MICELLAR EFFECT UPON THE RATE OF ACIDIC HYDROLYSIS OF CARBOXYLATE ESTERS

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ABSTRACT

The acidic hydrolysis of carboxylate ester (Ethylchloro acetate) in the presence of different surfactants has been studied. The rate of hydrolysis of this ester was determined under pseudo first order condition in which the concentration of HCl was kept in large excess over the [ester]. The cationic micelles of cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC) enhanced the rate of hydrolysis of esters to a maximum value and thereafter, the increasing concentration of surfactant decreased the reaction rate. The anionic micelles of sodium dodecyl sulfate (SDS) and (LDS) inhibited the rate of the hydrolysis. The reaction proceeds through the attack of H^+ ions on the carbonyl carbon forming tetrahedral intermediate. The tetrahedral intermediate is unstable and collapses immediately to yield respective acid and alcohol. The micelles influence the stability of tetrahedral intermediate, in turn, altering the rate of hydrolysis. The nonionic micelles of TritonX-100 and Brij-35 relatively small retard the rate of acid catalysed hydrolysis of Ethylchloroacetate. The variation in the rate of hydrolysis by micelles was treated by considering the pseudophase ion-exchange model.

Keywords: Ethylchloro acetate, Cationic micelles, Anionic micelles, Acidic hydrolysis, Micellar catalysis

I. INTRODUCTION

The kinetics provides the useful information about the Mechanism and rate of chemical reaction, which helps to run a chemical reaction successfully by a way of selecting optimum condition to get maximum yield. Ethyl chloroacetate use in organic synthesis, vat dyestuff, and military purposes .Halo derivative esters are most toxic in nature .Due to their toxicity there are immediate needs for innovative analytical and environmental friendly methods to decompose the toxic esters. Hydrolysis and oxidation are the most preferred reactions to detoxify them. The facile hydrolysis of this haloalkyl ester is found everywhere and has attracted a great consideration due to their great values in various chemical and biological reactions, thus it has become the subject of intense research to the chemist and biologists.

The hydrolysis of carboxylic acid esters involves bimolecular Electrophilic attack analogous to the SN2 mechanism on the saturated carbon. Ester functional groups are among the most common acid derivatives present in natural and man-made chemicals. Carboxylic acid esters are

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used industrially to make flavors, soaps, herbicides organic synthesis, vat dyestuff, and military purposes etc. The acid catalyzed or acidic hydrolysis of esters generally takes place via SN2 reaction]. The presence of water as solvent changes the rate and mechanism of hydrolysis reactions in many ways such as Electrophilic reagent, as a high dielectric-constant; and as a specific solvating agent for organic reactants and products.

Surfactants are the amphiphilic molecules consisting of the polar or charged head group and non-polar hydrocarbon chain. The surfactant molecules aggregate at concentrations above critical micellar concentrations (cmc) to form micelles. The micelles have a tendency to influence the reaction rates by enhancing it or by retarding the rates of reaction. The influence of cationic cetyltrimethylammonium bromide (CTAB), cetylpyridinium chloride (CPC) and anionic sodium dodecyl sulfonate (SDS) and (LDS) was investigated on the rate of acidic hydrolysis of elaborate the medium role on the rate of hydrolysis.

II. EXPERIMENT

Material and methods

All the solutions were prepared using triply distilled water. Ethylchloroacetate (98%, Merck, Germany), sodium dodecyl sulfate (SDS, 99%, BDH, England), Loryl lithium sulphate (LDS, 99%, BDH, England) and cetyltrimethylammoniumbromide (CTABr, 99%, BDH, England) ,cetylpyridinium chloride (CPC , 99%, BDH, England were used d as supplied. Anal R grade sodium hydroxide was used during the experimental work. Deionized double-distilled water with specific conductance; $1–2 \cdot 10\_6 \ X\_1 \ cm\_1$was used as a solvent throughout the experiment.

The progress of kinetics of hydrolysis has been studied by **Karl fisher Titrimeter** method. pseudo first order rate coefficients have been determined from the first order rate equation.

