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EFFECT OF NON-IONIC MICELLES OF POLY OXY ETHYLEN DODECYL ETHER ON THE REACTION OF HYDROXIDE ION WITH MONO-4-CHLORO-3-METHYL PHENYLPHOSPHATE ESTER

SINGH, A. P.
Department of Chemistry, B.S.A College, Mathura(U.P.)
Pal_abendra@rediffmail.com.

(Abstract)
The micellar catalysed reactions between hydroxide or hydroperoxide anion and mono-phosphate ester of 4-CMPP has been examined in buffered medium (at pH 8.0-10.0) with borate ions. First order rate constant (K_ψ) for the reaction of OH^- with 4-CMPP go through maxima increasing with the concentration of poly oxyethylene dodecyl ether (POEDE) micelles of POEDE are very effective catalysts to the reactions of phosphate mono ester.non-ionic detergent Poly oxy ethylene dodecyl ether have been investigated at 40±0.50C.

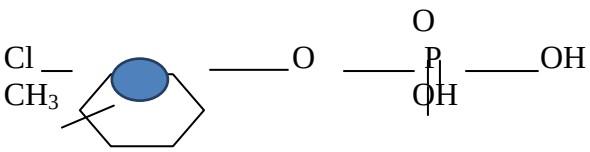
Key word: Micelles, Micellar catalysis, Mono-CMPP, PODE.

INTRODUCTION

The properties of poly oxy ethylated non-ionic surfactants in relation to their poly oxyethylene chain lengths. A large extent on the average number of oxyethylene units. The wide range of the chain lengths of poly oxyethylene in order better to understand the effect of chain lengths properties relationship [1,2] between poly oxy ethylene dodecyl ether. The purification of the Peg sample was carried out by the extraction method by counter current prtition[3] and liquid chromatography a mixture of n-butanol, acetone, water (4:1:5)[4] volume.

EXPERIMENTAL

Preparation Monoester of 4-chloro-3-methylphenyl phosphate the residue left after removing mono- 4-chloro -3- methyl phenyl phosphate at b_p 120-140 ^{0} C was washed several times with boiling distilled water and 0.2 NaOH solution to remove 4-chloro- 3-methyl phenyl phosphate monoester, unreacted phosphorus oxy tri-chloride and the phenol and finally digested in hot water 0.5 NaOH solution. It was filtered and the filtrate acidified with dilute HCl using phenolphthalein as an indicator. A white precipitate obtained was separated by filtration and made free from hydroxyl ions with repeated washings with boiling water. It was than dried at room temperature and recrystallised with absolute ethyl alcohol gave a white crystalline solid and it was identified to be Mono-4-chloro -3-methyl phenyl phosphate ester as under.



MONO-4-CHLORO-3-METHYL PHENYL PHOSPHATE ESTER

Cetyltrimethyl 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. Thecolourless amidolsolution so obtained was filtered in to a solution containing 100ml solution of sodium meta bisulphate (20%). The reagent obtained waskept in a dark at low temperature (0^0 C). This solution gradually decomposed and turned yellow after 6-8 days,then it was of no use and hence,discarded. Each time amidol was purified beforeuse.

Method: substrate in solution have 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 radiantenergy, 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 reacts with the ammonium molybdate and forms a phosphate molybdate complex $(NH_4)_3Po_4.12MoO_3$,which is reduced to molybdenumblue, a soluble complex by addition of mixture of 2,4-diamino phenyl hydrochloride (amidol,diamol or nerol)

Material: Phosphate mono esters were prepared by standard methods,purified by re crystallisation from absolute ethyl alcohol and examined by IR, POEDE used analytical grade, strength of borate buffer was prepared and purified by standard methods [5]

Kinetics: All kinetic runs were performed using doubly or triply distilled water. All reactions were carried out at 40 ± 0.5^0C and pH 9.0, reaction s was followed by spectrophotometer at the absorbance 662 nm. To obtain first order rate (K_ψ)

