



## Research Article

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## Kinetic Studies of Micelle-Assisted Redox reactions in aqueous Media

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### Abstract

The rate constant of three redox reactions: i)  $\text{Fe}^{3+} - \text{H}_2\text{O}_2$ , ii)  $\text{S}_2\text{O}_8^{2-} - \text{I}^-$  and iii)  $\text{BrO}_3^- - \text{I}^-$  were determined in aqueous media in the absence and presence of surfactants: cationic, CTAB; anionic, SLS and nonionic, Triton X-100 at 30<sup>o</sup>C and 44.3<sup>o</sup>C, respectively. The rate as well as rate constant of  $\text{Fe}^{3+} - \text{H}_2\text{O}_2$  system increases with increase in concentration of ionic (CTAB and SLS) and nonionic (TX -100) surfactants at room temperature. The trend of enhancement of rate constant of  $\text{Fe}^{3+} - \text{H}_2\text{O}_2$  system follows the order: CTAB > TX -100 > SLS at room temperature but at high temperature, the order: CTAB > SLS > TX -100. For  $\text{BrO}_3^- - \text{I}^-$  and  $\text{S}_2\text{O}_8^{2-} - \text{I}^-$  systems, the rate constant's enhancement follow the following order at both temperatures: CTAB > TX -100 > SLS. Thermodynamic properties as well as activation energies of activated state of these kinetics have been determined. With the help of Bruice's mathematical model and Menger and Portnoy's equation, the association constant,  $k_s$  and rate constant in micellar phase,  $k_m$  for the redox reactions in different surfactants micellar pseudo phase at 30<sup>o</sup>C and 44.3<sup>o</sup>C have been calculated.

**Keywords:** Redox reaction, Association constant, Micellar phase, Gouy -Chapman layer, binding ability

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### 1. Introduction

The role of micellar catalysis in recent years has become much popular in different areas such as chemical, pharmaceutical, oil recovery industry, environmental as well as Nano technological system. Numerous kinetics of chemical reactions has been studied in surfactants media. Research work on surfactants have gained widespread interest because above CMC value surfactants molecules can self aggregate to produce a variety of structures which can form a ideal system to study several biological processes involving electron transfer reactions. Many of the fundamental processes in Nature rely on the redox process of constituent biomolecules- e.g., cell respiration involves the stepwise oxidation of organic substrate via a cascade of redox reaction. The intrinsic mechanism of electron transfer reaction have become foci for extensive physical & biochemical investigations [1, 2]. Considering

these, we have focused on the redox reactions in micellar system. Very few redox reactions have been studied by Scientists. Some of them are cited here.

Hameed et al. [3] studied the redox reaction between malachite green and Fe (III) in aqueous and micellar media spectrophotometrically at a temperature range 20-40°C. They had noticed that CTAB has no effect but SLS inhibits the rate of reaction whereas rate increases with increasing  $[H^+]$ . Mallick et al. [4] investigated the redox reaction of methylene blue and  $SnCl_2$  in three different micelles. Cationic followed by nonionic micellar catalysis have been observed because of the binding of substrates onto the micellar surface by hydrophobic and/or electrolytic interaction.

Katre et al. [5] studied the kinetics of oxidation of dextrose by N-bromosuccinimide (NBS) in presence of CTAB in  $H_2SO_4$  media and found the rate of reaction reaches maxima at certain concentration of surfactant and also proposed pertinent mechanism. Redox reaction between Co(III) complex with Mohr salt ( $Fe^{+2}$ ) was investigated by Mukherjee et al.[6] in micelle and reverse micelle of diverse surfactants and reported the order of rates in surfactant as  $r_{SLS} > r_{TX-100} > r_{CTAB}$ . K. ud-Din et al.[7] pointed out the reaction site and gave probable mechanism from the study of redox reaction of glycolic acid with chromium(VI), catalysis by Mn(II) and cationic micelle of CTAB or CPB(cetyl pyridinium bromide). We have reported kinetics of three redox reactions i.e., i)  $Fe^{3+} - H_2O_2$ , ii)  $S_2O_8^{2-} - I^-$  and iii)  $BrO_3^- - I^-$  in aqueous and different surfactants media at two temperatures in this paper.

