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Micellar effect of anionic of sodium lauryl sulphate on hydroxide ion with mono-2-methoxy phenyl phosphoramide ester

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Abstract

Micellar catalysed reaction with hydroxide ion and mono phosphoramide ester of 2-methoxy phenyl phosphoramide (2-MPPA) sodium buffered solution at pH 8.0-10.0 with borate ions. The first order rate constant for the reaction of hydroxide (OH^-) ion with 2-MPPA through maximum inhibited the concentration of Sodium Lauryl Sulphate (NALS). Micelles 0f NALS are least and anionic micelles of (NALS) have little effect on the reaction rates probably because anionic micelles strongly inhibit the nucleophilic effect.

Keywords: micelles, micellar catalysis, mono-2-MPPA, NALS

Introduction

Self-diffusion of micelles of Sodium Lauryl Sulphate (NALS) in water and aquous sodium chloride solutions using the Porous Disc Method [1] which was developed to permit accurate self-diffusion measurements and micelles were tagged [2] with orange OT (1-0-Tolyl-azo-β-napthol). Principle of this method is to measure the rate of diffusion of tracer in NALS and sodium chloride solutions, which are uniform in concentration and immobilized by sintered glass throughout and diffusion column. The NALS has been used to determine the molecular weight of micelles of NALS by light scattering [3], the critical micelles concentrations (CMC) by several methods [4] and electrophoretic mobility of micelles have been reported [5].

Materials and Methods

The mono ester of 2-methoxy phenyl phosphoramide has been prepared by treating phosphorylating agent, phosphorus oxy tri chloride ($POCl_3$) with 2-methoxy phenol in dry benzene. Pure 2-methoxy phenol (16.25gm) was dissolved in dry benzene (100ml) in a round bottom flask. Phosphorus oxy tri chloride (10ml) was added drop wise with constant mechanical stirring to ice cooled phenol in one hour with the help of separating funnel. After addition of $POCl_3$, then the mixture was refluxed for 16 hrs. at constant temperature 60^0C to ensure complete reaction and distilled at reduced pressure. The first reaction of benzene and unreacted $POCl_3$ was removed by distillation at B.P. 120^0C. The second reaction of a pungent smelling liquid which was supposed to be 2-methoxy phenyl phosphoramide dichloride was distilled at B.P. $130\text{-}140^0$C. it was dissolved in ice cooled water (100ml) and kept overnight at low temperature. The 2-methoxy phenyl phosphoramide converted into 2-methoxy phenyl phosphoramide was extracted with solvent ether. After removing the solvent ether a light brown coloured crystalline solid was obtained after recrystallization with absolute ethyl alcohol gave a white crystalline solid and it was identified as mono-2-methoxy phenyl phosphoramide.

The basic principle of absorption is utilized in the measurement of various concentrations. The spectrophotometer was utilized a source of radiant energy to isolate a band of radiant energy which was focused to on the solution then measured with a detector. Kinetic study for the hydrolysis of all the di ester was followed by Spectrov photo metrically. This method was involved the quantitative estimation of inorganic phosphoramides formed from the hydrolysis of phosphoramide esters. The inorganic phosphoramide react with the ammonium molybdate and forms a phosphoramide molybdate complex, which is reduced to molybdenum blue. The phosphoramide mono esters were prepared by standard methods purified and recrystallisation from absolute alcohol and examined by IR. The NALS was used analytical grade and strength of borate were prepared and purified by standard method [6].

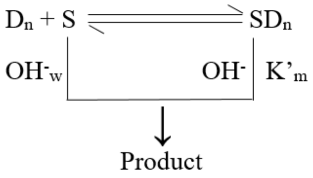
Results and Discussion

The micellar catalysed hydrolysis of mono-2-MPPA with different concentration of hydroxide (OH^-) ion in borate buffer in presence of anionic detergent (NALS) have been investigated at 40 ±0.5^0C. There is an insignificant contribution towards the enhancement of reaction rates at pH 9-10, where the di –mono- anion of 2-MPPA only reactive species at these pH values. The pseudo first order rate coefficient[7] have been determined at three different concentrations of hydroxide (OH^-) ion in borate buffer at pH 9.0-10 in presence of (NALS) micelles. The rate of coefficient and relation of rate constants with anionic detergent concentration have been given in Table-1.