The Ethyl Chloro acetate hydrolysis reaction is reversible and the reaction equilibrium constant is relatively small. Therefore, H+ ion is employed as the catalyst in order to increase the reaction rate strong acids such as sulfuric acid and hydrochloric acid can be used to produce an H^+ion and catalyze the reaction. The reaction is Hydrolysis of Ethyl Chloro acetate in acidic solution

$$ClCH_2COOC_2H_5 + H_2O \longrightarrow C_2H_5OH + ClCH_2COOH$$

An ester is a chemical condensed compound of an oxoacid and a hydroxyl compound. In our experiment, we will take a closer look at the acid catalysed hydrolysis of the Ethyl Chloro acetate, forming chloro acetic acid and ethanol. The formal reaction equation of the H+-ion catalysed hydrolysis of the Ethyl Chloro acetate where k_1 and k_2 describe the reaction rate constants of the forward and reverse reaction, respectively.

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$$K_1$$

$$\mathbf{ClCH_2COOC_2H_5} + H2O + H^+ \rightleftharpoons \mathbf{C_2H_5OH} + \mathbf{ClCH_2COOH} + H$$

$$K_2$$
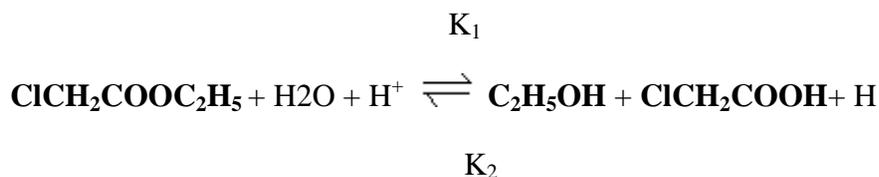
Free energy change (ΔG), enthalpy of activation (ΔH), entropy of activation (ΔS) and activation energy (Ea) were calculated from the rate data at two different temperatures using standard equations.

III. RESULT & DISCUSSION

Pseudo first order rate constant were determined in the aqueous medium, where a Hydrogen ion gave small values of rate constants without surfactant. The reactions of H^+ ions are very strongly catalysed by cationic micelles of CTAB. The rate constants have been calculated.

Kinetic measurement

(1) Determination of the rate constant

The rate equation of the ester hydrolysis may be written as:

d[EA]/ dt= k [EA][H O][H] k [S][HAc][H] --(1)

 [EA] = concentration of chloro ethyl acetate,

[HAc] = concentration of acetic acid,

[A] = concentration of alcohol.

Since the experiment is carried out in a solution of a strong acid (HCl) that serves as catalyst, the concentration of [H+] will not change during the reaction. Though the generation of chloro acetic acid from the hydrolysis goes along with a slight increase in the [H+] concentration, this effect is too little to have an effect on the reaction rate. The equation (1) can be simplified to:

d[EA]/ dt= k [EA][H O] k [HAc][A]   ----(2)

(2) Effect of surfactant

The pseudo-first order rate constants for the hydrolysis of Ethylchloroacetate in presence of different concentrations of cationic surfactants (cetyltrimethylammonium bromide CTAB), (cetylpyridinium chloride CPC) and anionic surfactants (sodium dodecyl sulfonate SDS) and lithium dodecyl sulfonate (LDS) beyond critical micelle concentration(CMC) are given in tables 1-2 respectively. It is observed that With increase in surfactant concentration the rate of acid

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hydrolysis of ester is decreased by CTAB and CPC both micelles and increased by SDS and LDS micelles. These rate acceleration or inhibition of acid hydrolysis of esters in cationic and anionic micellar solutions caused by the distribution of the substrate between micellar phase and bulk water phase as a result of electrostatic and hydrophobic interactions of the substrate with the surfactant aggregate.

The gradual decrease of the reaction rate on increase in concentration of cationic surfactant (CTAB, CPC) in ECA may be due to increase in no. of micelles and ester molecule are entrapped therefore the proton cannot approach the ester molecule to initiate the hydrolysis reaction. The acid catalyzed hydrolysis carried by protonation of an ester oxygen atom with the formation of carbonium ion intermediate which reacts with water to give chlorocarboxylic acid Pseudophase ion exchange model based on two assumptions which are:

1. Micelles act as a separate phase from water.

2. Changes in K_{obs} due to added surfactant depend largely up on the distribution of S and H^+ between micelles and bulk water.

