Research Article

EFFECT OF SODIUM DODECYL SULPHATE MICELLES ON THE OXIDATION OF L-SERINE BY PERIODATE IN PERCHLORIC ACID MEDIUM

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ABSTRACT
The kinetics of oxidation of L-serine(Ser) by periodate(Per) in presence of an anionic surfactant, sodium dodecyl sulphate(SDS) was studied spectrophotometrically at 280 nm in perchloric acid medium at 303 K. The reaction exhibited first order dependence on [Per], [Ser] and [H$^+$]. It was found that increase in [SDS] causes an increase in rate indicating that the reaction was catalysed by anionic micelles. The critical micelle concentration(CMC) for SDS was determined in 0.12 mol dm^{-3} ionic strength in presence of oxidant by surface tension measurements and found to be 1.0 x 10^{-4} mol dm^{-3}. The rate-[surfactant] profile shows a limiting behaviour indicative of unimolecular rate-determining reaction in the micellar pseudo-phase. 2-hydroxy acetaldehyde was identified to be the main product of oxidation by IR-spectroscopy. The activation parameters were computed using linear least squares method and the values of E_a and $\Delta S^{\#}$ are found to be 21.39 ± 1.64 kJ mol^{-1} and -312 ± 4.67 JK^{-1} mol^{-1} respectively.

Keywords: L-serine, periodate, micelles, kinetics, oxidation, 2-hydroxy acetaldehyde.

INTRODUCTION
Micelles are biologically important aggregates that are formed in aqueous solutions by surfactants, which are compounds possessing a water-solubilizing moiety (often an ionic group) and a water insoluble portion(a long hydrocarbon chain). Micelles are spherical aggregates of 20-200 molecules, containing hydrocarbon interiors and ionic surfaces. The presence of the surface active agent often brings about acceleration of reaction by 10-100 times and in a few cases $10^3 – 10^4$ times. Catalysis or inhibition of chemical reaction in solution is due to binding of the reactants by micelle. Micelles are formed after certain concentration of the detergent is reached, called critical micelle concentration(CMC). There is an abrupt change in physical properties of micellar solutions like conductance, refractive index etc. at and above the CMC and thus a sudden drift in property is used to determine the CMC. The CMC decreases in the presence of multivalent ions or high ionic concentrations.

In the oxidation of picolinic acid[1], formaldehyde[2], ethanol and propan-1-ol[3], D-glucose[4], dimethyl sulfoxide[5] by chromium(VI), Vanadium(IV)[6], DL-Aspartic Acid[7] it was reported that the SDS accelerated the reaction. Very few reports are available on the oxidation of L-serine using peroxydiphosphate[8,9], manganese(VII)[10,11], N – bromo p-toulenesulphonamide[12,13], ruthenium(III) -catalysed oxidation by peroxodiphosphate[14], manganese(III)[15-18], N – bromonicotinamide(NBN)[19], diperiodatocuprate(III)[20], iridium(III) and iridium(III) – manganese(II) catalysed oxidation by cerium(IV)[21], chromium(VI)[22] in perchloric acid medium at 50 ^{0}C, periodate in alkaline medium, the product of oxidation is glycolaldehyde. Periodate is a two electron oxidant with redox potential of 1.60 V in acid medium[23] and is a more suitable reagent for the study of oxidation reactions of both organic and inorganic substrates[24-28]. In continuation of our studies on the oxidation of L-serine (Ser) using oxidant Au(III)[29] with an attempt to evaluate the degradation mechanism it was proposed to investigate these reactions in hydrophobic environments by mimicking the conditions existing inside the protein molecule. The hydrophobic environment is necessary for most of the enzymatic reactions to avoid the interference of bulk water present in the physiological fluids.

Hence, these redox reactions were carried out in different micellar media, known to create hydrophobic environments by decreasing the dielectric constant of the medium. These reactions were investigated in *vitro* under mimicked physiological conditions so that these results can be extended to real life systems. Further, so far no attempt has been made to investigate the oxidation of serine in micellar medium. While the cationic micelle, cetyltrimethyl ammonium bromide(CTAB) and the neutral micelle, Triton-X did not significantly alter the reaction rates with all these oxidants, the anionic surfactant, SDS accelerated the rate of oxidation of serine with periodate.

