

Effect of Anionic Micelles of Sodium lauryl sulphate on the reaction of Hydroxide Ion with Mono-4-chloro-3-methyl phenyl phosphate ester

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Abstract: The micellar catalysed reaction with hydroxide ion and mono phosphate ester Of 4-chloro-3-methyl phenyl (4-CMPP) has been examined in buffered solution medium (at pH 8.0-10.0) with borate ions. First order rate constant for the reaction of OH⁻ ion with 4-CMPP through maxima inhibited the concentration of sodium lauryl sulphate (Nals), micelles of Nals are least reactive. Anionic micelles of [Nals] have little effect on the reaction rates probably because anionic micelles strongly inhibit the nucleophilic effect.

Key words: Micelles, Micellar catalysis, Mono-4-CMPP, Nals.

Introduction

The self diffusion of micelles of sodium lauryl sulphate¹ (Nals) in water and in dilute aqueous sodium chloride solutions using the porous disc method which was developed to permit accurate self diffusion measurements and has been recently described² micelles were tagged³ with orange OT(1-0-Tolyl-azo- β -naphthol). The principle of the method is to measure the rate of diffusion of the tracer in solutions of Nals and sodium chloride which are uniform in concentration and immobilized by sintered glass throughout and diffusion column. As reported elsewhere, the same Nals has been used to determine the molecular weight of micelles of Nals by light scattering⁴ the critical micelles concentration (CMC) by several methods⁵ and electrophoretic mobility of micelles⁶.

Material & Methods

Mono ester of 4-chloro-3-methylphenyl has been, prepared by treating excess of phosphorylating agent (phosphorus oxy tri chloride POCl_3) with 4-chloro-3-methyl phenol in dry benzene. Pure 4-chloro-3-methyl phenol (14.25 gm) was dissolved in dry benzene (100ml) in a round bottom flask. Phosphorus oxy tri chloride (9.03 ml) was added drop by drop with constant stirring to the ice cooled phenol in about half an hour with the help of separating funnel. After addition of POCl_3 , mixture was refluxed for about 18 hours on the sexheat heater at constant temperature 65 °C In order to ensure complete reaction and then distilled at reduced pressure. The first reaction of benzene and un reacted POCl_3 , was removed by distillation at b_p 120 °C. The second reaction of a pungent smelling liquid which was supposed to be 4-chloro-3-methyl phenyl phosphate dichloride was distilled at b_p 120-140 °C. It was dissolved in ice cooled water (100ml) and kept at low temperature over to night .The 4-chloro-3-methyl phenyl phosphate di chloridate converted in to 4-chloro-3-methyl phenyl phosphate di hydrogen was extracted with solvent ether. After removing the solvent ether a light brown coloured crystalline solid was obtained which, on recrystallisation with absolute ethyl alcohol gave a white crystalline solid and it was identified to be as mono 4-chloro -3-methyl phenyl phosphate.

Cityltrimethyl ammonium bromide was purified by given method 4-chloro-3-methyl phenyl phosphate were washed with anhydrous ether acetone until no amine is detected in the eluent recrystallised from methanol

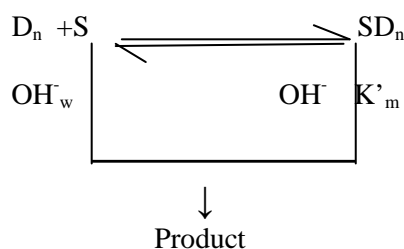
and then at least 4 times from methanol with addition of anhydrous ether. Amidol (1.4gm) was taken in conical flask covered with carbon paper, activated charcoal (2gm) and water (10ml) were added in to the conical flask and then it was shaken thoroughly for 15-20 min. The colourless, amidol solution so obtained was filtered in to a solution containing 100ml solution of sodium metabisulphate (20%). The reagent was obtained kept in dark at low temperature (0°C). This solution gradually decomposed and turned yellow after 6-8 days, than it was of no use and hence, discarded each time amidol was purified before use.

