Catalytic effect of sodium dodecyl sulfate on the oxidation of propanal by potassium permanganate in acidic medium

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The effect of anionic micelles of sodium dodecyl sulfate (SDS) on the oxidation of propanal by potassium permanganate in acidic medium was spectrophotometrically investigated. The oxidation reaction showed first order to each [$KMnO_4$], [propanal] and fractional order to [H^+]. The surfactant micelles catalyzed the reaction. The catalysis increased with increase in [SDS] and reached a maximum. Activation parameters were obtained from Eyring's equation as 20.41 kJ mol^{-1}, -0.23 kJ K^{-1} mol^{-1} and 88.95 kJ mol^{-1} for $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$, respectively. Quantitative kinetic analysis of kψ –[SDS] data was performed based on the pseudo-phase model by Menger-Portnoy and the Piszkiewicz cooperativity model.

Keywords: Propanal, activation parameters, sodium dodecyl sulfate (SDS), thermodynamics.

INTRODUCTION

The effect of surfactant micelles on chemical reactions has received great attention over the years. The use of cationic, anionic, neutral and zwitterionic micelles [1-10] has been reported. The chemistry of the micellar effect has been explained *via* electrostatic and hydrophobic interactions between the micelles and the substrates. Several models like the Menger-Portnoy pseudo-phase model, Piszkiewicz cooperativity model and Raghvan-Srinivasan model have been used to explain the mechanism of influence of surfactants on chemical reactions. Interaction of surfactant molecules with substrates can either catalyze or inhibit a chemical reaction. The oxidation of propanal is a very important reaction which has not been reported in the micellar system using $KMnO_4$ as oxidant. Therefore, this paper seeks to investigate the influence of SDS on the oxidation of propanal by potassium permanganate in acidic medium. Studies of the micellar effect on the oxidation of aldehydes using various oxidants like Cr (VI), N-bromophthalimide, and bromate [11-14] have been reported with the exception of $KMnO_4$. Potassium permanganate is a versatile oxidant used in various organic and inorganic redox reactions, which prompted the need to investigate its oxidation effect on propanal in the micellar system.

EXPERIMENTAL

Materials

Propanal (Merck, India), SDS (Fluka, Switzerland), H_2SO_4 (Merck, India), KNO_3, $KMnO_4$ (BDH) were of Analar grade and used without further purification. All solutions were prepared in mole litre^{-1} using doubly distilled CO_2-free water. The results were obtained in duplicate.

Kinetic runs

Requisite volumes of SDS, KNO_3, H^+, propanal and distilled water except $KMnO_4$ were placed in the reaction vessel fitted with a double-wall spiral condenser to check evaporation in a water bath thermostat. Furthermore, at constant temperature of the mixture in the reaction vessel, $KMnO_4$ solution thermostated at the same temperature was transferred to the mixture in the reaction vessel. For the purpose of this study, aliquots of the reaction mixtures were withdrawn at definite time intervals, quenched in ice bath and absorbance was taken. The progress of the reaction was monitored by measuring the decrease in absorbance of the reaction mixture at 525 nm using a double-beam Unicam-1800 Schimadzu spectrophotometer equipped with a thermo-regulated cell compartment. The pseudo-first order rate constants k$_\psi$ (s^{-1}) were calculated from the slope of the plot of log absorbance *versus* time.

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RESULTS AND DISCUSSION

The observed pseudo first-order rate constants (k_ψ) at various initial concentrations of the reactants are shown in Table 1. The log k_ψ *versus* log [X] where X = KMnO$_4$, propanal and H$^+$ showed first-order dependence to each [KMnO$_4$] and [propanal] and fractional order to [H$^+$] with no effect on the ionic strength of the mixture suggesting the presence of a neutral molecule in the rate-determining step.

Table 1. Effect of [Reactants]

10^5[KMnO$_4$] (mol dm^{-3})	10^3[Propanal] (mol dm^{-3})	10^3[H$^+$] (mol dm^{-3})	$10^2 k_\psi$/s^{-1}
1.00	3.00	1.00	0.15
2.00	3.00	1.00	0.54
3.00	3.00	1.00	0.79
4.00	3.00	1.00	1.00
5.00	3.00	1.00	1.29
6.00	3.00	1.00	1.46
7.00	3.00	1.00	1.67
3.00	1.00	1.00	0.08
3.00	2.00	1.00	0.19
3.00	3.00	1.00	0.25
3.00	4.00	1.00	0.35
3.00	5.00	1.00	0.45
3.00	6.00	1.00	0.53
3.00	7.00	1.00	0.61
3.00	3.00	1.00	0.25
3.00	3.00	2.00	0.33
3.00	3.00	3.00	0.43
3.00	3.00	4.00	0.52
3.00	3.00	5.00	0.58
3.00	3.00	6.00	0.68
3.00	3.00	7.00	0.75