MATERIALS AND METHODS

A 0.1 mol dm^{-3} solution was prepared afresh by dissolving in required volume of double distilled water. A 0.01 mol dm^{-3} solution of periodate was prepared by dissolving the requiste amount of sodium periodate in water and the solution was standardized by iodometric method[10]. All the chemicals used were of analytical reagent grade.

Kinetic measurements were carried out under the conditions, [H$^+$] > [SDS] > [Ser] > [Per] in 0.01 mol dm^{-3} perchloric acid medium. The progress of the reaction was followed by measuring the absorbance of periodate at 280 nm (Fig. 1). The plots of log(absorbance) versus time were found to be linear upto 80% completion of the reaction indicating that the reaction was first order with respect to [Per]. The pseudo-first order rate constants calculated from these plots were denoted by k$^/$ and the rate constants were found to be reproducible within ± 4%.

Milton Roy spectronic 1201 UV-Visible spectrophotometer was used to measure the absorbance. The temperature was kept constant using a JULABO constant temperature liquid circulatory bath.
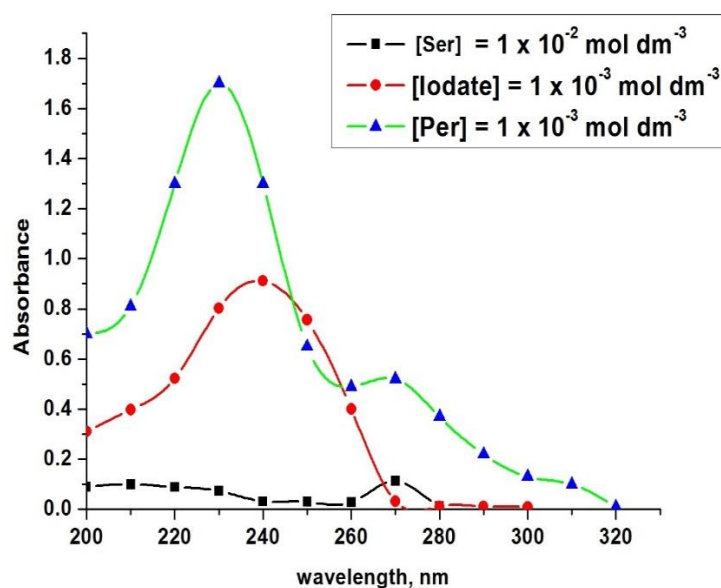

Fig. 1: Spectra of Periodate, Iodate and Serine in 0.01 mol dm^{-3} HClO$_4$
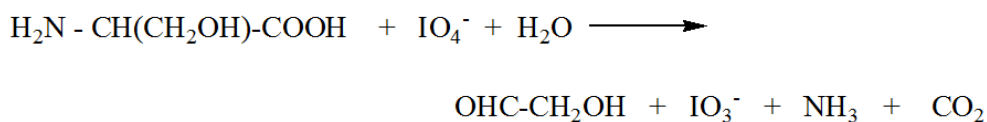
RESULTS AND DISCUSSION

Test for free radicals

The test for free radicals was carried out by taking L-serine, perchloric acid, SDS in a thumberg tube and acrylonitrile and periodate in a bent tube. After evacuating the system the solutions were mixed by tilting the tube. The reaction mixture was kept aside and even after 24 h no precipitate was observed indicating the absence of free radical formation.

Stoichiometry

Known amounts of L-serine was allowed to react completely with a known excess of periodate at 303 K and in 0.01 mol dm^{-3} perchloric acid medium in presence of SDS and after 24 h the amount of iodate formed (which equals the amount of periodate consumed) was estimated by measuring the absorbance of the reaction mixture .

