ROLE OF MIXED SURFACTANTS ON THE OXIDATION OF MALACHITE GREEN BY NITRITE IONS

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Abstract:

The oxidation of malachite green $\left(MG^{+}\right)$ with nitrite ions in aqueous solutions of sodium dodecyl sulphate (SDS), Triton X-100 (TX-100), and their mixtures at 25°C has been used as a probe for investigating the catalytic/inhibitive property of SDS/TX-100 mixed systems. The results showed that the composition of the mixed surfactants has quite significant influence on the rate constant of the oxidation reaction when compared with the reaction in the single surfactant system and the effect of SDS was found crucial. The results indicated 62-85% lower reactivity as the mole fraction increased and a higher pseudo-first order rate constant in aqueous solution than in the surfactants or their mixtures were also observed with a rapid decrease until saturation was reached in pure SDS indicating an overall inhibition. The kinetic mechanism of the micellar effects was probed and rationalized using existing Clint's, Menger and Portnoy, Rubingh's and Maeda's theories for mixed micellar systems. Strong electrostatic attraction between the protonated species and the anionic surfactant aggregates was important in the reaction process.

Keywords: *malachite green, oxidation reaction, nitrite ions, kinetics, surfactant*

INTRODUCTION

Much attention has been focused on experimental and theoretical aspects of mixed micellar systems (Bergstrom and Eriksson, 2000; Ruiz and Agula, 1999; Garamus, 2003; Rodgers *et al.,* 2003). In the majority of industrial applications, it is common practice to employ mixtures of surfactants in place of individual ones because these mixed surfactant systems possess superior qualities in terms of detergency, improved synergy, lower interfacial tension, solubilisation and in the modification of rheological properties of polymers (Magnus and Jan Christer, 2000; Lutz *et al.,* 2004; Rakshit and Palepu, 2003; Aiysha *et al.,* 2005). Surfactants are surface active agents which form a larger class of molecules that have significant technological and biological importance. They are characterised by their dual properties; one part consisting of hydrophilic (water loving) and a hydrophobic (oil/air loving) part. This dual property is responsible for their association behaviour in solution (micelles, bilayers, vessels etc.), (Laurier *et al*., 2003).

However, mixed surfactant systems that exhibit synergistic behaviour may be exploited to reduce the total amount of surfactant employed in an application and thereby reduce the cost and environmental impact (Bergstrom and Eriksson, 2000; Blankschtein and Shiloach, 1998). The tendency to form a micellar structure in mixed surfactant solutions will be substantially different from that in pure surfactant solutions (Yoshikazu *et al.,* 1994).

Several workers have worked on studies involving the effect of mixed surfactants on reaction rates (Aiysha *et al.,* 2005; Khan and Ismail, 2004; Reinsborough *et al.,* 1990; Soriyan *et al*., 2009; Mandan *et al*., 2007). Khan and co-worker (Khan and Ismail, 2004

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in their study on the effects of non- ionic and cationic micelles on the aqueous cleavages of phenylbenzoate and phenylsalicylate in alkaline solution described the micellar effect in terms of a pseudo phase model of micelles coupled with changes in the micellar environment.

4-[(4-dimethylaminophenyl)-phenylmethyl]-N,N-dimethyl-aniline, also known as malachite green (MG^+), is a basic organic dye used for materials such as silk, wool, jute, ceramics, leather, paper, in aquaculture and as cytochemical staining agent. However, nitrite accumulation in blood and tissues represents a biological pool for nitric oxide (NO) generation since several different mammalian enzymes and metalloproteinase possess nitrite reductase activity such as xanthine oxidoreductase (XOR) and aldehyde oxidase (AO), heme proteins and mitochondrial respiratory chain enzymes (Xu et al., 2003; Furchgoh, 1998). The recent appreciation of the mechanism and observations that nitrite vasodilates the human circulation at near physiological concentrations supports a role for nitrite in hypoxic vasodilation (Huang et al., 2005; Hunter et al., 2004).