## 2. Experimental

The surfactants: nonionic, Triton X-100(p-octyl phenoxy polyethoxy ethanol), anionic, SLS (sodium lauryl sulphate) and cationic, CTAB (N, N cetyl trimethyl ammonium bromide), supplied by Sigma Chemical (USA) and BDH (England) were used without further purification. All the chemicals used for kinetics of redox reactions which are  $H_2O_2$ ,  $FeCl_3$ ,  $H_2SO_4$ ,  $KMnO_4$ ,  $Na_2S_2O_3$ ,  $KBrO_3$ , KI, HCl and starch were of AR grade. The solution of surfactants and other chemicals were prepared in doubly distilled water.

The three redox reactions i.e., i)  $Fe^{3+} - H_2O_2$ , ii)  $S_2O_8^{2-} - I^-$  and iii)  $BrO_3^- - I^-$  have been studied in aqueous and surfactant media at two different temperatures. The concentrations of surfactants were varied from below CMC to above CMC with upper limit. Redox reaction,  $Fe^{3+} - H_2O_2$  is of 1st order. The reaction can be studied permanganometrically [8], the volume of permanganate solution  $v_t$  required being proportion to the concentration of  $H_2O_2$ , (a-x) remaining at time t after the initiation of the reaction. The rate constant, k of this kinetics is given by  $t_n = 2.303/k \log v_1/v_n$  where  $v_1$  and  $v_n$  are the volume of  $KMnO_4$  at times  $t_1$  and  $t_n$ , respectively and  $t_n - t_1$  is expressed as  $t_n$ . Rate constant, k can be determined from the slope by plotting  $\log v_1/v_n$  vs.  $t_n$ .

Redox reaction,  $S_2O_8^{2-} - I^-$  is of 2nd order. When the concentration of both reactants are equal, the rate constant, k is given by the expression  $k = x/t(a-x)$  where a is the initial concentration of reactant and x is the concentration that has reacted at time, t. The reaction rate can be followed by measuring the rate of liberation of iodine along with the knowledge of the initial concentration of the reactants. The rate constant, k can be determined from slope by plotting  $x/a(a-x)$  vs. t.  $BrO_3^- - I^-$  is another 2nd order reaction. The expression and measurement of rate constant is same as  $S_2O_8^{2-} - I^-$  system. The thermodynamic parameters of activated state of these reactions i.e.,  $G^\ddagger$ ,  $S^\ddagger$ ,  $H^\ddagger$  and  $E_a$  are calculated based on Transition State (T.S.) Theory.

## 3. Results and Discussion

### $Fe^{3+} - H_2O_2$ system:

This redox reaction was studied in aqueous and three surfactants, CTAB, SLS and TX-100 media (below and above critical micelle concentration, CMC) at 30°C and 44.3°C. The rate constants of this kinetics were determined by plotting  $\log v_1/v_n$  with  $t_n$ . The variation of  $\log v_1/v_n$  of  $Fe^{3+} - H_2O_2$  system in 0.01M SLS at different temperature is shown in Fig.1. Physicochemical parameters of activated state [9] of this kinetics,  $G^\ddagger$  is calculated based on rate constant and using ARRT (Absolute Reaction Rate Theory) i.e.,

$$k = KT/hK \text{ -----(1)}$$

$$G^\ddagger = -RT \ln K \text{ -----(2)}$$

Where k, K and K are rate constant, Boltzmann constant and equilibrium constant for the activated state. Entropy of activation,  $S^\ddagger$  is calculated using thermodynamic approach on the T.S. theory, i.e.

$$k = KT/h e^{(1-n)} e^{S^\ddagger/R} e^{-E_a/RT} \text{ -----(3)}$$

Where  $E_a$  is activation energy and  $n = 0$  for unimolecular reaction. So, eqn.(3) can be expressed as  $S^\ddagger = R \ln (kh/KT) - R + E_a/T$  -----(4)

Activation energy,  $E_a$  is calculated using Arrhenius eqn.,  $k = A e^{-E_a/RT}$  -----(5)

Where A is frequency factor. Enthalpy of activation,  $H^\ddagger$  is calculated using standard equation,

$H = G + T S$  ----- (6). All these parameters of  $Fe^{3+} - H_2O_2$  system in three surfactants media at different temperatures are presented in Tables 1.1-1.3.