The stoichiometry of the reaction was found to correspond to the equation

$$H_2N - CH(CH_2OH)\text{-}COOH \quad + \quad IO_4^- + H_2O \longrightarrow$$

$$OHC\text{-}CH_2OH \quad + \quad IO_3^- \quad + \quad NH_3 \quad + \quad CO_2$$

Product analysis
The reaction product was isolated by a solvent extraction method using an organic solvent diethyl ether and was identified by IR Spectrum(Fig. 2), in which the absorption band at 3435.15 cm^{-1} corresponds to O-H stretching, the band at 2919.66 cm^{-1} corresponds to C-H stretching, 2863.12 cm^{-1} corresponds to O=C-H stretching and 1643.23cm^{-1} corresponds to C=O stretching.
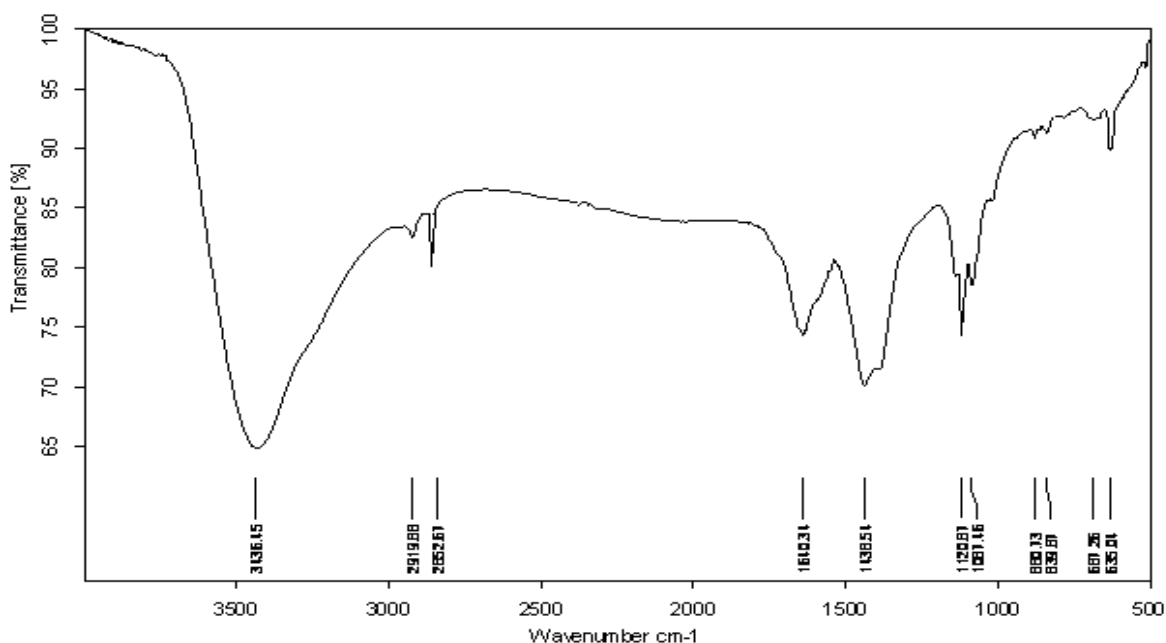

Fig. 2: FT-IR spectrum of 2- hydroxy acetaldehyde

Determination of CMC of SDS under the experimental conditions employed
The CMC of SDS has a value of 8.0×10^{-3} mol dm^{-3} in the presence of any added ions[30], but the value decreases as the ionic strength of the medium increases. It is necessary to ascertain whether SDS has the same value of CMC at the ionic strength(μ) of 0.12 mol dm^{-3} with sodium perchlorate instead of NaCl and also in presence of serine by determining the surface tension of the mixture at different concentrations of SDS using stalagmometry. The value of surface tension was plotted against logarithm of SDS concentration (Fig. 3). The decrease in surface tension with increase in [SDS] is very pronounced at SDS $\leq 1.0 \times 10^{-4}$ mol dm^{-3} and above this concentration of SDS, the decrease in surface tension is much less pronounced. The plot has been found to yield two straight lines intersecting at [SDS] = 1.0×10^{-4} mol dm^{-3} and hence, the CMC under experimental conditions was considered to be 1.0×10^{-4} mol dm^{-3}(Table-1).