The influence of mixed surfactants on reaction rate has become a new field in kinetics that is receiving much attention (Khan and Ismail, 2004; Reinsborough et al., 1990; Soriyan et al., 2009). The kinetics and mechanisms of the oxidation reaction of MG^+ with nitrite ion have been studied in aqueous acidic medium (Mohammed et al., 2010) and one step in such reaction as reported is an electron transfer process. However at the moment, information and knowledge of the redox reaction of MG^+ by nitrite ions mediated by mixed surfactants are limited. This paper, in continuation of the work on the reaction of MG^+ (Soriyan et al., 2009; Bamgbose et al., 2013), reports the investigation of the effect of mixed surfactants of SDS and Triton X-100 on the oxidation of MG^+ by nitrite ions. It is of interest to investigate how the distribution of MG^+ in the bulk solution is going to affect the redox reaction when compared to the same reaction occurring in micelle free medium.

EXPERIMENTAL PROCEDURES

Materials and Methods

All the materials and reagents used in this work are analar grades and were used as received. Sodium nitrite (NaNO2) and SDS used were products of BDH chemicals. The critical micelle concentration was determined in order to test its degree of purity in aqueous medium at 25oC. This gave 8.16 x 10-3 M which agrees with literature values (Soriyan et al., 2009; William et al., 1955; Soriyan and Ige, 1986). Malachite green was obtained from Bektoh (Germany). The Triton X-100 (TX-100) was an Aldrich product. A wavelength scan of the aqueous solution of Triton X-100 shows a maximum absorbance peak at 276nm which agrees with the work of Gratzer and Beaven in 1969 who reported a $\lambda_{\max}$ of 278 nm and an extinction coefficient of 1670 dm^{-3} mol^{-1} cm^{-1} for TX-100 in water. The Critical Micellar Concentration (CMC) of each surfactant and their mixtures was determined by conductometric method using electric conductivity meter DDS-307 made by Jenway at controlled temperature $25 \pm 1^{o} C$.

The Sodium nitrite used was a product of BDH chemicals. All the solutions were prepared as mole fractions with glass distilled water. Thermo Helios Zeta UV/visible Spectrophotometer (Thermo Scientific) was used to monitor the absorbance of the reaction complex at a

$\lambda_{\max}$ of 620 nm by measuring the absorbance against different wavelengths from 400 to 700nm and at a molar extinction coefficient of 105 $M^{-1}cm^{-1}$ which is in agreement with literature value (Raducan et al., 2008).

Kinetic Studies

Kinetic studies for the reaction of MG^{+} and Nitrite ions NO_2^- in the presence of SDS, TX-100 and their mixtures were performed by monitoring the decrease in absorbance of the MG^{+} at absorption maximum $\lambda_{\max}$ of 620 nm as a function of time using a thermostated double beam Helios zeta UV/visible spectrometer at an interval of 5 minutes and 25.0 ± 0.1 ^{0}C. All the stock solutions were put in the thermostated water bath to ensure constant temperature in the kinetic run. 0.00, 0.27, 0.42, 0.52, 0.63, and 1.00 mole fractions of SDS (X_{SDS}) were employed in the reaction. The spectrophotometric titration was done using the individual surfactants separately. At each mole ratio, the surfactant and various concentrations of the nitrite (without the dye) were mixed, first in a 5 ml standard flask from which 3ml was pipetted into a cuvette of 4 x 1cm quartz cell and the dye added immediately for each kinetic run. Care was taken to prevent exposing the MG^{+} to light. The concentration of the dye was constant at 5.77 x10^{-5} mol/dm^3 (0.208 Absorbance) for all the reactions while the oxidant concentrations were varied for at least 50 fold in excess. All the spectrophotometric titrations were done under pseudo-first order kinetics. The pseudo-first order rate constants (k) were obtained from the slopes of the plot of $\ln(A_t - A_\infty)$ versus time in minutes. A_t and A_∞ are absorbance at different times and at infinity times respectively.

Results

The effect of mixed surfactants of SDS and TX- 100 on the oxidation of MG^{+} by nitrite ions was determined at 0.00, 0.27, 0.42, 0.52, 0.63, and 1.00 mole fractions of SDS (X_{SDS}) by spectrophotometrically monitoring the decrease in absorbance of the MG^{+} at 620 nm as a function of time. The linear plots of $\ln(A_t - A_\infty)$ versus time (min) for the redox reaction of Malachite green and NO_2^- in aqueous solution, SDS, and in mixed SDS and TX-100 respectively are presented in Figures 1A, B & C.