At fixed ionic strength μ= 0.05 mol dm^{-3} maintained by KNO$_3$, [SDS] 3 ×10^{-2} mol dm^{-3} at 298K

Activation parameters obtained from the temperature-dependent study using equations (1) and (2) are shown in Table 2.

$$In\left(\frac{k}{T}\right) = \frac{-\Delta H^\#}{RT} + In\left(\frac{K^/}{h}\right) + \left(\frac{\Delta S^\#}{R}\right) \qquad (1)$$

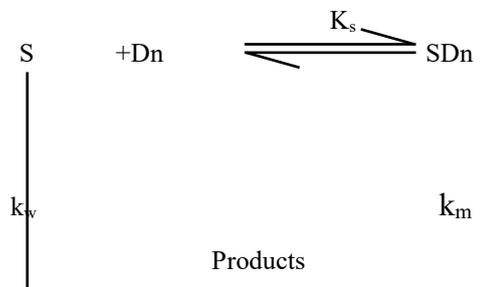where $In\left(\frac{K^/}{h}\right) = 23.76$

$$\Delta G^\# = \Delta H^\# - T\Delta S^\# \qquad (2)$$

k = rate constant; T= temperature; $\Delta H^\#$ = enthalpy of activation; $\Delta S^\#$ = entropy of activation; $\Delta G^\#$ = free Gibbs energy of activation; R = molar gas constant; k$^/$ = Boltzmann's constant; h= Plank's constant.

Table 2. Activation parameters

Substrate	$\Delta H^\#$/kJ mol^{-1}	-$\Delta S^\#$/kJ K^{-1} mol^{-1}	$\Delta G^\#$/kJ mol^{-1}
Propanal	20.41	0.23	88.95

[KMnO$_4$] = 3 × 10^{-5} mol dm^{-3}, [propanal] = 3 × 10^{-3} mol/dm^{-3}, [H$^+$] = 1 × 10^{-3} mol dm^{-3}, μ = 0.05.

Scheme 1. Menger-Portnoy model (D$_n$= micellar SDS surfactant; S = free substrate; SD$_n$= associated substrate)
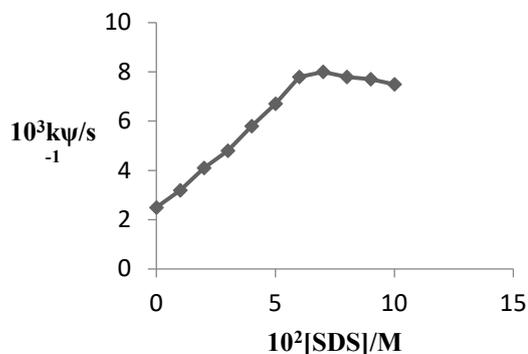

Fig. 1. Plot of k_ψ *versus* [SDS] Menger-Portnoy model.

A pseudo-phase kinetic model proposed by Menger and Portnoy was used to interpret the catalytic activity of sodium dodecyl sulfate and to evaluate the binding constant between the substrate and the surfactant.

$$k_\psi = \frac{(k_w + k_m K_s[D_n])}{(1 + K_s[D_n])} \qquad (3)$$

The critical micelle concentration (CMC) of SDS in the reaction mixture is 8.20×10^{-3} mol dm^{-3} [15, 16]. k_w is the pseudo-first order rate constant in aqueous phase; k_m is the pseudo-first order rate constant in micellar phase; Ks is the binding constant of the substrate with the surfactant; [D$_n$] is the concentration of the micelle surfactant; [D]$_T$ is the stoichiometric concentration of the surfactant.