Table 1: Determination of CMC
[Ser] = 1.0 x 10^{-2} mol dm^{-3} ; [H^+] = 1.0 x 10^{-2} mol dm^{-3} ;
μ = 0.12 mol dm^{-3} ; T = 303 K

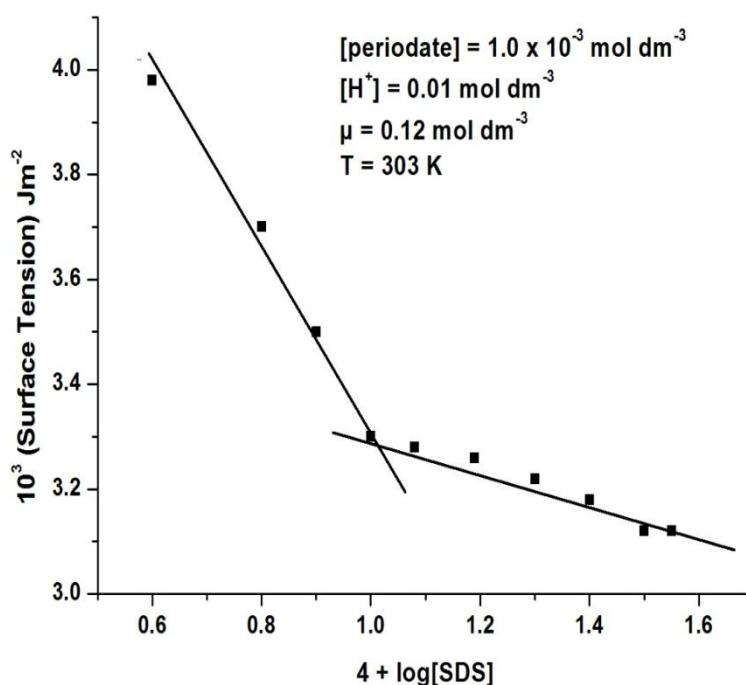| [SDS] x 10^3, mol dm^{-3}	Surface Tension x 10^3, Jm^{-2}
0.0	6.00
0.4	5.25
0.6	3.97
0.8	3.30
1.0	3.25
1.5	3.20
2.0	3.15
2.5	3.11
3.0	3.11
3.5	3.10

Fig. 3: Plot of surface tension versus log[SDS].
The [SDS] at point of intersection corresponds to CMC

Determination of binding constant of serine
To determine the binding constant of serine with the SDS micelles (at [H^+] = 0.01 mol dm^{-3} and μ = 0.12 mol dm^{-3}) spectra of serine was scanned at different SDS concentrations under the conditions [SDS] > [serine]. A plausible wavelength is chosen (λ = 210 nm) and A_m the absorbance in presence of micelle was determined for various SDS concentrations (Fig. 4). A_w, the absorbance in the absence of micelle was also found to be 0.352 (Table-2). The binding constant of serine is calculated using the equation[31]

$1/A_m – A_w^0 = [1/A_m^0 – A_w^0](1 + 1/K_b D_n)$

and plotting $1/A_m – A_w^0$ versus $1/D_n$ where A_m^0 is limiting absorbance in presence of micelle where D_n is ([SDS] – CMC).

**Table 2: Absorbance data of serine at 210 nm
at different SDS concentrations
[Serine] = 1.0 x 10^{-2} mol dm^{-3} ; [H$^+$] = 1.0 x 10^{-2} mol dm^{-3} ;
μ = 0.12 mol dm^{-3} ; CMC = 1.0 x 10^{-4} mol dm^{-3} ; T = 303 K**