Stoichiometric studies show that one mole of the dye is consumed by one mole of the nitrite ions as shown in equation 1.

$$MG^{+} + NO_2^- \rightarrow MGNO_2 \qquad (1)$$

The results showed that the SDS/TX-100 system composition has quite significant influence on the rate constant of the oxidation of MG^{+} when compared with the reaction in the single surfactant systems. There is a higher pseudo-first order rate in aqueous solution than in the surfactants or their mixtures. Table 1 presents the mean pseudo–first-order rate constants (k_1, k_2, k_3) of the reaction of malachite green and nitrite in aqueous medium, SDS, TX-100 and various ratios of their mixtures.

The mean pseudo-first order rate constant, k_1 was in the range 0.0110 - 0.1612 s^{-1} in aqueous medium, k_2 0.0086 - 0.0882 s^{-1} in SDS. k_3 0.0110 - 0.1518 s^{-1} in TX-100 and k_4 0.0044 - 0.0606 s^{-1} in the mixed surfactants. The results showed a higher pseudo- first order rate constant in aqueous solution than in the surfactants or their mixtures. The SDS/TX-100 effect on k for the redox reaction reveals 62-85% lower reactivity as the mole fraction increases.

The experimental results of the observed pseudo-first order rate constant, k as a function of total surfactant concentration at different mole fraction of SDS as presented in Figure 2.

The reaction rate was very sensitive to the medium effects since k_2 decreases with increasing total surfactant concentration for all mole fractions of SDS. Figure 3 also shows that the observed rate constant increases as the mole fraction of TX-100 (X_{TX-100}) increases at fixed total surfactant concentration. The Critical Micellar Concentration (CMC) of the mixed surfactants was determined. The observed CMC of the mixed surfactants is presented in table 2. The kinetic mechanism of the micellar effects was probed and discussed using existing Clint's, Menger and Portnoy, Rubingh's and Maeda's theories for mixed micellar systems.

Discussion

In table 1, there is a higher pseudo-first-order rate in aqueous solution than in the surfactants or their mixtures. These results show that the reaction is faster in bulk water phase than in micellar phase. This observation is highly influenced by the MG^+ distribution between the bulk water and the surfactant aggregates. The decrease in the k_2 of the reaction in SDS surfactant compared with the k_1 of the aqueous solution is due to the electrostatic attraction between the SDS and MG^+. This is in agreement with the interactions between dyes and anionic surfactants (Malik and Jhamb, 1970). The observed rate inhibition in the mixed micelle implies that either the rate of electron attachment is different in the micellar pseudo-phase than in the bulk aqueous phase or that the penetration of electron present in aqueous solution to the site of solubilized malachite green cation is hindered electrostatically by the negatively charged SDS micellar surface. The dye is assumed to be locally concentrated on the SDS micellar phase where the microenvironment was non-aqueous, thus, there is a strong binding of the triarylmethylcation to the negatively charged SDS micelle and hence, the SDS renders the substrate less available to nucleophilic attack by the NO_2^- ion (Fendler and Fendler, 1975). However, the effects of the TX-100 (a non-ionic) surfactant compared with the anionic surfactant, SDS on the reaction suggest that the non-ionic TX-100 did not alter the rate of reaction significantly. This is in conformity with previous work (Bunton *et al.*, 1968).

The observed rate constant decreased rapidly until saturation is reached in pure SDS, suggesting an overall inhibition. This inhibition is as a result of the negative charge on the SDS micellar phase attracting the triarylmethyl cation, which leads to the local concentration of the dye in SDS micellar phase being greater than that in the bulk phase and, on the other hand, they repelled the nitrite ions. There is also the possibility that the nitrite ion would be predominant in the bulk water region due to the columbic repulsion between the negatively charged surfactant aggregates and the nitrite ions. Also, there is inhibition because strong hydrophobic interaction would keep a greater proportion of MG^+ within the micelle and this would remove the bulk of the complex from the bulk water region and thus inhibit the reaction rate. This repulsion also leads to the local concentration of the dye in the SDS micellar phase being lower than in the bulk phase. Consequently, when nitrite ions approach the triarylmethyl cations to form the transition state, they are repelled by the negative charges on SDS micellar phase.