### $S_2O_8^{2-}-I^-$ and $BrO_3^- - I^-$ systems:

Like  $Fe^{3+} - H_2O_2$  system, other two redox reactions i.e.,  $S_2O_8^{2-}-I^-$  and  $BrO_3^- - I^-$  systems were studied with and without surfactants of different concentrations at two temperatures. The rate constant,  $k$  was calculated by plotting  $x/a(a-x)$  vs.  $t$ . With the help of eqns. (1) to (5) and using  $k$  obtained from graphs, all the parameters of the activated state were calculated. In the case of  $S$ , the value of  $n = -1$  is considered for bimolecular reaction and equation,

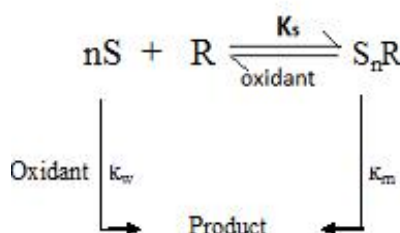
$S = R \ln(kh/KT) - 2R + E_a/T$  is used instead of eqn. (4). All the data were inserted in Tables 2.1-2.3 and 3.1-3.3 for  $S_2O_8^{2-}-I^-$  and  $BrO_3^- - I^-$ , respectively. The activation energy,  $E_a$  of these redox reactions have been determined with and without surfactants which are presented in Table 4. The experimental data presented in the tables are the direct titrimetric evidence of the influence of surfactants on the redox reactions. Since, surfactants are basically electrolyte in nature, so the rate of redox reaction of same charge substituents will be enhanced whereas the rate will not be affected if one substituent of the reaction is neutral.

Theoretically, it can be expected that  $S_2O_8^{2-}-I^-$  and  $BrO_3^- - I^-$  redox reactions will show more enhanced rates in CTAB and SLS compared to TX-100. The  $Fe^{3+} - H_2O_2$  redox system will not be influenced by any surfactant. But the table 1 shows that  $Fe^{3+} - H_2O_2$  system exhibits enhanced rate constant with SLS at room temperature and higher temperature compared to aqueous media. It is observed that rate as well as rate constant of  $Fe^{3+} - H_2O_2$  system increases with increase in concentration of ionic (CTAB and SLS) and nonionic (TX -100) at room temperature. The trend of enhancement of rate constant of  $Fe^{3+} - H_2O_2$  system follows the order: CTAB > TX -100 > SLS at room temperature but at high temperature, the order: CTAB > SLS > TX -100. For  $BrO_3^- - I^-$  and  $S_2O_8^{2-}-I^-$  systems, the rate constant's enhancement follows the following order at both temperature: CTAB > TX -100 > SLS.

In general, surfactants (ionic and nonionic) form micelle at certain concentrations. So, there are two types of environment for reactants i.e., micelle and aqueous (bulk phase) which are the reason for the kinetics in surfactant media. The reductant species of all three redox reaction are either oriented near the Stern layer or Gouy -Chapman layer depending on the charge of the layer and charge of reductant species. Simultaneously, some reductant was also solvated by water. So, the oxidant substrate which reacts with reductant can remain in either micelle or aqueous environment. As a result, the rates as well as rate constants of unimolecular and bimolecular redox reaction increase irrespective of the nature of surfactant.

Irrespective of order, all the redox reactions form activated state anionic species i.e.,  $FeO_4^{2-}$ ,  $S_2O_8I^{3-}$  and  $Br^-$  for  $Fe^{3+} - H_2O_2$ ,  $S_2O_8^{2-}-I^-$  and  $BrO_3^- - I^-$  which prefer cationic micelle i.e., CTAB. So, the rate constants are high for all the three redox reactions in cationic compared to anionic and nonionic surfactants media due to attachment of transition state species at the Stern layer of CTAB. Compared to anionic surfactant, nonionic's Gouy-Chapman layer, having low positive charge density, attracts the T.S. species. In case of SLS, T.S. species are bounded by cations in Gouy-Chapman layer and may have resultant negative charge. As a result, repulsion may occur between Stern layer and T.S. species bounded in Gouy-Chapman layer. So, the rate constants of the redox reactions are lower compared to other two types of surfactants.

It is also interesting to mention that surfactant is active even when it is below CMC values. This might be due to formation of submicellar aggregates at concentration lower than the CMC [10, 11]. At high temperature, more number of micelle will be formed as aggregate number becomes lower. As a result, rate and rate constant should be enhanced at high temperature which is observed in the present work. To discuss the rate dependence on surfactant, a theoretical mathematical model of Bruice (Scheme-I) [12] is considered. For the kinetics of unimolecular and bimolecular redox reaction, consider reductant, R and n, number of surfactant molecules(S) aggregate to form catalytic micelles  $S_nR$  which may further gives the products.