[D$_n$] = ([D]$_T$ – CMC)

Rearrangement of equation (3) gives:

$$\frac{1}{(k_\psi - k_w)} = \frac{1}{(k_m - k_w)} + \frac{1}{(k_m - k_w)K_s[D_n]} \qquad (4)$$

Fig. 2 shows the validity of Menger-Portnoy pseudo-phase model. The obtained value of k_m was $7.45 \times 10^{-3}\,\text{s}^{-1}$.
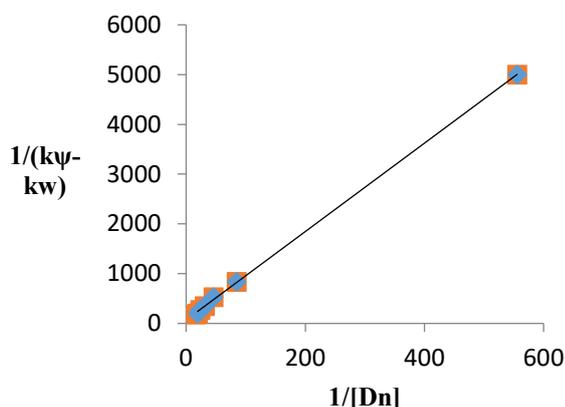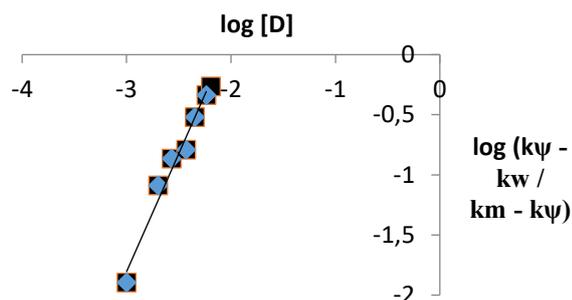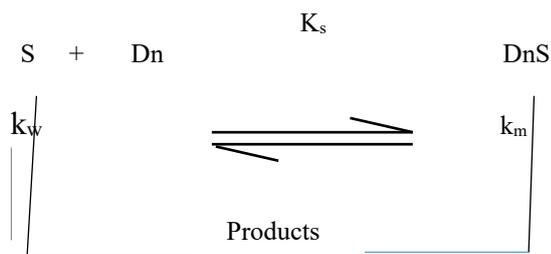

Fig. 2. Validity of Menger-Portnoy model

Fig. 3. Plot of $log\frac{(k_\psi - k_w)}{(k_m - k_\psi)}$ *versus* log[D]

Piszkiewicz cooperativity model

Piszkiewicz cooperativity model which is analogous to Hill model applied to enzyme-catalyzed reactions helps to explain the reactions in micellar systems. It gives a more accurate dependence of the observed rate constants on surfactant concentrations at low concentrations as shown in Scheme 2.

Scheme 2. Piszkiewicz cooperativity model

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Piszkiewicz cooperative model shows that:

$$k_\psi = k_m[D]^n + \frac{K_D k_w}{K_D + [D]^n} \qquad (5)$$

Re-arranging Equation 5:

$$log\frac{(k_\psi - k_w)}{(k_m - k_\psi)} = nlog[D] - logK_D \qquad (6)$$

K_D is the dissociation constant of micellized substrate back to its free components; K is the association constant of the micelle-substrate complex.

Applying Equation 6 and using the earlier obtained value of k_m from Menger-Portnoy model, the plot of $log\frac{(k_\psi - k_w)}{(k_m - k_\psi)}$ *versus* log[D] was linear for this reaction.

Sodium dodecyl sulfate (SDS) micelles catalyzed the oxidation reaction, the plot of kψ *vs* [SDS] shows a rate maximum at [SDS] 7×10^{-2} mol dm^{-3}, increase in [SDS] > 7×10^{-2} mol dm^{-3} led to a decrease in the reaction rate as shown in Fig. 1. The kψ *vs* [SDS] profile can be explained using the pseudo-phase model proposed by Menger and Portnoy. The overall increment of rate constant at low [SDS] can be attributed to the fact that the reactants get associated /incorporated at the stern layer of the micellar phase. Consequently, the decrease in kψ beyond [SDS] greater than 7×10^{-2} mol dm^{-3} can be explained as follows: At higher [SDS] all the substrate has been incorporated into the micellar phase. When bulk of the substrate is incorporated into the micelle, addition of more SDS generates more SDS and more Na$^+$ counter-ions in the Guoy-Chapman layer of the micelles. The overall increase in the positive charge in the Guoy-Chapman layer of the micelles results in the repulsion of the positively charged substrates and thereby inhibiting the partitioning of the substrate into the stern layer of the micelle. The dissociation constant of the micellized surfactant back to its component (K_D) and the index of cooperativity (n) were obtained by the Piszkiewicz model. The value of Ks was 7.09, n was 2 which is greater than unity and suggests positive cooperativity. This means that the binding of the first molecule of a substrate allows subsequent molecules to bind easily [17]. The value of n is far less than the number of surfactant molecules in the micelle, hence the existence of premicellar aggregates cannot be ignored. K_D was obtained to be 9.68×10^{-5}.

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