Theories and Mechanism of the reaction of MG^+ and nitrite ions in SDS/TX-100

The Clint's, Rubingh's and Maeda's theories for ideal mixed miceller systems were employed to analyse the experimental data. For ideal mixed miceller systems, Clint's equation (Clint, 1975) can be employed to determine the expected critical micellar concentration (CMC) of the reaction mixture. Our first approach utilized Clint's equation 2 to determine the expected CMC of the mixture and the results shown in Table 2;

$$\frac{1}{CMC_{mix}} = \sum_{i=1}^{2} \frac{\alpha_i}{CMC_i} \qquad (2)$$

where CMC_{mix}, α_i and CMC_i are the expected CMC of the mixture, the mole fraction of component i in the solution and the CMC of the pure component i respectively. Our results show that the experimental CMC is lower when compared with the expected CMC (Table 2). This deviation from ideal behaviour is due to the different composition of surfactant monomers in the micelle compared to the bulk solution (Rubingh, 1979).

The actual composition of the mixed micellar phase was calculated using the regular solution approximation. The following equation was employed;

$$\frac{X_1^2 \ln\left({CMC_{mix}\alpha_i} \middle/ {CMC_1 X_1} \right)}{[1-X_1]\ln\left({CMC_{mix}[1-\alpha_1]} \middle/ {CMC_2[1-X_1]} \right)} = 1 \qquad (3)$$

X_1 is the mole fraction of surfactant 1 in the mixed micelle, α_1 is the mole fraction of surfactant 1 in the bulk solution and CMC_{mix} is the experimental CMC value. From equation 3, X_1 was calculated and the interaction parameter (β) obtained from equation 4 (Rubingh, 1979). The β which is an index of surfactant interaction in the mixed micelle has negative values (Table 2) indicating that the system exhibit synergism and that the surfactant monomers are attracting one another.

$$\beta = \frac{\ln\left({CMC_{mix}\alpha_i} \middle/ {CMC_i X_i} \right)}{(1 - X_i)^2} \qquad (4)$$

The excess free energy of mixing, ΔG_{ex}^{o}, was determined from the values of the interaction parameter and those of activity coefficients of the surfactants using Rubingh's approach in equation 5. The values are shown in Table 2.

$$\Delta G_{ex}^{o} = RT \sum_{i=1}^{2} X_i \ln \gamma_i \qquad (5)$$

where γ_1 and γ_2 are activity coefficients for each of the surfactants.

From Table 2, it is observed that the TritonX-100 possesses a much lower CMC than the SDS. This indicates that more of the TritonX-100 will be incorporated into the mixed micelle as a result of the decrease in ionic head group repulsion caused by the positioning of the ionic surfactant monomer between the charged head groups (Aiysha *et al*., 2005).

The negative values of excess free energy of mixing indicate favourable mixing of the surfactant monomer within the mixed micelles. Also the smaller values of the activity coefficients for each of the surfactants show that both surfactants deviate from the standard state in the mixed micelle (Aiysha *et al*., 2005). Maeda observed that a mixed ionic-non-ionic surfactant system often exhibits a CMC much lower than the CMC predicted by employing Clint's equation (Clint, 1975). This is attributed to the decrease in ionic head group repulsion caused by the presence of the non-ionic surfactant between the ionic head groups.

Using Maeda's approach (equation 6), the free energy of micellization was calculated as a function of the ionic component X_2 in the mixed micelle (Maeda, 1995);

$$\Delta G^{o}_{mic} = RT\left(B_o + B_1 X_2 + B_2 X_2^2\right) \quad (6)$$

Where: $B_o = \ln C_1$ (7)

$$B_1 + B_2 = \ln\left(\frac{C_2}{C_1}\right) \quad (8)$$

$$B_2 = -\beta \quad (9)$$

In equations 7 - 8, C_1 is the CMC of the pure non-ionic surfactant on the mole fraction scale, C_2 is the CMC of the pure ionic surfactant on the mole fraction scale, and β is the interaction parameter. B_1 is a parameter indicative of the chain-chain interactions. A negative value of B_1 indicates that chain-chain interactions served to stabilize the mixed micelle (Clint, 1975). According to the values of both B_1 and β, the mixed micelle is most stable at lower contents of the SDS surfactants (Table 3).