Scheme- I

where  $K_s$  is the binding constant of the micelle with reductant,  $k_m$  and  $k_w$  are the rate constants in the presence and absence of micelle, respectively. Taking the kinetic steps involved into consideration, Menger and Portnoy have derived an expression (Equation 1) which has been successfully applied to micelle catalyzed unimolecular and bimolecular reaction [13].

$$1/k_{obs} - k_w = 1/k_m - k_w + [N/k_s(k_m - k_w)] \cdot 1/(C_D - CMC) \text{-----(1)}$$

where  $k_{obs}$  is observed rate constant,  $C_D$ , concentration of surfactant,  $N$ , aggregation number of surfactant molecules,  $k_w$  and  $k_m$  are mentioned earlier and  $k_s$  is association constant related with  $K_s$  as  $k_s/N = K_s$ . The kinetic data of all three redox reactions with varying concentration of CTAB up to 0.04 M are fitted to the above equation. Plots of  $1/k_{obs} - k_w$  vs  $1/(C_D - CMC)$  are linear in three redox kinetics with CTAB at the two temperatures. From the slope and intercept of each of the plot, the value of  $k_s/N$  is calculated. Using the value of  $N$  for CTAB [10] to be 78, the association constants,  $k_s$  and  $k_m$  for the three redox kinetics in CTAB are calculated and are given in Table 5. The values of  $k_s$  indicate that there is a substantial binding of all reductant molecules with CTAB molecules. Using the value of  $N$  [14] for SLS- 62 and Triton X-100 -121,  $k_w$  and  $k_m$  of all the three kinetics with SLS are calculated like CTAB and inserted in Table 5.

From Table 5, it is observed that the binding ability of CTAB with reductant substitute for three redox systems follows the order:  $S_2O_8^{2-} - I^- > Fe^{3+} - H_2O_2$  and for SLS:  $BrO_3^- - I^- > S_2O_8^{2-} - I^- > Fe^{3+} - H_2O_2$  whereas at high temperature, the order becomes reversed. The  $k_m$  values are remarkably large due to increase in the effective concentrations of both reactants in a small volume of micellar phase. Similarly, binding ability of TX -100 with reductant of redox kinetics can be determined, if aggregation number is available in literature. Among the thermodynamic parameters of activated state, fairly high negative entropy of activation and positive  $\Delta H^\ddagger$  suggest more order of the transition state complex. However, there is not much deviation in the  $\Delta G^\ddagger$  values due to change in the medium of the reaction. The values of energy of activation show that the redox reactions are more favored in the presence of surfactant compared to aqueous media.

**Table 1.1:** Thermodynamic properties of  $Fe^{3+} - H_2O_2$  system in SLS media at 30°C and 44.3°C

| Conc. of SLS (M) | Rate constant, k (sec <sup>-1</sup> ) |        | G (kJmol <sup>-1</sup> ) |        | - S (Jmol <sup>-1</sup> deg <sup>-1</sup> ) |        | H (kJmol <sup>-1</sup> ) |        |
|------------------|---------------------------------------|--------|--------------------------|--------|---|--------|--------------------------|--------|
|                  | 30°C                                  | 44.3°C | 30°C                     | 44.3°C | 30°C  | 44.3°C | 30°C                     | 44.3°C |
| 0.00             | 0.028                                 | 0.065  | 83.237                   | 85.096 | 129.82                                      | 130.20 | 43.901                   | 43.783 |
| 0.005            | 0.029                                 | 0.219  | 83.175                   | 81.878 | 247.14                                      | 232.29 | 8.291                    | 8.173  |
| 0.008            | 0.035                                 | 0.224  | 82.729                   | 81.819 | 245.67                                      | 232.10 | 8.290                    | 8.174  |
| 0.01             | 0.036                                 | 0.263  | 82.636                   | 81.398 | 245.36                                      | 230.78 | 8.291                    | 8.172  |
| 0.02             | 0.039                                 | 0.275  | 82.440                   | 81.278 | 244.71                                      | 230.40 | 8.292                    | 8.172  |
| 0.04             | 0.045                                 | 0.290  | 82.065                   | 81.137 | 243.48                                      | 229.96 | 8.290                    | 8.171  |