Substrate is solution the specific property of absorbing light of wave length characteristic of the particular substance. The basic principle of absorption is utilized in the measurement of various concentrations. The spectrophotometer instrument utilize a source of radiant energy, a means to isolate a band of radiant energy which is focused to on the solution and then measured with a detector. Kinetic study for the hydrolysis of all the mono-,di-,and tri ester was followed spectrophotometrically. This method involved the quantitative estimation of inorganic phosphates formed from the hydrolysis of phosphate esters. The inorganic phosphate react with the ammonium molybdate and forms a phosphate molybdate complex $(\text{NH}_4)_3\text{Po}_4 \cdot 12\text{MoO}_3$, which is reduced to molybdenum blue, a soluble complex by addition of mixture of 2, 4-diamino phenyl hydrochloride (amidol, diamol or nerol). Phosphate mono esters were prepared by standard methods purified and recrystallisation from absolute ethyl alcohol and examined by IR, Nals used analytical grade, and strength of borate buffer were prepared and purified by standard methods.

Result & Discussion

Micellar catalysed hydrolysis of mono-4-CMPP with different concentration oh $[\text{OH}^-]$ in borate buffer in presence of anionic detergent [Nals] have been investigated at $40 \pm 0.5^\circ\text{C}$. There is insignificant contribution towards the enhancement its reaction of rates at PH 9.0 to 10.0 where the di anions of 4CMPP only reactive species at these higher pH values. Pseudo first order rate coefficients have been determined at three different concentrations of $[\text{OH}^-]$ in borate buffer at pH 9.0 to 10.0 in presence of [Nals] micelles Table (1) summarises the rate coefficient and relation of rate constants with anionic detergent concentration has been shown in fig.(1) . Anionic micelles of [Nals] have little effect on the reaction rates probably because anionic micelles strongly inhibit the nucleophilic attack of $[\text{OH}^-]$ ion on the phosphorous atom of di anion of mono-4-CMPP must overcome the columbic repulsion between di an ions and counter ion in the stern layer of the micelles. Micellar effect at very low concentration of detergent [Nals] the di-anions of mono-4-CMPP are more reactive and there is an insignificant inhibition the reaction rates which fig.(1) Where the values of K_ψ is extra plotted against anionic detergent Nals at constant $[\text{OH}^-]$ ions.

We assume that nucleophile $[\text{OH}^-]$ ion reacts with the di anions of mono-4-CMPP in both aqueous and micellar phase, following usual approximations of scheme -1.



We make use of the equation (3) of section (1) part 'A' which suggest that the ploat of $1/K_\psi - K'_w$ against $1/(C_D - \text{cmc})$ should be linear equation (3)

$$1/K_\psi - K'_w = 1/K_m - K'_w + 1/K'_m - K'_w \{N/K_s(C_D - \text{cmc})\} \dots(1)$$

The results of micellar catalysis for [Nals] appear not to fit it in eq. (1) because there is inhibition below the CMC, as measured by conventional methods. Di anions of mono-4-CMPP are taken up strongly by micelles or sub micellar aggregates that the reaction could not be studied at detergent concentrations much above the CMC because it is too slow. Whereas with other substrates which are less soluble in aqueous detergent, it is possible to work at higher detergent concentrations, where approximations made in deriving eq. (1) are relatively unimportant. $K'_m = 0$ for the reaction on hydroxide ion with mono-4CMPP in micelles of [Nals]. This assumption is correct for other anionic molecular reactions^{7,8} eq. (1) then gives eq. (2)-

$$K'_w/K_\psi - 1 = K_s/N (C_D - \text{cmc}) \dots (2)$$

and we find that plotted $K'_w/K_\psi - 1$ against C_D curve upward sharply as the detergent concentration increases and is approximately linear. Figure (2) is shows relationship and Table (2) summarises the variation in inhibited rates of reaction by changing detergent concentrations. The slop of this curve is gives $K_s/N = 0.21739 \times 10^{-3} \text{ moldm}^{-3}$ for NaOH in addition, the assumption, $K'_m = 0$ may be correct and the consequent error would be most important at higher detergent concentrations. Therefore, it is better to use equation (1) provided that $C_D \gg \text{cmc}$, so that uncertain in the values of cmc can be ignored.

Because of the powerful inhibition by [Nals], the values of K_ψ are very small at higher concentration therefore determination of binding constant aggregation number, ion exchange model, effect of substrate concentration, effect of electrolyte and temperature etc. could not be studied. Consequently, we carried out detailed studies of micellar catalysis of CTABr detergent.

Table-1: Pseudo First Order Rate Constants for reaction of $[20.8 \times 10^{-3}] \text{ moldm}^{-3}$ NaOH with Mono-4-chloro-3-methyl phenyl phosphate in $[5 \times 10^{-2}] \text{ moldm}^{-3}$ Borate Buffer Solution In Presence Of [NaLS] AT pH 9.0 and temp. $40 \pm 0.50^\circ\text{C}$.