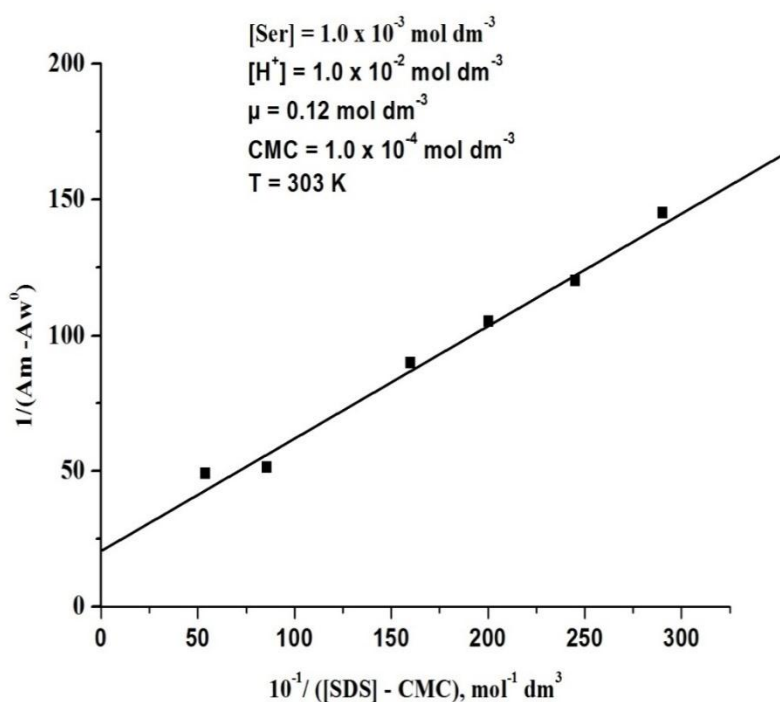| [SDS] x 10^3 mol dm^{-3}	Absorbance A_m	$1/(A_m - A_w^0)$	$1/D_n$ mol^{-1} dm^{-3}
0.0	0.352	-	-
4.0	0.358	166.60	288.85
8.0	0.363	90.90	134.01
12.0	0.368	62.50	87.24
16.0	0.371	52.60	64.67
20.0	0.374	45.45	51.38
40.0	0.377	40.00	25.06
50.0	0.381	34.48	20.04
60.0	0.383	32.25	16.69
70.0	0.384	31.25	14.30

Fig. 4: Plot of $1/(A_M - A_w)$ Vs $1/$ ([SDS]-CMC)

From the slope and intercept of the plot given in (Fig. 4), the binding constant of serine was found to be 62.8 dm^{-3} mol^{-1} at 303 K.

Effect of ionic strength
The effect of ionic strength was studied by varying the ionic strength in the range 0.1-0.2 mol dm^{-3} using sodium perchlorate and it was observed that the rate of the reaction decreased with increase in ionic strength (Table-3).

Table 3: Effect of ionic strength, 'μ' on the
pseudo-first order rate constant, k/
[serine] = 1.0 x 10^{-2} mol dm^{-3} ; [periodate] =1.0 x10^{-3} mol dm^{-3} ;
[H^+] = 0.01 mol dm^{-3}; [SDS] = 50.0 x 10^{-3} mol dm^{-3} ; T = 303 K

μ, mol dm^{-3}	k/ x 10^4, sec^{-1}
0.1	6.98
0.12	6.16
0.14	5.33
0.16	4.31
0.18	3.28
0.2	2.25

Effect of [periodate]

The effect of periodate on the rate of the reaction, was studied by carrying out kinetic runs at 303 K and by varying the concentration of periodate from 0.1-2.5 x 10^{-3} mol dm^{-3}, keeping the concentrations of all other ions constant. The plots of log(absorbance) versus time were found to be linear upto 80% completion of the reaction indicating that the reaction was first order with respect to [IO_4^-] (Table – 4).

Table 4: Effect of [periodate] on the
pseudo-first order rate constant, k/
[Serine] = 1.0 x 10^{-2} mol dm^{-3} ; [H^+] = 0.01 mol dm^{-3};
[SDS] = 1.0 x 10^{-2} mol dm^{-3} ; μ = 0.12 mol dm $^{-3}$; T = 303 K

[periodate] x 10^3, mol dm^{-3}	k/ x 10^4, sec^{-1}
0.5	5.95
1.0	6.16
1.5	5.95
2.0	6.03
2.5	6.16
3.0	6.08

Effect of [iodate]

To study the effect of product, iodate on the rate of reaction, kinetic runs were carried out keeping the concentrations of all other reactants constant and varying the concentration of iodate from 0.10 - 2.50 x 10^{-3} mol dm^{-3}. It was observed that [iodate] did not show any effect on the reaction rate (Table-5).