**Table 1.2:** Thermodynamic properties of  $Fe^{3+} - H_2O_2$  system in CTAB media at 30°C and 44.3°C

| Conc. of CTAB (M) | Rate constant, k (sec <sup>-1</sup> ) |        | G (kJmol <sup>-1</sup> ) |        | - S (Jmol <sup>-1</sup> deg <sup>-1</sup> ) |        | H (kJmol <sup>-1</sup> ) |        |
|-------------------|---------------------------------------|--------|--------------------------|--------|---|--------|--------------------------|--------|
|                   | 30°C                                  | 44.3°C | 30°C                     | 44.3°C | 30°C  | 44.3°C | 30°C                     | 44.3°C |
| 0.00              | 0.028                                 | 0.065  | 83.237                   | 85.096 | 129.82                                      | 130.20 | 43.901                   | 43.783 |
| 0.001             | 0.049                                 | 0.068  | 81.845                   | 84.973 | 213.87                                      | 214.47 | 17.042                   | 16.921 |
| 0.005             | 0.063                                 | 0.092  | 81.200                   | 84.165 | 211.75                                      | 211.92 | 17.039                   | 16.922 |
| 0.01              | 0.078                                 | 0.589  | 80.661                   | 79.270 | 209.97                                      | 196.49 | 17.040                   | 16.923 |
| 0.02              | 0.102                                 | 0.853  | 79.988                   | 78.293 | 207.75                                      | 193.41 | 17.043                   | 16.924 |
| 0.04              | 0.145                                 | 1.023  | 79.103                   | 77.813 | 204.83                                      | 191.90 | 17.039                   | 16.924 |

**Table 1.3:** Thermodynamic properties of  $Fe^{3+} - H_2O_2$  system in Triton X- 100 media at 30°C and 44.3°C

| Conc. of Triton X-100 (M) | Rate constant, k (sec <sup>-1</sup> ) |        | G (kJmol <sup>-1</sup> ) |        | - S (Jmol <sup>-1</sup> deg <sup>-1</sup> ) |        | H (kJmol <sup>-1</sup> ) |        |
|---------------------------|---------------------------------------|--------|--------------------------|--------|---|--------|--------------------------|--------|
|                           | 30°C                                  | 44.3°C | 30°C                     | 44.3°C | 30°C  | 44.3°C | 30°C                     | 44.3°C |
| 0.00                      | 0.028                                 | 0.065  | 83.237                   | 85.096 | 129.82                                      | 130.20 | 43.901                   | 43.783 |
| 0.001                     | 0.042                                 | 0.049  | 82.256                   | 85.808 | 239.59                                      | 240.35 | 9.661                    | 9.545  |
| 0.002                     | 0.045                                 | 0.052  | 82.037                   | 85.658 | 238.87                                      | 239.88 | 9.659                    | 9.543  |
| 0.01                      | 0.053                                 | 0.079  | 81.671                   | 84.573 | 237.65                                      | 236.46 | 9.663                    | 9.544  |
| 0.02                      | 0.072                                 | 0.084  | 80.883                   | 84.404 | 235.05                                      | 235.93 | 9.662                    | 9.543  |
| 0.04                      | 0.075                                 | 0.093  | 80.759                   | 84.133 | 234.65                                      | 235.08 | 9.660                    | 9.542  |

**Table 2.1:** Thermodynamic properties of  $S_2O_8^{2-}-I^-$  system in SLS media at 30°C and 44.3°C

| Conc. of SLS (M) | Rate constant, k ( $dm^3 mol^{-1} min^{-1}$ ) |        | G ( $kJ mol^{-1}$ ) |        | - S ( $J mol^{-1} deg^{-1}$ ) |        | H ( $kJ mol^{-1}$ ) |        |
|------------------|---|--------|---------------------|--------|-------------------------------|--------|---------------------|--------|
|                  | 30°C  | 44.3°C | 30°C                | 44.3°C | 30°C                          | 44.3°C | 30°C                | 44.3°C |
| 0.00             | 0.067   | 0.156  | 81.042              | 82.774 | 129.27                        | 129.66 | 41.873              | 41.633 |
| 0.008            | 0.132   | 0.706  | 79.341              | 78.791 | 224.65                        | 213.54 | 11.272              | 11.034 |
| 0.01             | 0.161   | 0.758  | 78.847              | 78.605 | 223.02                        | 212.96 | 11.271              | 11.033 |
| 0.02             | 0.812   | 0.960  | 74.771              | 77.980 | 209.57                        | 210.99 | 11.271              | 11.032 |
| 0.04             | 0.864   | 1.150  | 74.616              | 77.504 | 209.06                        | 209.49 | 11.270              | 11.032 |
| 0.06             | 0.924   | 1.196  | 74.447              | 77.401 | 208.50                        | 209.16 | 11.271              | 11.034 |

