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Effect of surfactants on the Acid catalyzed hydrolysis of aliphatic esters having variation in chain length of their alkyl part

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A B S T R A C T

The kinetics of acidic hydrolysis of simple aliphatic esters in aqueous and surfactant media has been studied. Different acetate esters having variation in numbers of carbons in alkyl part and surfactants; cationic: CTAB, anionic: SLS and non-ionic: TX-100 have been considered for the present work. The effect of temperature, concentration of surfactants and H^+ on the kinetics assists to establish to probable reaction path as well as the role of surfactants in this hydrolysis.
Keywords: Activation parameters, Micelle, CMC, Association constant, binding ability.

A R T I C L E   I N F O

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1. Introduction

The surfactants and micellar solutions have versatile uses in the field of Chemistry, Biochemistry, Medicine, Detergents, Paints, Dyestuffs, Cosmetics, Agrochemicals, Fibers, Mining, Petroleum, Foods and Plastics. In last few years, the use of surfactants for synthesis and also to control different reactions has been reported. Smith et al. [1] investigated the kinetics of alkaline hydrolysis of benzocaine in the presence of nonionic surfactant. The

effect of surfactant on the solubility and on wavelength of substrate in UV region was studied. Possidonio et al. [2] studied the pH-independent hydrolysis of bis (2, 4-dinitrophenyl) carbonate in presence of sodium lauryl sulphate (SLS), sodium dodecylbenzene sulfonate and cationic surfactants spectrophotochemically. Ghosh et al. [3] also determined the rates of acidic hydrolysis of hydroxamic acids in perfluorooctanoic acid and also with sodium 1-dodecanesulphonate and sodium dodecyl sulphate. They also noticed that pseudo-first order rate constants depend on concentration of reactive and non-reactive surfactants and explained the results based on pseudo-phase ion-exchange kinetic model. To investigate the effect of surfactant of different nature on reaction kinetics, acidic catalyzed hydrolysis of aliphatic esters having variation in chain length of their alkyl part have been studied in aqueous and different micellar media. The effect of temperature, concentration of surfactants and H^+ are examined and all the activated parameters are reported. In the present work, the micellar inhibition / catalysis and binding capability of surfactant to the ester substrate is pointed out.

2. Experimental
The aliphatic esters used are methyl, ethyl, n-propyl and n-butyl acetate procured from E.Merck (India) Ltd and Sigma Aldrich Chemical (India) and used after purification. Methyl acetate was refluxed for 6 hours with acetic anhydride, followed distillation through fractional column. The liquid passing out from fractional column at 56-57ºC is mixed with anhydrous potassium carbonate for few minutes, filtered and redistilled. The other esters were purified as per standard procedures [4]. Different surfactants e.g., cationic, CTAB (N, N-cetyl trimethyl ammonium bromide), anionic, SLS (sodium lauryl sulphate) and Triton X-100 (iso-octyl phenoxy polyethoxy ethanol) were obtained from BDH (England) and Sigma Chemical (USA) and used without further purification. All other chemicals were of AR grade. All solutions were prepared in double distilled water. The kinetics of aliphatic ester hydrolysis has been studied in aqueous and surfactant media at different temperatures. The concentration of different surfactants in ester solutions were maintained above CMC and below CMC of them. The rate constants of acidic hydrolysis of esters have been calculated varying concentration of acid, HCl in this kinetics.

The equation, k = 1/t ln a/a-x ----------- (1) is employed to evaluate pseudo first order rate constant of these kinetics. The volume change at infinite time was measured by refluxing the sample at 60-70˚C for an hour and then reading was taken after 24 hours. All these activated parameters e.g., G , H , S and activation energy (E_a) were evaluated from the rate data at different temperatures using standard equations.

3. Results and Discussion
The mechanism of acid catalyzed hydrolysis involves protonation of an ester oxygen atom followed the special type mechanism $A_{AC}{}^1$ where cleavage of C-O bond i.e., International Journal of Chemistry and Pharmaceutical Sciences

formation of acyl carbonium ion is the rate determining step, whereas combination of this carbonium ion with water is a fastest step (Scheme I). Scheme I has been proposed assuming the hydrolysis of ester with and without surfactants.
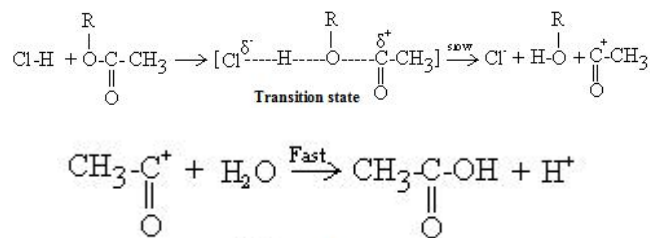
Scheme I

where R = methyl, ethyl, n-propyl or n-butyl.