The importance of the chemical reactions in the micellar phase, bulk water phase and simultaneously in surfactant solutions are crucial in this work. To this end, the Menger and Portnoy Pseudo phase kinetic (equation 10), (Menger and Portnoy, 1967) was employed.s

$$\log\left\{\frac{k_\psi - k_w}{k_m - k_\psi}\right\} = n\log[D] - \log K_D \quad (10)$$

where k_ψ= observed rate constant in the mixed micelles, k_w= rate constant in the bulk phase, k_m= rate constant in the micellar phase, n= number of surfactant molecule D to form micelle D^n, K_D= the dissociation constant between the substrate and the micelle

Typical plots of $\log\left\{\frac{k_\psi - k_w}{k_m - k_\psi}\right\}$ against log $[D]$, were linear for the reaction at all the mole fractions of SDS considered, from which n and K_D were obtained. The dissociation constant (K_D) decreased as the mole fraction of SDS increased as shown in Table 4. This is in agreement with the observed rate constant which decreased with SDS concentration as a result of stronger binding of the triarylmethyl cation to the negatively charged SDS micelle. The 0.76 which represents the mean number of surfactant, n obtained in SDS/TX-100 mixed micelle in this study is lower than that obtained for SDS alone (n= 3.59 and n= 1.98), in previous reports which is an indication of looser packing of hydrocarbon chains in the mixed micelle (Soriyan *et al*., 2009; Park *et al*., 1989).

The variation of inhibition factor with mole fraction of SDS is shown in Table 5. The energy of the transition state of the oxidation of the MG^+ in SDS micellar phase is presumed to be higher than in the bulk phase. This is supported by the increase in the inhibition factor $\left({k_w}/{k_\psi} \right)$ as the mole fraction of the SDS increases. The (k_w) is defined as the rate constant for the reaction in bulk aqueous medium and in the absence of surfactant while k_ψ is the observed rate constant in the mixed micelles. Thus, the reaction will be faster in bulk water phase than in micellar phase. There is increase in the inhibition factor $\left({k_w}/{k_\psi} \right)$ as the mole fraction increased (Table 5). This is evident in Figure 3, which shows k_ψ – X_{TX-100} profile at fixed total surfactant concentrations of 8.4 x 10^{-3}, 1.05 x10^{-2}, 1.3 x10^{-2} and 1.57 x 10^{-2} mol dm^{-3}.This observation is ascribed to reduced charged density on SDS when mixed with TX-100. The reduction in charged density of SDS will reduce the number of MG^+ bound to SDS micelle, thus more of the MG^+ will be in the bulk phase where the reaction is faster. This is in agreement with the previous work on the properties of the mixed micelle of SDS and TX-100 (Fendler and Fendler, 1975), in which the workers interpreted the non-ideality in the mixed surfactants in terms of charged density reduction and decrease in activity coefficient of SDS in the mixed micellar phase.

CONCLUSION

The catalytic or the inhibitive property of mixed surfactants of SDS/TX-100 on the oxidation of malachite green and nitrite ions has been investigated. The SDS/TX-100 mixed system lowers the reactivity of MG^+ with nitrite ions as the mole fraction of SDS increases. The results showed that the SDS/TX-100 system composition has relatively significant influence on the rate constant of the oxidation of the MG^+ when compared with the reaction in the single surfactant systems. The results also showed a higher pseudo- first order rate in aqueous solution than in the surfactants or their mixtures. The effect of SDS/TX-100 on rate constant for the oxidation of malachite green with nitrite revealed 62-85% lower reactivity as the mole fraction increased. The experimental data were analysed within the frame work of the existing kinetic mechanisms of micellar system.