**Table 2.2:** Thermodynamic properties of  $S_2O_8^{2-}-I^-$  system in CTAB media at 30°C and 44.3°C

| Conc. of CTAB (M) | Rate constant, k ( $dm^3 mol^{-1} min^{-1}$ ) |        | G ( $kJ mol^{-1}$ ) |        | - S ( $J mol^{-1} deg^{-1}$ ) |        | H ( $kJ mol^{-1}$ ) |        |
|-------------------|---|--------|---------------------|--------|-------------------------------|--------|---------------------|--------|
|                   | 30°C  | 44.3°C | 30°C                | 44.3°C | 30°C                          | 44.3°C | 30°C                | 44.3°C |
| 0.00              | 0.067   | 0.156  | 81.042              | 82.774 | 129.27                        | 129.66 | 41.873              | 41.633 |
| 0.001             | 0.156   | 1.103  | 78.928              | 77.615 | 177.05                        | 165.68 | 25.281              | 25.045 |
| 0.005             | 0.357   | 1.171  | 76.842              | 77.456 | 170.16                        | 165.18 | 25.283              | 25.044 |
| 0.01              | 0.414   | 1.338  | 76.471              | 77.105 | 168.94                        | 164.08 | 25.282              | 25.042 |
| 0.02              | 1.150   | 1.432  | 73.895              | 76.925 | 160.44                        | 163.50 | 25.281              | 25.046 |
| 0.04              | 1.196   | 1.543  | 73.797              | 76.729 | 160.12                        | 162.89 | 25.280              | 25.043 |

**Table 2.3:** Thermodynamic properties of  $S_2O_8^{2-}-I^-$  system in Triton X-100 media at 30°C and 44.3°C

| Conc. of Triton X-100 (M) | Rate constant, k ( $dm^3 mol^{-1} min^{-1}$ ) |        | G ( $kJ mol^{-1}$ ) |        | - S ( $J mol^{-1} deg^{-1}$ ) |        | H ( $kJ mol^{-1}$ ) |        |
|---------------------------|---|--------|---------------------|--------|-------------------------------|--------|---------------------|--------|
|                           | 30°C  | 44.3°C | 30°C                | 44.3°C | 30°C                          | 44.3°C | 30°C                | 44.3°C |
| 0.00                      | 0.067   | 0.156  | 81.042              | 82.774 | 129.27                        | 129.66 | 41.873              | 41.633 |
| 0.002                     | 0.329   | 1.140  | 77.043              | 77.527 | 189.11                        | 165.40 | 19.743              | 25.045 |
| 0.01                      | 0.336   | 1.382  | 76.997              | 77.021 | 188.96                        | 163.80 | 19.742              | 25.046 |
| 0.02                      | 0.362   | 1.522  | 76.811              | 76.765 | 188.35                        | 163.00 | 19.741              | 25.044 |
| 0.04                      | 1.080   | 1.651  | 74.053              | 76.550 | 179.25                        | 162.33 | 19.740              | 25.042 |
| 0.06                      | 1.086   | 1.725  | 74.039              | 76.435 | 179.20                        | 161.96 | 19.742              | 25.045 |

**Table 3.1:** Thermodynamic properties of  $BrO_3^- - I^-$  system in SLS media at 30°C and 44.3°C

| Conc. of SLS (M) | Rate constant, k ( $dm^3 mol^{-1} min^{-1}$ ) |        | G ( $kJ mol^{-1}$ ) |        | - S ( $J mol^{-1} deg^{-1}$ ) |        | H ( $kJ mol^{-1}$ ) |        |
|------------------|---|--------|---------------------|--------|-------------------------------|--------|---------------------|--------|
|                  | 30°C  | 44.3°C | 30°C                | 44.3°C | 30°C                          | 44.3°C | 30°C                | 44.3°C |
| 0.00             | 0.029   | 0.099  | 83.132              | 83.953 | 136.17                        | 65.90  | 41.872              | 63.042 |
| 0.008            | 0.414   | 0.461  | 76.471              | 79.913 | 222.14                        | 223.73 | 9.162               | 8.923  |
| 0.01             | 0.470   | 0.601  | 76.149              | 79.216 | 221.08                        | 221.53 | 9.161               | 8.924  |
| 0.02             | 0.752   | 0.913  | 74.964              | 78.112 | 217.17                        | 218.05 | 9.162               | 8.925  |
| 0.04             | 0.823   | 1.016  | 74.738              | 77.832 | 216.42                        | 217.17 | 9.163               | 8.923  |
| 0.06             | 0.980   | 1.753  | 74.297              | 76.392 | 214.97                        | 212.63 | 9.161               | 8.925  |