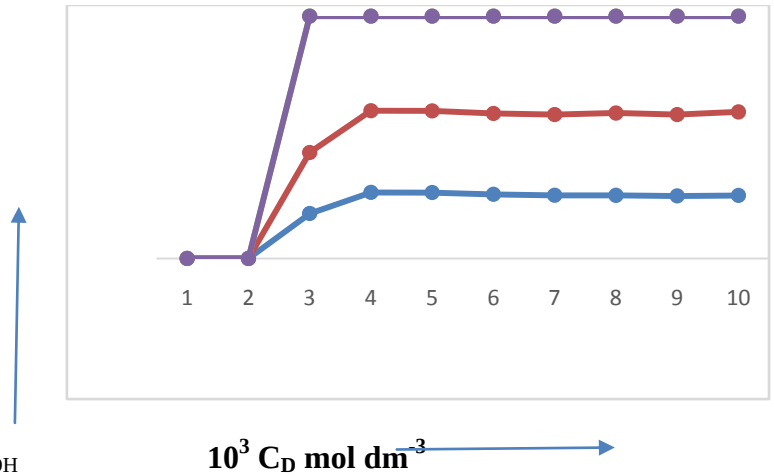
RESULT & DISCUSSION.

FFFECT OF ANIONIC MICELLES OF [POEDE] ON THE REACTION OF HYDROXIDE ION WITH MONO-4-CHLRO-3-METHYLPHENYLPHOSPHATE

Micellar catalysed hydrolysis of mono-4-CMPP with different concentration of [OH^-] in borate buffer in presence of Poly oxy ethylene dodecyl ether [POEDE] [6,7]detergent have been investigated at 40 ± 0.5^0C. There is insignificant contribution towards the enhancement of reaction rate at pH 9.0 to 10.0 where the di-anions of 4-CMPP only reactive species at these higher Ph values, pseudo first order rate coefficients have been determined at three different concentrations of [OH-] in borate buffer at pH 9.0 to 10.0 in presence of [POEDE] micelles Table(1) summaries rate coefficients and relation of rate constants with anionic detergent concentration has been shown in fig.(1) Non-ionic micelles of [POEDE] have little effect on the reaction rates probably because anionic micelles strongly inhibit the nucleophilic attack of [OH-] ion on the phosphorus atom of dianion of 4-CMPP because of hydrophobic interactions of dianions of 4-CMPP must overcome the coulombic repulsion between dianions and counterions in the stern layer of the micelles. Micellar effect at very low concentration of detergent [POEDE] the dianions of 4-CMPP are more reactive and there is a insignificant inhibition in the reaction rates which fig. Where, values of K_ψ extra ploated against the anionic detergent PODE, at constant [OH^-] ions.

Table (1)PSEUDO FIRST ORDER RATE CONSTANTS FOR REACTION OF 4.0, [20.8X10^{-3}],43.8 mol.dm^{-3} NaOH WITH MONO-4-CHLORO-3-METHYLPHENYL PHOSPHATE IN [5X10^{-2}] mol.dm^{-3} BORATE BUFFER SOLUTION IN PRESENCE OF POEDE AT pH. (8.0-10.0)AND TEMP. 40±0.5^{0}C.

[OH]$^{-}$	PH	10^5K'w	$10^5K_{\psi s}^{-1}$ in presence of POEDE							
			0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
4.0	8.0	4.17	8.59	8.23	7.79	7.34	6.86	6.58	5.95	5.58
20.8	9.0	5.67	10.62	10.18	9.83	9.36	8.95	8.56	7.87	7.23
43.8	10.0	12.67	12.31	11.83	11.83	11.43	10.54	10.37	9.04	9.51



$-K_{\psi}10^5$ sec^{-1}/m$^{s}_{OH}$ **10^3 C_D mol dm^{-3}**

Fig. (1) **MONO-4-CHLORO-3-METHYLPHENYL PHOSPHATE IN [5X10^{-2}] mol.dm^{-3} BORATE BUFFER SOLUTION IN PRESENCE OF POEDE.**

CONCLUSION

The comparative study of rate constants for the reaction of mono-4-CMPP with hydroxides ion&nonionic in presence of 10^{-3} [POEDE] detergent besides of this effect of pH and borate buffer has been examined. There is negligible effect of pH and on the rate of reaction theirs, it was postulated dianions of 4-CMPP are buried in interior of nonionic micelles, where it is difficult for the nucleophile to attack the phosphorus atom of dianion.

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