Table 5: Effect of [iodate] on the
pseudo-first order rate constant, k/
[Serine] = 1.0 x 10^{-2} mol dm^{-3} ; [periodate] =1.0 x10^{-3} mol dm^{-3} ;
[H^+] = 0.01 mol dm^{-3}; [SDS] = 50.0 x 10^{-3} mol dm^{-3} ;
μ = 0.12 mol dm^{-3} ; T = 303 K

[iodate] x 10^3 mol dm^{-3}	k/ x 10^4 sec^{-1}
0.1	5.95
0.5	6.16
1.0	6.23
1.5	5.94
2.0	6.19
2.5	6.12

Effect of [serine]

To find out the dependence of rate on [serine], kinetic runs are performed varying the initial concentration of threonine in the range of 0.5 -3.0 x 10^{-2} mol dm^{-3} keeping the concentration of all other reactants and temperature constant. The pseudo-first order rate constants obtained were found to increase with the concentration of serine (Table-6).

Table 6: Effect of [serine] on the pseudo-first order rate constant, $k^/$
[periodate] =1.0 x10^{-3} mol dm^{-3} ; [H^+] = 0.01 mol dm^{-3};
[SDS] = 50.0 x 10^{-3} mol dm^{-3} ; µ = 0.12 mol dm^{-3} ; T = 303 K

[serine] x 10^2, mol dm^{-3}	$k^/$ x 10^4, sec^{-1}
0.5	3.2
1.0	6.16
1.5	9.36
2.0	12.5
2.5	15.6
3.0	18.81

**Effect of hydrogen ion concentration**

In order to study the effect of [H^+] on the rate of the reaction, kinetic runs were carried out keeping the concentrations of all other reactants constant and varying the [H^+] from 0.01 to 0.06 mol dm^{-3} with perchloric acid. The pseudo-first order rate constants were found to decrease with increase in [H^+] (Table-7).

Table 7: Effect of [H^+] on the pseudo-first order rate constant, $k^/$
[serine] = 1.0 x 10^{-2} mol dm^{-3} ; [periodate] =1.0 x10^{-3} mol dm^{-3} ;
[SDS] = 50.0 x 10^{-3} mol dm^{-3} ; µ = 0.12 mol dm^{-3} ; T = 303 K

| [H^+] x 10^2, mol dm^{-3}	$k^/$ x 10^4, sec^{-1}
0.01	6.16
0.02	5.12
0.03	4.38
0.04	3.12
0.05	2.87
0.06	2.05

Effect of sodium dodecyl sulphate concentration

To investigate the effect of the concentration of SDS on rate, the rate constants, k, (Fig. 5) were determined at different concentrations of SDS, keeping the concentrations of serine and other reactants constant. The pseudo first order rate constants thus obtained indicate that the rate increases with the concentration of SDS, reaches a maximum and remains constant with further increase in [SDS] (Table-8).
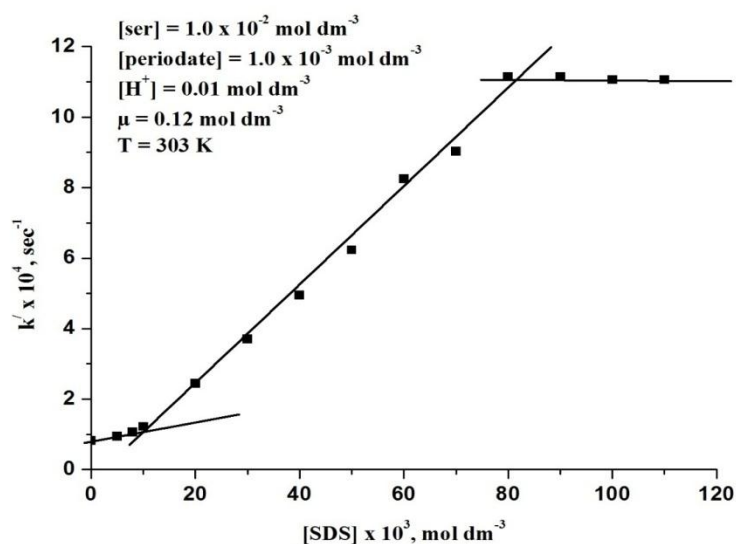
Fig. 5: Plot of k / versus [SDS]