**Table 3.2:** Thermodynamic properties of  $BrO_3^- - I^-$  system in CTAB media at 30°C and 44.3°C

| Conc. of CTAB (M) | Rate constant, k ( $dm^3 mol^{-1} min^{-1}$ ) |        | G ( $kJ mol^{-1}$ ) |        | - S ( $J mol^{-1} deg^{-1}$ ) |        | H ( $kJ mol^{-1}$ ) |        |
|-------------------|---|--------|---------------------|--------|-------------------------------|--------|---------------------|--------|
|                   | 30°C  | 44.3°C | 30°C                | 44.3°C | 30°C                          | 44.3°C | 30°C                | 44.3°C |
| 0.00              | 0.029   | 0.099  | 83.132              | 83.953 | 136.17                        | 65.90  | 41.872              | 63.042 |
| 0.001             | 0.049   | 0.246  | 81.825              | 81.576 | 119.35                        | 113.94 | 45.661              | 45.422 |
| 0.01              | 0.362   | 1.171  | 76.810              | 77.457 | 102.80                        | 100.44 | 45.662              | 45.587 |
| 0.02              | 0.658   | 1.246  | 75.303              | 77.293 | 97.83                         | 100.43 | 45.661              | 45.426 |

**Table 3.3:** Thermodynamic properties of  $\text{BrO}_3^- - \text{I}^-$  system in Triton X-100 media at  $30^\circ\text{C}$  and  $44.3^\circ\text{C}$ 

| Conc. of Triton X-100 (M) | Rate constant, k ( $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$ ) |                      | G ( $\text{kJmol}^{-1}$ ) |                      | - S ( $\text{Jmol}^{-1} \text{deg}^{-1}$ ) |                      | H ( $\text{kJmol}^{-1}$ ) |                      |
|---------------------------|--|----------------------|---------------------------|----------------------|--|----------------------|---------------------------|----------------------|
|                           | $30^\circ\text{C}$   | $44.3^\circ\text{C}$ | $30^\circ\text{C}$        | $44.3^\circ\text{C}$ | $30^\circ\text{C}$                         | $44.3^\circ\text{C}$ | $30^\circ\text{C}$        | $44.3^\circ\text{C}$ |
| 0.00                      | 0.029  | 0.099                | 83.132                    | 85.953               | 136.17                                     | 65.90                | 41.872                    | 63.042               |
| 0.002                     | 1.092  | 1.326                | 74.026                    | 77.128               | 236.98                                     | 236.82               | 2.221                     | 1.984                |
| 0.01                      | 1.223  | 1.489                | 73.741                    | 76.822               | 236.04                                     | 235.86               | 2.220                     | 1.983                |
| 0.02                      | 1.361  | 1.543                | 73.471                    | 76.729               | 235.15                                     | 235.57               | 2.221                     | 1.982                |
| 0.04                      | 1.528  | 1.683                | 73.179                    | 76.500               | 234.18                                     | 234.85               | 2.222                     | 1.982                |
| 0.06                      | 1.658  | 1.812                | 72.974                    | 76.304               | 233.51                                     | 234.22               | 2.220                     | 1.986                |

**Table 4:** Determination of Activation energy,  $E_a$  of different redox reaction with and without surfactants

| System                                   | $E_a$ ( $\text{kJ mol}^{-1}$ ) in different media |       |               |       |
|--|---|-------|---------------|-------|
|  | Aqueous   | SLS   | Triton X- 100 | CTAB  |
| $\text{Fe}^{3+} - \text{H}_2\text{O}_2$  | 46.42   | 10.81 | 12.18         | 19.56 |
| $\text{S}_2\text{O}_8^{2-} - \text{I}^-$ | 46.91   | 16.31 | 24.78         | 30.32 |
| $\text{BrO}_3^- - \text{I}^-$            | 68.32   | 14.20 | 7.26          | 50.70 |

**Table 5.1:** Association constants,  $k_s$  and Rate constant in micellar phase,  $k_m$  for the redox reactions in CTAB micellar pseudo phase at  $30^\circ\text{C}$  and  $44.3^\circ\text{C}$ 