Table 1: Pseudo first order rate constant for reaction of (20.8×10^{-3}) mol dm^{-3} NaOH with mono-2-methoxy phenyl phosphoramide in (5×10^{-3}) mol dm^{-3} borate buffer solution in presence of (NaLS) at pH 9.0 and temp. 40 ± 0.5^{0}C.

S. No.	**10^{3} (NaLS) mol dm^{-3}**	**10^{-5} $K_{\Psi}S^{-1}$**
1.	0.2	22.72
2.	0.4	10.06
3.	0.6	6.58
4.	0.8	3.34
5.	1.0	2.86
6.	1.2	2.24
7.	1.4	2.12
8.	1.6	1.96
9.	1.8	1.84
10.	2.0	1.68

Anionic micelles of Sodium Lauryl Sulphate have little effect on the reaction rates probably because anionic micelles strongly inhibit the nucleophilic attack of hydroxide ion on the phosphorus atom of di anion of the mono-2-MPPA must overcome the columbic repulsion between di anions and concentration in the stem layer of the micelles. Micellar effect at very low concentration of detergent, the di anions of mono -2- MPPA are more reactive and there is an insignificant inhibition the reaction rates. We assume that nucleophile hydroxide (OH^{-}) ion reacts with di anions of mono-2-MPPA in both aqueous and micellar phase, as shown in following equation.



We make the use of above equation which suggest that the $1/K_{\Psi} - K`_{w}$ against $1/(C_{D}- cmc)$ should be linear equation.

$$1/K_{\Psi} - K`_{w} = 1/K_{m} - K`_{w} + 1/K`_{m} - K`_{w} \{N/K_{S}(C_{D}-cmc)\} \text{ --- } (1)$$

Results of micellar catalysis for Sodium Lauryl Sulphate appear was not fit in equation (1) because there is inhibition below the CMC, as measured by conventional methods. The di anions of mono-2-MPPA 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 are less soluble in aqueous detergent and is possible to work at higher detergent concentrations, where made in equation (1) are relatively unimportant. The K`m=0 for the reaction on hydroxide ion with mono-2- MPPA in micelles of (NALS) and this assumption is correct for other anionic molecular reactions[8,9,10] and equation (1) is then gives in equation (2).

$$K`_{w}/K_{\Psi} -1 = K_{S}/ N (C_{D}-cmc) \text{ --- } \qquad (2)$$

Table-2 showed the relation between reaction rate and micellar concentration were summarises the variation in inhibited rates of reaction by changing detergent concentrations. The data is gives $K_{S}/N = 0.21738\times10^{-3}$ mol dm^{-3} for sodium hydroxide solution in addition and the assumption K`w -0 may be correct and the consequent error would be most important at higher detergent concentrations. Therefore, it is better use in equation (1) provided that C_{D}>>CMC, so that uncertain in the value of CMC can be ignored.

Table 2: Relation between reaction rate and micellar concentration in borate buffer for (NALS) with (5×10^{-5}) mol dm^{-3} mono-2-methoxy phenyl phosphoramide at pH 9.0 and 40 ± 0.5^{0}C

S.No.	**10 ^{3} (NaLS)**	**10 5 $K_{\Psi}s^{-1}$**	**$K`_{w}/ K_{\Psi}$ -1**
1.	0.2	22.72	-
2.	0.4	10.06	-
3.	0.6	6.58	-
4.	0.8	3.34	0.78
5.	1.0	2.86	1.18
6.	1.2	2.24	1.72
7.	1.4	2.12	1.86
8.	1.6	1.96	2.68
9.	1.8	1.84	2.74
10.	2.0	1.68	2.92

The powerful inhibition by Sodium Lauryl Sulphate showed the values of K_{Ψ} are very small at higher concentration, therefore the 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 CTAB detergent [11].

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