S.N.	$10^3[\text{NaLS}] \text{ moldm}^{-3}$	$10^5 K_\psi \text{ s}^{-1}$
1	0.2	22.67
2	0.4	10.01
3	0.6	6.41
4	0.8	3.20
5	1.0	2.60
6	1.2	2.03
7	1.4	2.00
8	1.6	1.98
9	1.8	1.94

Table-2: Relation Between Reaction Rate And Micellar concentration in Borate Buffer For [NaLS] with $[5 \times 10^{-3}] \text{ moldm}^{-3}$ Mono-4-chloro-3-methyl phenyl phosphate at Ph -9.0 AND $40 \pm 0.5^\circ\text{C}$.

S.N.	$10^3[\text{NaLS}]$	$10^5 K_\psi \text{ s}^{-1}$	$K'_w/K_\psi - 1$
1	0.2	22.67	-
2	0.4	10.01	-
3	0.6	6.41	-
4	0.8	3.20	0.76
5	1.0	2.60	1.16
6	1.2	2.03	1.77
7	1.4	2.00	1.81
8	1.6	1.98	2.51

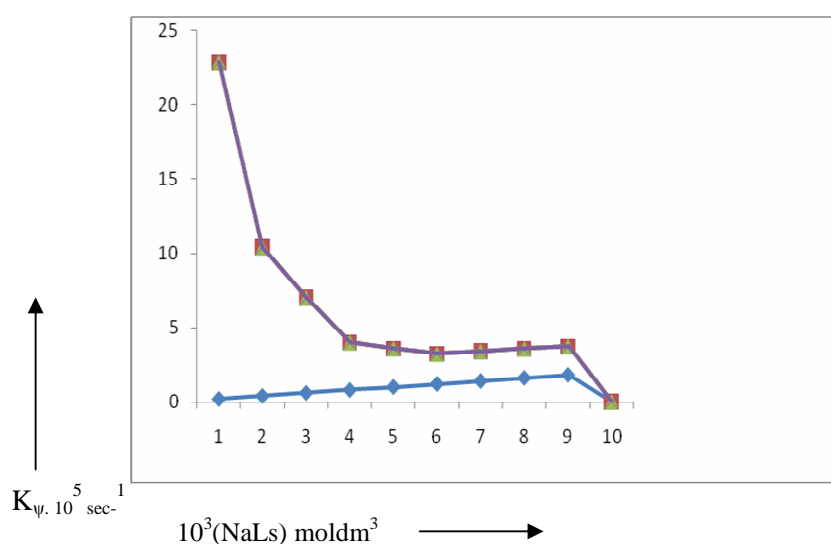


Fig. (1)

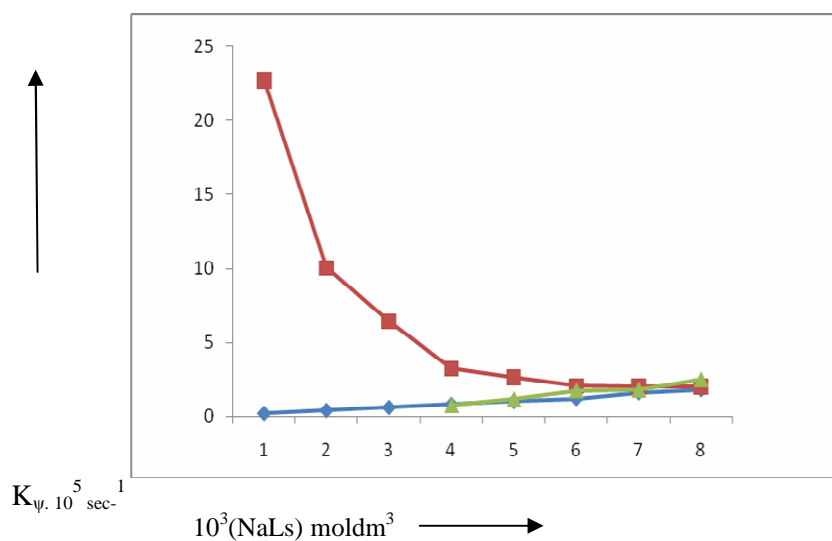


Fig. (2)

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