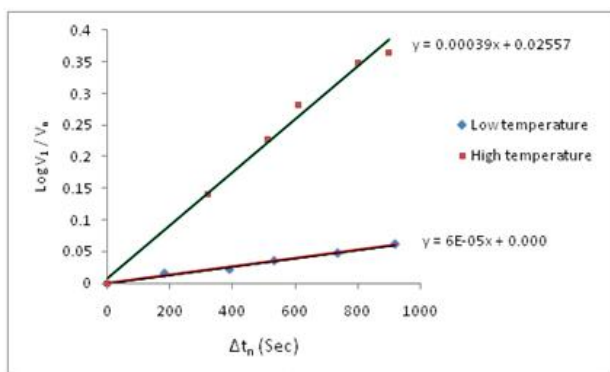
| Media | System                                   | $k_s$               |                      | $k_m$              |                      |
|-------|--|---------------------|----------------------|--------------------|----------------------|
|       |  | $30^\circ\text{C}$  | $44.3^\circ\text{C}$ | $30^\circ\text{C}$ | $44.3^\circ\text{C}$ |
| CTAB  | $\text{Fe}^{3+} - \text{H}_2\text{O}_2$  | $2.775 \times 10^3$ | $4.610 \times 10^3$  | 0.229              |                      |
|       | $\text{S}_2\text{O}_8^{2-} - \text{I}^-$ | $2.516 \times 10^3$ | $42.00 \times 10^3$  | 2.567              |                      |
|       | $\text{BrO}_3^- - \text{I}^-$            | -                   | -                    | -                  |                      |

**Table 5.2:** Association constants,  $k_s$  and Rate constant in micellar phase,  $k_m$  for the redox reactions in SLS micellar pseudo phase at  $30^\circ\text{C}$  and  $44.3^\circ\text{C}$ 

| Media | System                                   | $k_s$               |                      | $k_m$              |                      |
|-------|--|---------------------|----------------------|--------------------|----------------------|
|       |  | $30^\circ\text{C}$  | $44.3^\circ\text{C}$ | $30^\circ\text{C}$ | $44.3^\circ\text{C}$ |
| SLS   | $\text{Fe}^{3+} - \text{H}_2\text{O}_2$  | $1.162 \times 10^4$ | $16.443 \times 10^4$ | 0.047              | 0.291                |
|       | $\text{S}_2\text{O}_8^{2-} - \text{I}^-$ | $1.761 \times 10^4$ | $5.115 \times 10^4$  | 0.267              | 1.112                |
|       | $\text{BrO}_3^- - \text{I}^-$            | $2.317 \times 10^4$ | $3.419 \times 10^4$  | 1.000              | 1.061                |

**Table 5.3:** Association constants,  $k_s$  and Rate constant in micellar phase,  $k_m$  for the redox reactions in Triton X -100 micellar pseudo phase at  $30^\circ\text{C}$  and  $44.3^\circ\text{C}$ 

| Media        | System                                   | $k_s$                |                      | $k_m$              |                      |
|--------------|--|----------------------|----------------------|--------------------|----------------------|
|              |  | $30^\circ\text{C}$   | $44.3^\circ\text{C}$ | $30^\circ\text{C}$ | $44.3^\circ\text{C}$ |
| Triton X-100 | $\text{Fe}^{3+} - \text{H}_2\text{O}_2$  | $4.436 \times 10^3$  | $6.445 \times 10^3$  | 0.119              | 0.105                |
|              | $\text{S}_2\text{O}_8^{2-} - \text{I}^-$ | $95.287 \times 10^3$ | $39.484 \times 10^3$ | 0.385              | 1.769                |
|              | $\text{BrO}_3^- - \text{I}^-$            | $43.358 \times 10^3$ | $38.118 \times 10^3$ | 1.580              | 1.810                |



**Figure 1:** The variation of  $\log v_1/v_n$  of  $\text{Fe}^{3+} \text{H}_2\text{O}_2$  system in 0.01M SLS at different temperature.

#### 4. Conclusion

First of all, the rate and rate constant of three redox reactions are enhanced in diverse surfactants media compared to aqueous due to formation of multi pockets following pseudo phase kinetics principle. Negatively charged T.S. species of redox reactions move towards the stern region of CTAB compared to TX-100 where positive charge arises on H atom of  $-\text{OH}$  head group due to electro negativity differences. Gouy-Chapman layer of SLS play the role to bind the T.S. species. Secondly, enhancement of rate constant of redox reactions in three surfactants follows the order: CTAB > TX-100 > SLS which is explained considering the binding affinity of T.S. species towards different micellar regions of surfactants.

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