

Role of mixed Surfactants on the Oxidation of Malachite Green by Nitrite ions

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Abstract: The oxidation of malachite green, (MG^+) 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 revealed 62-85% lower reactivity as the mole fraction increased. We also observed a higher pseudo-first order rate in aqueous solution than in the surfactants or their mixtures. A rapid decrease in the observed pseudo-first order rate constant (k) was observed 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.

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1. Introduction

Much attention has been focused on experimental and theoretical aspects of mixed micellar systems [1, 2, 3, 4]. In many applications, surfactants are usually mixtures as a result of blending process that aims to improve synergy [5]. However, in the majority of industrial applications, it is common practice to employ mixtures of surfactants in place of individual ones because these mixed surfactants systems possess superior qualities in terms of detergency, lower interfacial tension, solubilisation and in the modification of rheological properties of polymers [6, 7, 8]. 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 [1, 9]. The tendency to form a micellar structure in mixed surfactant solutions will be substantially different from that in pure surfactant solutions [10].

Several workers have worked on studies involving the effect of mixed surfactants on reaction rates, [8, 11, 12, 13, 14]. Khan and co-worker [11] in their study on the effects of non-ionic and cationic micelles on the aqueous cleavages of phenyl benzoate and phenyl salicylate 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, known as malachite green, (MG^+), is a basic organic dye used for materials such as silk, wool, jute, ceramic, leather, paper, in aquaculture and as cytochemical staining agent. However, nitric accumulation in blood and tissues represent 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 [15, 16]. 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 [17, 18].

The influence of mixed surfactants on reaction rate has become a new field in kinetics which is receiving increasing attention [12, 11, 13]. The kinetics and mechanisms of the oxidation reaction of MG^+ with nitrite ion have been studied in acidic medium [19] and one step in such reactions reported is frequently 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 our work on the reaction of MG^+ [13, 20], 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 taken place in micelle free medium.

2. Experimental Procedures

Materials and Methods

All the materials and reagents used in this work are analar grades and were used as received. The SDS used was a product of BDH chemicals. The critical micelle concentration was determined in order to test its degree of purity in aqueous medium at 25°C. This gave $8.16 \times 10^{-3} M$ that agrees with literature values [13, 21, 22]. Malachite green was obtained from Bektöh (Germany). The Triton X-100 (TX-100) was an Aldrich product. A wavelength scan of its aqueous solution shows a maximum absorbance peak at 276nm which agrees with the work of Gratzner and Beaven [23] which reported a λ_{max} of 278 nm and an extinction coefficient of $1670 \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ for TX-100 in water. The CMC of each surfactant was determined by conductometric method using electric conductivity meter, DDS-307 made by Jenway at controlled temperature $25 \pm 1^\circ C$.

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 λ_{max} of 620 nm and a molar extinction coefficient of $105 \text{ M}^{-1} \text{ cm}^{-1}$ which is in agreement with the literature value [24].

3. 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 λ_{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 at a fixed temperature of $25.0 \pm 0.1^\circ C$. All the stock solutions were put in the thermostated water bath to ensure constant temperature in the kinetic run. The

spectrophotometric titration was done using the individual surfactants separately. The surfactant and 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 maintained at $5.77 \times 10^{-5} \text{ mol/dm}^3$ (0.208 Absorbance) for all the reactions. The concentration of MG^+ was kept constant for all the reactions while the oxidant concentrations were 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 $\ln(\text{Absorbance})$ versus time (min).

4. Results and Discussion

The effect of mixed surfactants of SDS and TX-100 was monitored at 0.00, 0.27, 0.42, 0.52, 0.63, and 1.00 mole fractions of SDS (X_{SDS}). The linear plots of $\ln(\text{Absorbance})$ versus time (min) are presented in Figures 1A, B & C.