Table 1

EFFECT OF CATIONIC & ANIONIC SURFACTANTS ON THE ACIDIC HYDROLYSIS OF ETHYLCHLOROACETATE AT 30^0C

10^3 [surfactant] M	$K_{obs} 10^3 s^{-1}$			
	CTAB	**CPC**	**SDS**	**LDS**
00	18.0	18.0	18.0	18.0
11	15.0	14.0	17.5	18.2
22	13.0	12.0	17.8	18.5
33	11.0	10.0	18.5	19.5
44	10.0	09.0	20.6	21.8
55	09.0	080	21.5	22.4
66	08.0	07.0	22.4	23.5
77	07.0	06.0	23.6	24.8
88	06.0	05.0	24.8	25.7

Table 2

EFFECT OF CATIONIC & ANIONIC SURFACTANTS ON THE ACIDIC HYDROLYSIS OF ETHYLCHLOROACETATE AT 40^0C

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10^3 [surfactant] M	K_{obs} 10^3 s^{-1}			
	CTAB	**CPC**	**SDS**	**LDS**
00	25.0	25.0	25.0	25.0
11	22.2	21.0	25.5	25.7
22	21.0	19.2	25.8	26.0
33	18.0	17.4	26.5	26.8
44	17.1	15.6	28.0	28.8
55	15.0	13.5	28.5	29.4
66	13.0	11.4	29.4	30.2
77	11.1	10.4	30.0	30.8
88	10.2	9.6	31.8	32.0

Table 3

EFFECT OF NON -IONIC SURFACTANTS ON THE ACIDIC HYDROLYSIS OF ETHYLCHLOROACETATE AT 30^0C

[surfactant] M	K_{obs} 10^3 s^{-1}	
	Triton x-100	**Brij-35**
0.35	28	26
0.45	28	26
0.55	27	25
0.65	26	24
0.75	24	24
0.85	23	22
0.95	22	21
1.05	20	19
1.15	18	17

Table 4

EFFECT OF NON-IONIC SURFACTANTS ON THE ACIDIC HYDROLYSIS OF ETHYLCHLOROACETATE AT 40^0C

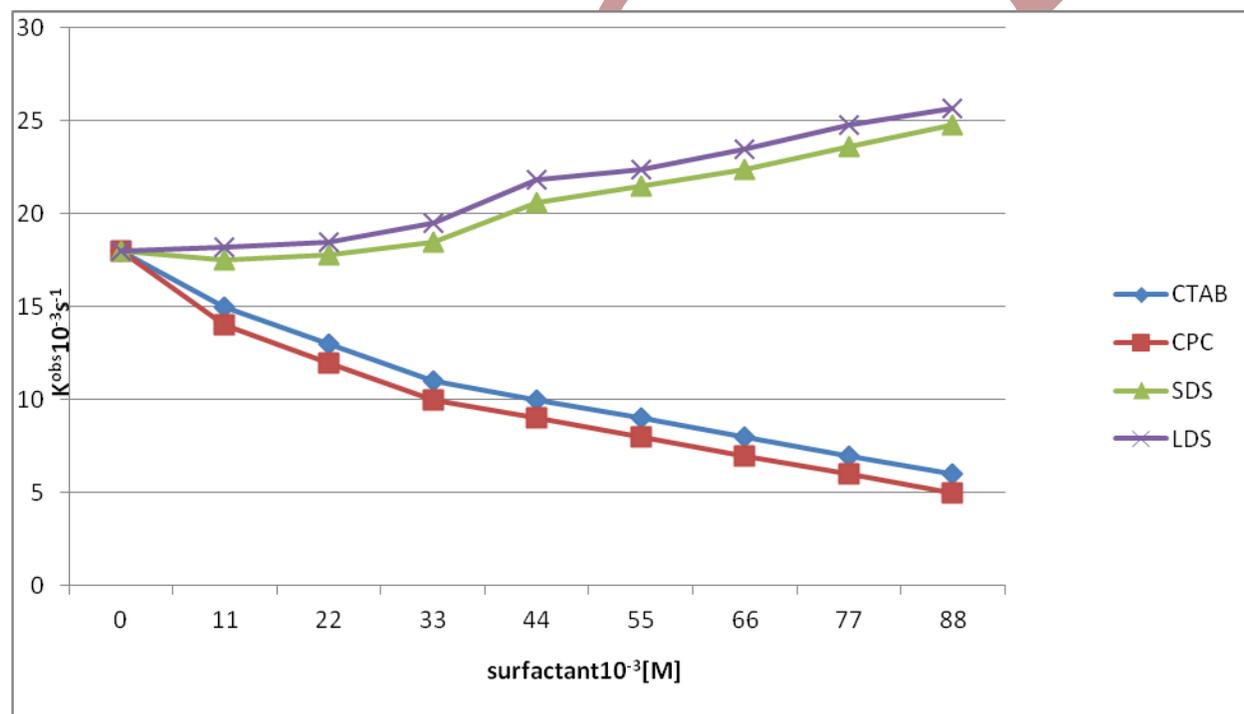| [surfactant] M	K_{obs} 10^3 s^{-1}	
	Triton X-100	**Brij-35**
0.35	35	33
0.45	34	32
0.55	34	32
0.65	33	30
0.75	32	30
0.85	30	29
0.95	29	28
1.05	28	27
1.15	28	26