It is important to note that in pure TX-100 (X_{TX} = 1), the surfactant solution has little or no effect on the redox reaction of MG^+ and nitrite ion, hence the reduced inhibition by TX-100 at fixed SDS is significant. k decreases rapidly until saturation is reached in pure SDS, indicating an overall inhibition. This inhibition is due to the negative charge on the SDS micellar phase attracting the triarylmethyl cation. Thus, when nitrite ions approach the triarylmethyl cation to form the transition state, they are repelled by the negative charges on SDS micellar surface. The overall inhibition observed in the mixed surfactants is ascribed to the strong electrostatic interactions between the SDS and MG^+.

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Table 1: Mean pseudo-first-order rate constant (k) of the reaction of malachite green and nitrites in Aqueous medium, SDS, TX-100 and various ratios of their mixtures. $[MG^+]$ = $5.77\text{x}10^{-5}$ mol/dm^3, [SDS] = 7.8 x10^{-3} mol/dm^3, [TX-100] = $2.28\text{x}10^{-4}$ mol/dm^3, $[NO_2^-]$ = (1.154 – 2.890) x 10^{-3} moldm^{-3} , Temperature = 25.0 ± 0.1^{O}C

$10^3[NO_2^-]$ mol/dm^3	k_1 (without surfactant)	k_2 (with SDS)	k_3 (with TX-100)	k_4 (with mixed surfactant)
1.154	0.1612	0.0882	0.1581	0.0606
8.240	0.1096	0.0621	0.0884	0.0420
6.410	0.0852	0.0508	0.0832	0.0224
4.810	0.0691	0.0432	0.0602	0.0105
4.120	0.0362	0.0185	0.0303	0.0095
2.890	0.0110	0.0086	0.0110	0.0044

Table 2: Rubingh's parameters and the excess free energy of mixing values

System	Mole Fraction (α_{SDS})	Mole Fraction ($\alpha_{TritonX-100}$)	CMC (observed) mM	CMC (expected) mM	β	γ_1	γ_2	ΔG^o_{ex} (kJ/mol)
SDS-TritonX-100	0.78	0.22	0.566	0.943	-4.575	0.215	0.446	-2.759
	0.63	0.37	0.353	0.588	-6.614	0.108	0.347	-3.836
	0.52	0.48	0.277	0.461	-7.907	0.056	0.249	-4.996
	0.42	0.58	0.231	0.385	-9.078	0.037	0.202	-5.728
	0.27	0.73	0.185	0.309	-6.144	0.107	0.338	-3.883

Table 3: Maeda's Parameters and free energy of micellization

System	Mole Fraction (α_{SDS})	B_1	ΔG^o_{mic} (kJ/mol)
SDS-TritonX-100	0.78	-3.300	-22.206
	0.63	-5.339	-23.436
	0.52	-6.632	-24.217
	0.42	-7.803	-24.923
	0.27	-4.869	-23.153

Table 4: Variation of the binding constant (K_D) and n with changes in mole fraction of SDS

X_{SDS}	K_D	n
1.00	2.11×10^{-2}	1.901
0.78	4.70×10^{-2}	1.014
0.63	7.14×10^{-2}	0.958
0.52	3.25×10^{-1}	0.408
0.42	2.14×10^{-1}	0.407
0.27	1.32×10^{-1}	0.376
0.00	1.30×10^{-1}	0.261

Table 5: Variation of inhibition factor with mole fraction of SDS

Mole fraction SDS	Inhibition factor $\left(k_W / k_\varphi \right)$
1.00	1.78
0.78	1.62
0.63	1.54
0.52	1.40
0.42	1.26
0.27	1.13

