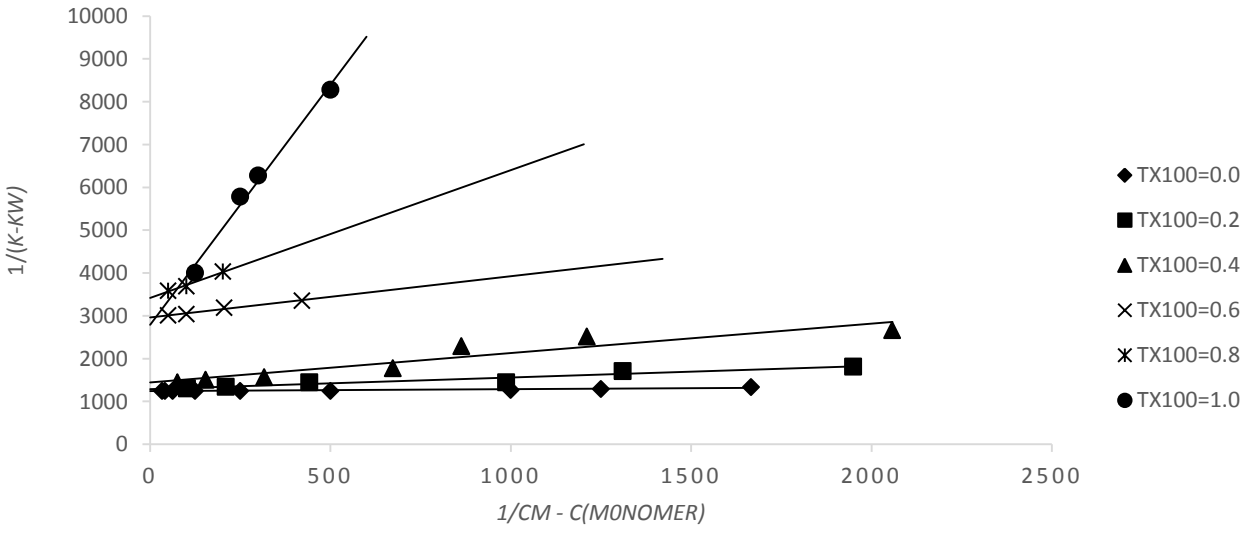

Fig.3. 1/(k-k_w) vs. 1/$C_m$at different mole fractions of TritonX-100 α_a=0.2, α_a=0.4, α_a=0.6, α_a=0.8 ,T=293K