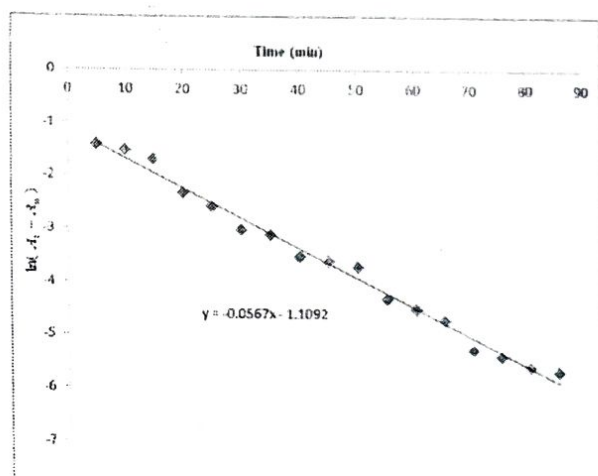


Figure 1A: Plot of $\ln(A_t - A_\infty)$ versus Time (min) for the redox reaction of Malachite green and NO_2^- in aqueous solution, $[MG^+] = 5.77 \times 10^{-5} \text{ mol/dm}^3$, $[NO_2^-] = 6.41 \times 10^{-3} \text{ mol/dm}^3$, $MG^+_{D_0} = 0.208$, $\lambda_{max} = 620 \text{ nm}$, Temperature = $25.0 \pm 0.1^\circ C$, $A_\infty = 0.065$, Pseudo-first order rate, $k_1 = 0.1306$

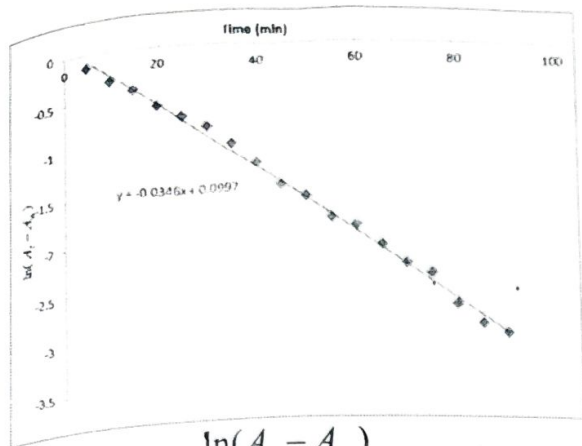


Figure 1B: Plot of $\ln(A_t - A_\infty)$ versus Time (min) for the redox reaction of Malachite green and NO_2^- in SDS surfactant, $[MG^+] = 5.77 \times 10^{-5} \text{ mol/dm}^3$, $[NO_2^-] = 6.41 \times 10^{-3} \text{ mol/dm}^3$, $MG_{D_0}^+ = 0.205$, $\lambda_{\text{max}} = 620 \text{ nm}$, $[SDS] = 8.2 \times 10^{-3} \text{ mol/dm}^3$, Temperature = $25.0 \pm 0.1^\circ \text{C}$, $A_\infty = 0.063$, Pseudo-first order rate, $k_2 = 0.0796$

Stoichiometric studies show that one mole of the dye is consumed by one mole of the nitrite ions. 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 rates (k) of the reaction of malachite green and nitrite in aqueous medium, SDS, TX-100 and various ratios of their mixtures.