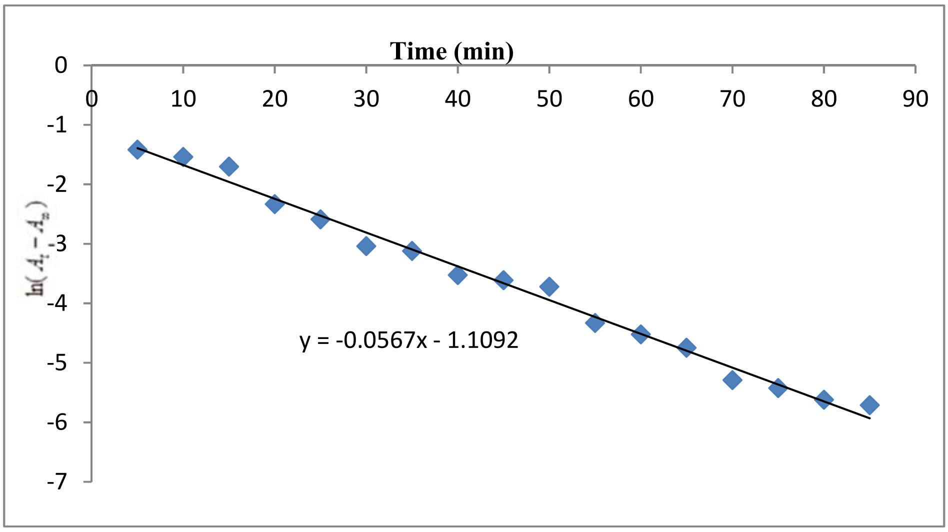

Figure 1A: Plot of $\ln(A_t - A_\infty)$ versus Time (min) for the redox reaction of Malachite green and NO_2^- in aqueous solution, $[MG^+] = 5.77\times10^{-5}\,mol/dm^3$, $[NO_2^-] = 6.41\times10^{-3}\,mol/dm^3$, $MG^+_{D_o} = 0.208$, $\lambda_{\max} = 620nm$, Temperature = 25.0 ± 0.1^oC, $A_\infty = 0.065$, Pseudo-first order rate constant, $k_1 = 0.1306$ s^{-1}

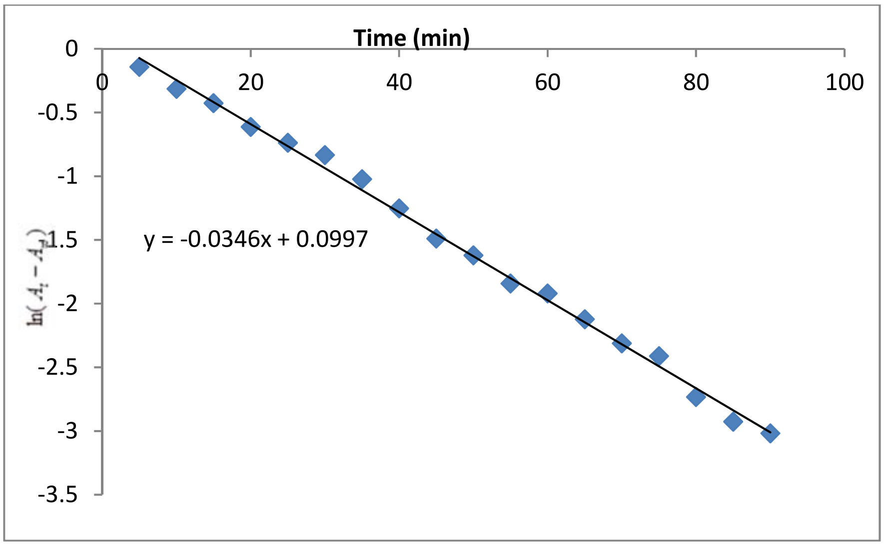

Figure 1B: Plot of $\ln(A_t - A_\infty)$ versus Time (min) for the redox reaction of Malachite green and NO_2^- in SDS surfactant, $[MG^+] = 5.77\times10^{-5}\,mol/dm^3$, $[NO_2^-] = 6.41\times10^{-3}\,mol/dm^3$, $MG^+_{D_o} = 0.205$, $\lambda_{\max} = 620nm$, $[SDS] = 8.2\times10^{-3}\,mol/dm^3$, Temperature = 25.0 ± 0.1^oC, $A_\infty = 0.063$, Pseudo-first order rate constant, $k_2 = 0.0796$ s^{-1}