Table 8: Effect of [SDS] on the pseudo-first order rate constant, k/
[serine] = 1.0×10^{-2} mol dm^{-3} ; [periodate] = 1.0×10^{-3} mol dm^{-3} ;
[H$^+$] = 0.01 mol dm^{-3}; μ = 0.12 mol dm $^{-3}$; T = 303 K

[SDS] x 10³, mol dm⁻³	k/ x 10⁴, sec⁻¹
0.0	0.82
5.0	0.95
8.0	1.06
10.0	1.22
20.0	2.45
30.0	3.71
40.0	4.95
50.0	6.23
60.0	8.25
70.0	9.03
80.0	11.15
90.0	11.15
100.0	11.06
110.0	11.06

DISCUSSION
L-serine possesses two pK_a values[32], one corresponding to the carboxylic acid group (pK_1 = 2.2) and the other to amino group (pK_2 = 9.2).
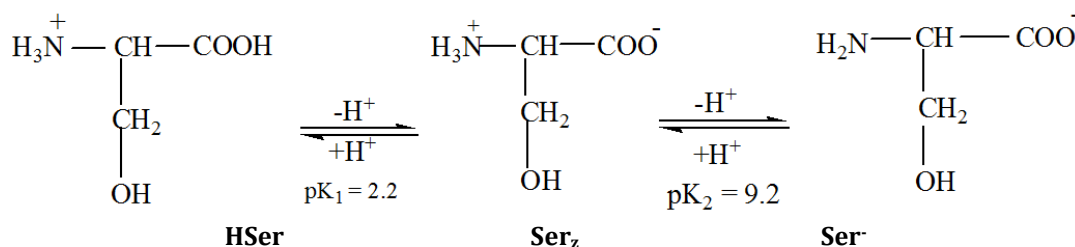
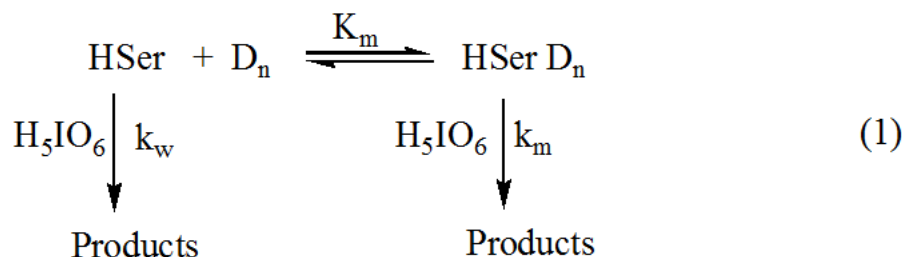Under the present experimental conditions ([H⁺] = 1.0×10^{-2} mol dm⁻³), serine exists in the protonated form (HSer) to an extent of 91.9% and the remaining in the zwitterionic form (8.1%). The cationic species (HSer) was the active species participating in the reaction . It was further confirmed by the decrease in rate with increase in [H⁺] which increases the concentration of cationic species.
Periodate is a stable two electron oxidant, capable of oxidising many organic substrates in acid, neutral and alkaline media. The species of the periodate varies with pH[33]. At pH 1, 75% of it exists as H_5IO_6; at pH

2.5-7.0 as $H_4IO_6^-$. Hence in the present experimental conditions, $[H^+] = 0.01$ mol dm^{-3}, periodate is present in the form of H_5IO_6.

HSer forms an outer -sphere complex with H_5IO_6 and this positively charged complex is bound by the SDS micelles. Thus the negatively charged SDS micelles promotes the positive charge transfer from cationic species of serine stabilizing the transition state resulting in the acceleration of reaction as proposed in the following scheme

$$\text{HSer} + D_n \underset{}{\overset{K_m}{\rightleftharpoons}} \text{HSer } D_n \qquad (1)$$

$$H_5IO_6 \downarrow k_w \qquad\qquad H_5IO_6 \downarrow k_m$$

$$\text{Products} \qquad\qquad\qquad \text{Products}$$

Where Hser is $H_3C\text{-(CHOH)-CH}(\overset{+}{NH_3})\text{-COOH}$ and the oxidation products are $H_3C(CHOH)CHO$, NH_3 and CO_2.