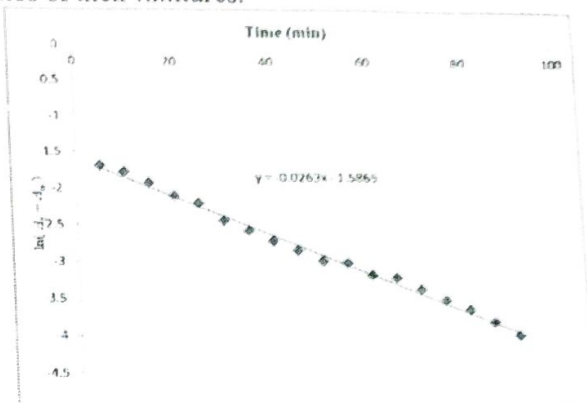


Figure 1C: Plot of $\ln(A_t - A_\infty)$ versus Time (min) for the redox reaction of Malachite green and NO_2^- in mixed surfactant, $[MG^+] = 5.77 \times 10^{-5} \text{ mol/dm}^3$, $[NO_2^-] = 6.41 \times 10^{-3} \text{ mol/dm}^3$, $MG_{D_0}^+ = 0.206$, $\lambda_{\text{max}} = 620 \text{ nm}$, $[SDS] = 8.2 \times 10^{-3} \text{ mol/dm}^3$, $[TX-100] = 2.28 \times 10^{-4} \text{ mol/dm}^3$, Temperature = $25.0 \pm 0.1^\circ \text{C}$, $A_\infty = 0.085$, Pseudo-first order rate, $k_4 = 0.0606$

Table 1: Mean pseudo-first-order rates (k) of the reaction of malachite green and nitrites in Aqueous medium, SDS, TX-100 and various ratios of their mixtures. $(MG^+) = 5.77 \times 10^{-5} \text{ mol/dm}^3$, $[SDS] = 7.8 \times 10^{-3} \text{ mol/dm}^3$, $[TX-100] = 2.28 \times 10^{-4} \text{ mol/dm}^3$, $(NO_2^-) = (1.154-2.89) \times 10^{-3} \text{ mol/dm}^3$, Temperature = $25.0 \pm 0.1^\circ \text{C}$

$10^3 [NO_2^-] \text{ mol/dm}^3$	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	0.0014

These results show that the reaction is faster in bulk water phase than in micellar phase. The decrease in the k of the reaction in SDS surfactant compared with the k 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 [25]. 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 and there is thus a strong binding of the triarylmethylation to the negatively charged SDS micelle and hence the SDS renders the substrate less available to nucleophilic

attack by the NO_2^- ion [26]. However, the effects of the TX-100 (a non-ionic) surfactant compared with the anionic surfactant SDS on the reaction of nitrite ion and MG^+ suggest that the non-ionic TX-100 did not seriously alter the rate of reaction. This is qualitatively in conformity with previous work [27].

The mean pseudo-first order rate, k was in the range 0.0110 - 0.1612 s^{-1} in aqueous medium, 0.0086-0.0882 s^{-1} in SDS, 0.0110- 0.1518 s^{-1} in TX-100 and 0.0044 - 0.0606 s^{-1} in the mixed surfactants. The results showed a higher pseudo- first order rate in aqueous solution than in the surfactants or their mixtures. This result is highly influenced by the MG^+ distribution between the bulk water and the surfactant aggregates. The SDS/TX-100 effect on k for the oxidation of malachite green with nitrite 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 is presented in figure 2 below.

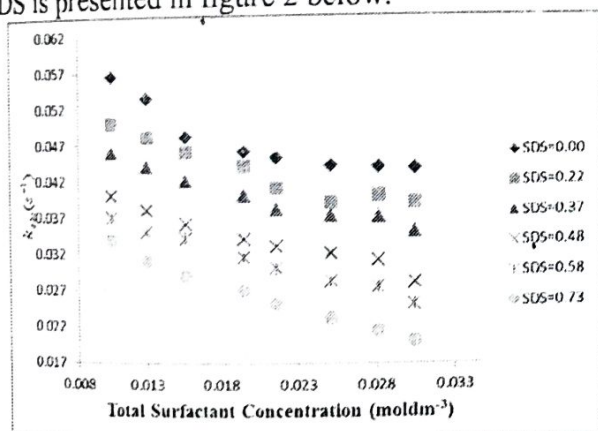


Figure 2: Variation of the observed rate constant (k_{obs}) as a function of the Total surfactant concentration for the redox reaction of Malachite green at various fixed mole fraction of SDS. $(NO_2^-) = 1.154 \times 10^{-3} mol / dm^3$ and Temperature = $25.0 \pm 0.1^\circ C$

It is observed in figure 2 that the rate is very sensitive to the medium effects as k 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.