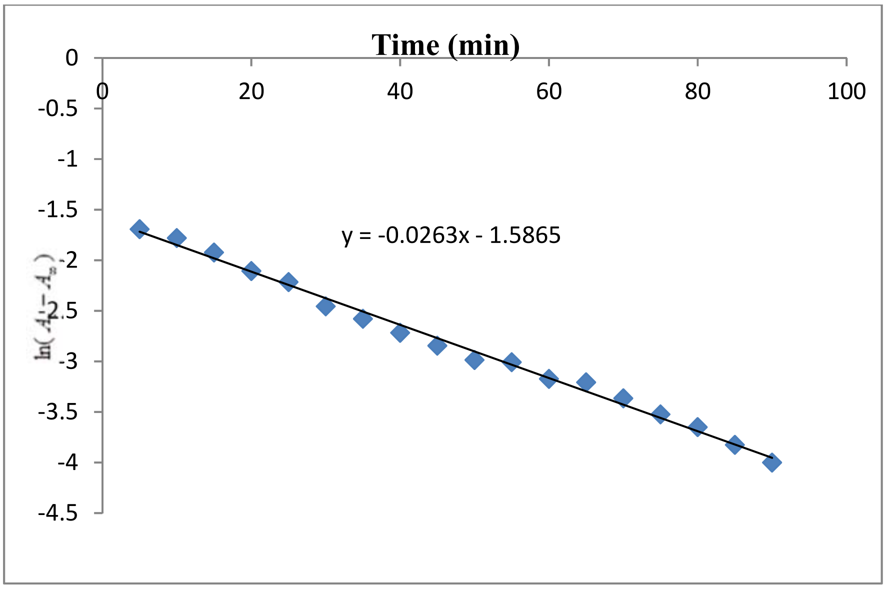

Figure 1C: Plot of $\ln(A_t - A_\infty)$ versus Time (min) for the redox reaction of Malachite green and NO_2^- in mixed surfactant, $[MG^+] = 5.77\times10^{-5}\, mol/dm^3$, $[NO_2^-] = 6.41\times10^{-3}\, mol/dm^3$ $MG^+_{D_o} = 0.206$, $\lambda_{\max} = 620nm$, $[SDS] = 8.2\times10^{-3}\, mol/dm^3$, $[TX-100] = 2.28\times10^{-4}\, mol/dm^3$, Temperature = 25.0 $\pm 0.1^oC$, $A_\infty = 0.085$, Pseudo-first order rate constant, $k_4 = 0.0606$ s^{-1}

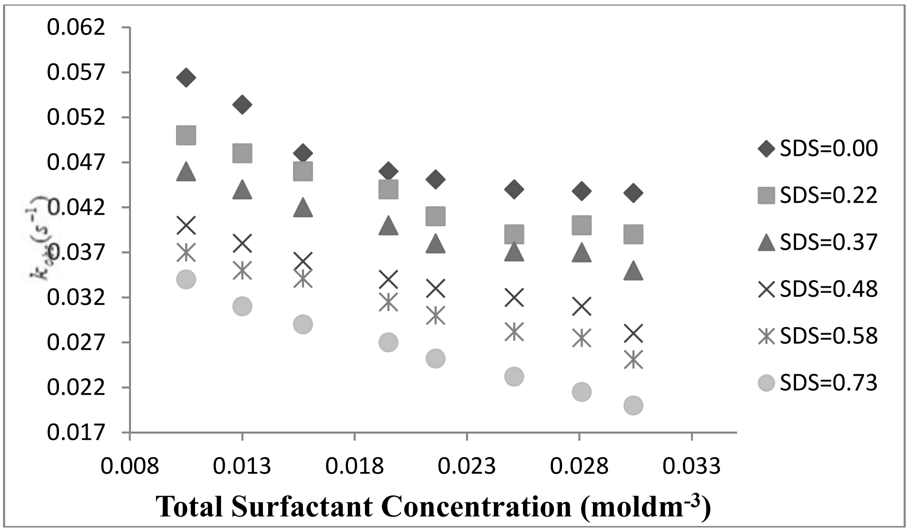

Figure 2: Variation of the observed rate constant (k_{obs}) as a function of the Total surfactant concentration for the redox reaction of Malachite green at various fixed mole fraction of SDS. $(NO_2^-) = 1.154\times10^{-3}\, mol/dm^3$ and Temperature = 25.0 $\pm\pm\, 0.1^oC$

Figure 3: k_{obs} -$X_{TX\text{-}100}$ profiles for the redox reaction of Malachite green at various fixed total concentrations of mixed surfactants. $[NO_2^-] = 1.154 \times 10^{-3}$ moldm^{-3} and Temperature = 25.0±0.1°