Further, k_w and k_m are the pseudo first order rate constants in absence and presence of micelle respectively.

D_n the concentration of micelle is given by
$[D_n] = ([SDS] -CMC)/ N$

where CMC is the critical micellar concentration (1.0×10^{-4} mol dm^{-3}) and N is the aggregation number. The binding constant, K_m between the micelle and serine has been evaluated by considering the pseudo-phase kinetic model reported by Menger and Portnoy[34]. The proposed micellar catalysed unimolecular path is in conformity with the rate - surfactant profile which exhibits a limiting behaviour (Fig. 5). The rate law for the proposed scheme can be represented as

$$k_{exp} = \frac{k_w + k_m K_m[D_n]}{1 + K_m[D_n]} \qquad (2)$$

Which rearranges to

$$\frac{1}{k_{exp}- k_w} = \frac{1}{k_m - k_w} + \frac{1}{k_m - k_w}\left[\frac{1}{K_m[D_n]}\right] \qquad (3)$$

where k_{exp} is the observed second order rate constant in presence of micelle. Equation (3) predicts the plot of $1/k_{exp} – k_w$ versus $(1/[SDS] – CMC)$ should be linear with a positive intercept on Y -axis. Exactly similar plot (Fig . 6) was obtained experimentally thus supporting the proposed scheme.
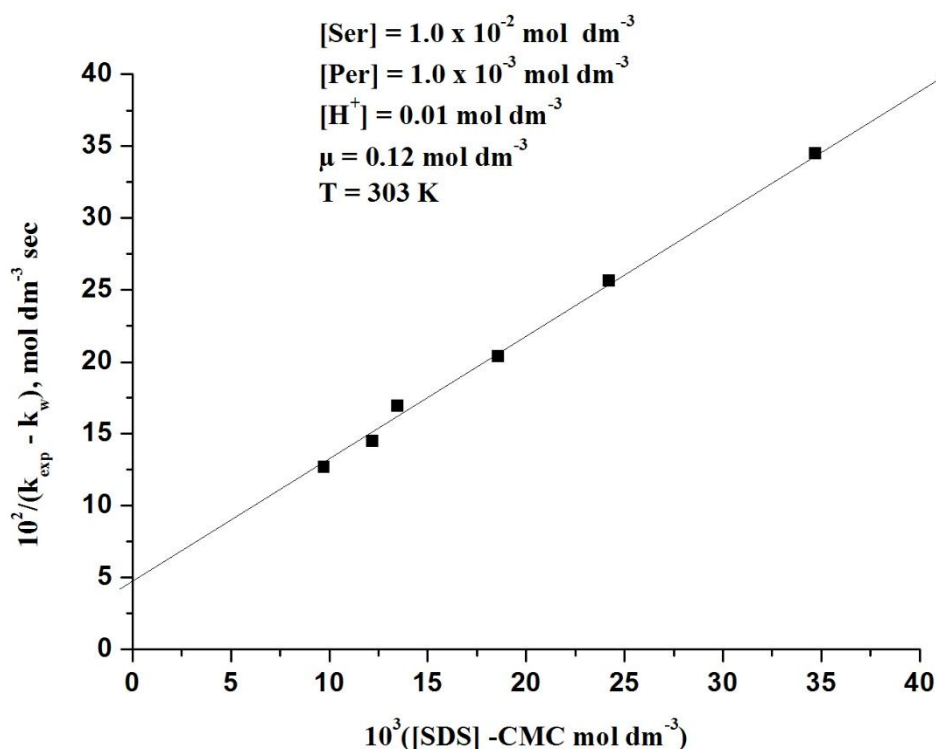
Fig. 6: Plot of $1/k_{exp} – k_w$ versus $1/[SDS]$-CMC

From the ratio of intercept to slope of Fig. 6 the binding constant, K_m was found to be 53.2 mol^{-1} dm^3 which is in reasonable agreement with the value obtained by spectrophotometric method (K_s = 62.8 mol^{-1} dm^3) at 303 K (Fig. 4).

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