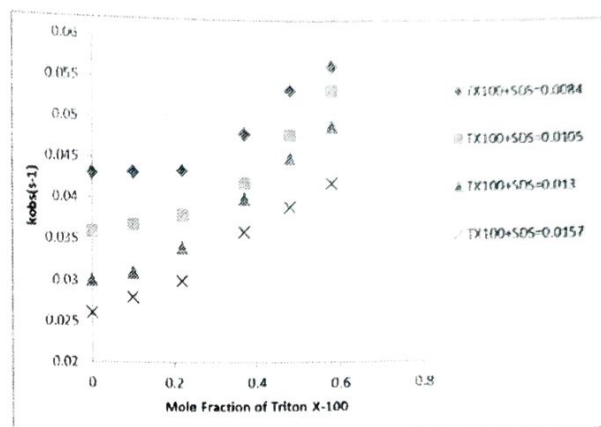


Figure 3: $k_{obs} - X_{TX-100}$ profiles for the redox reaction of Malachite green at various fixed total concentrations of mixed surfactants. $(NO_2^-) = 1.154 \times 10^{-3} moldm^{-3}$ and Temperature = $25.0 \pm 0.1^\circ C$

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 predominantly 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. 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 [28] can be employed to determine the expected CMC of the mixture. Our first approach utilized Clint's equation 1 to determine the expected CMC of the mixture and the results shown in table 2;

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

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 differing composition of surfactant monomers in the micelle compared to the bulk solution [29].

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

$$\frac{X_1^2 \ln \left(\frac{CMC_{mix} \alpha_1}{CMC_1 X_1} \right)}{[1-X_1] \ln \left(\frac{CMC_{mix} [1-\alpha_1]}{CMC_2 [1-X_1]} \right)} = 1 \quad (2)$$

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 2, X_1 was calculated and the interaction parameter (β) obtained from equation 3 [29]. 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 also suggesting that the surfactant monomers are attractively interacting with one another.

$$\beta = \frac{\ln \left(\frac{CMC_{mix} \alpha_i}{CMC_i X_i} \right)}{(1-X_i)^2} \quad (3)$$

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 4. The values are shown in table 2.

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_{ex}^o (kJ/mol)
SDS-	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
TritonX-100	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

$$\Delta G_{ex}^o = RT \sum_{i=1}^2 X_i \ln \gamma_i \quad (4)$$

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 [8].

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 [8]. 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. This is attributed to the decrease in ionic head group repulsion caused the presence of the non-ionic surfactant between the ionic head groups.

Using Maeda's approach (equation 5), the free energy of micellization was calculated as a function of the ionic component X_2 in the mixed micelle [30];

$$\Delta G_{mic}^{\circ} = RT(B_0 + B_1 X_2 + B_2 X_2^2) \quad (5)$$

Where:

$$B_0 = \ln C_1 \quad (6)$$

$$B_1 + B_2 = \ln \left(\frac{C_2}{C_1} \right) \quad (7)$$

$$B_2 = -\beta \quad (8)$$

In equations 6 - 7, 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 are serving to stabilize the mixed micelle [28]. 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).

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

System	Mole Fraction (α_{SDS})	B_1	ΔG_{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

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 (9), [31] was employed to explain this;

$$\log \left\{ \frac{k_{\psi} - k_w}{k_m - k_{\psi}} \right\} = n \log [D] - \log K_D \quad (9)$$

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 [13, 32].

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

The variation of inhibition factor with mole fraction of SDS is shown in Table 5 below.

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

Mole fraction SDS	Inhibition factor $\left(\frac{k_w}{k_\psi}\right)$
1.00	1.78
0.78	1.62
0.63	1.54
0.52	1.40
0.42	1.26
0.27	1.13

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 $\left(\frac{k_w}{k_\psi}\right)$ 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 $\left(\frac{k_w}{k_\psi}\right)$ as the mole fraction increased (Table 5). This is evident in figure 3, which

shows $k_\psi - X_{TX-100}$ profile at fixed total surfactant concentrations of 8.4×10^{-3} , 1.05×10^{-2} , 1.3×10^{-2} and $1.57 \times 10^{-2} \text{ mol dm}^{-3}$. 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 [26], 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.

5. 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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