Figure1-Effect of cationic & anionic surfactants on the acidic hydrolysis of Ethylchloroacetate at 30^0C
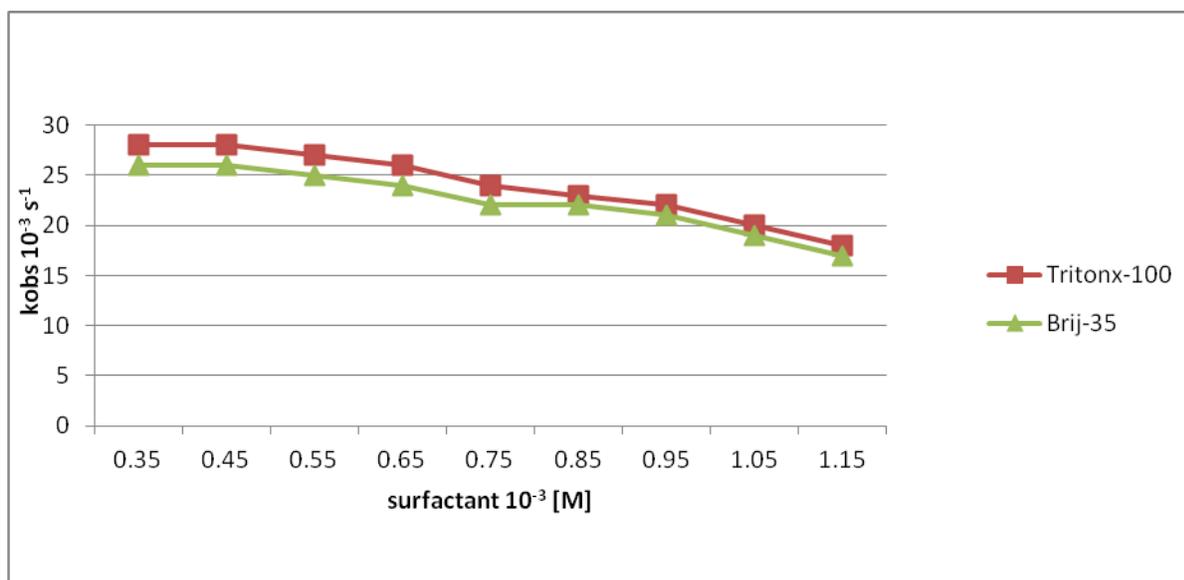
Figure2-Effect of Non-ionic surfactants on the acidic hydrolysis of Ethylchloroacetate at 30^0C

IV. CONCLUSION

Ethylchloroacetate hydrolysis is a major process in PVA and PTA plants an appropriate and simple kinetics is required that can be added to optimization software. Such a model would be based on a data bank of experimental information. The effects of different parameters such as temperature, initial molar ratio, different concentration of surfactants were studied. It is found that the increase of concentration of anionic surfactant increase the hydrolysis reaction rate whereas increase of concentration of cationic surfactant decrease the hydrolysis reaction rate. Relatively small retardation of the rate of the acid catalysed hydrolysis of Ethylchloroacetate in nonionic surfactants have been observed. Because of the importance of nonionic surfactant in industry ,as well as the fundamental aspects of understanding the kinetics ,as the electrical effect is absent from these surfactants ,it was decided to study the effect of these surfactants of the rate of hydrolysis. Nonionic surfactants decreases the rate of hydrolysis of Ethylchloroacetate. Furthermore, the temperature variation has considerable influence on the reaction rate. The study of hydrolysis reactions indicates typical in nature. Hydrolysis of haloesters in acidic medium has been studied for the first time.

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