i. Effect of surfactants and its concentration
The rate constant of pseudo first order for acidic hydrolysis of methyl, ethyl, n-propyl and n-butyl acetate in presence of varying concentration of SLS above and below CMC at room temperature is obtained from the slope by plotting log (v -v$_t$) vs. t (Fig.1). The parameters, a and a-x of equation (1) are replaced by v -v$_o$ and v -v$_t$ where v$_o$, v$_t$ and v are the value of tritant (NaOH) at time initial , t and infinity, respectively. The above kinetics in SLS media was also studied in high temperature. The rate constant of acidic hydrolysis of these esters in CTAB and TritonX-100 (TX-100) environment at different temperatures were calculated similarly and are inserted in the Tables 1-3, respectively. It is observed that with increase in surfactant concentration, the rate of acid hydrolysis of ester is retarded by CTAB micelles and enhanced by SLS micelles but no significant change of rate was observed with TX-100. The acceleration or inhibition of rate of ester hydrolysis in ionic micellar may be due to the distribution of the substrate between micellar and bulk water phase as a result of electrostatic and hydrophobic interactions of the substrate with different regions of ionic micelles. Moreover, different rates of hydrolysis of ester in two environments will be considered for overall rate of hydrolysis.

The alkyl chain of esters preferably enters in the core of either ionic micelle, keeping acyl groups in the stern layer. Whereas electrophilic H^+ is oriented either nearby or away from stern layer depending on the nature of micelles, thereby favoring or preventing the formation of the transition state (Scheme I). The electrostatic stabilization of the positively charged transition by anionic micelles and destabilization of the same by cationic micelle are responsible for the observed change in the rate of hydrolysis. The gradual decrease of the reaction rate on increasing CTAB concentration in all the cases (Table 1) may be attributed to the increase in number of micelles wherein more number of ester molecules are entrapped leading to decrease in the effective concentration of esters in the bulk.

The acidic proton cannot approach the ester molecule to initiate the hydrolysis due to electrostatic repulsion between the proton and positive head groups of these micelles.

Similar effect of cationic surfactants on acid catalyzed hydrolysis of aromatic and aliphatic esters [5, 6] has been reported. In the presence of SLS, the rate of hydrolysis of all esters increases with a gradual increase in the concentration of SLS from 0.005 to 0.04M (Table 2). The rate enhancement occurs due to the increase in effective concentration of H^+ at the micellar surface which can attack on carbonyl carbon atom of esters present close to the interface. The transition state (acyl carbonium ion) is also stabilized due to favorable columbic interaction. The gradual incorporation of more and more ester molecules into the micelles causes the rate enhancement till saturation. The ester localized in one micelle can't interact with H^+ present in other micelle [7].

The effect of the non-ionic micelles (TX-100) on the rate of hydrolysis is found to be negligible (Table 3). Generally, non-ionic surfactants either decrease or have insignificant effects on the rate of hydrolytic reactions of carboxylic esters[8]. From the Table 2, it is observed that enhancement of the magnitude of the rate constant of acidic aliphatic ester hydrolysis in SLS shows a break at CMC of SLS, and then remain more or less steady value at above CMC (Fig.2). So, SLS molecules even in below CMC form aggregated structure having less number of molecule compared to CMC of it, which is also effective to create two different pockets for the hydrolysis of esters. As a result, rate constants of ester hydrolysis increases compared to aqueous media [9, 10].

The variation of rate constant of methyl acetate in CTAB media shows one break at CMC value like SLS media but in reverse manner which is shown in (Fig.3). For TX-100 media, rate constants of ester hydrolysis are not enhanced below CMC and also above CMC compared to aqueous media (Table 3).

ii. Effect of Temperature
At high temperature, number of surfactant aggregation becomes lower and consequently more number of micelle will be formed. As a result, rate and rate constant should be enhanced at high temperature. Experimental data are also in accordance with this theory. With increase in temperature, the rate is found to increase in all the cases (Tables 1-3). All the activated parameters of this kinetic are enlisted in Table 4. From the Table 4, it is observed that the high negative entropy of activation suggests more ordering of the transition state complex. However, there is not much deviation in the ΔG values due to the change in the medium of the reaction. In the case of SLS only, activation energy, E_a of ester hydrolysis is lower than aqueous media which indicates the positive catalytic enhancement of SLS to kinetics.

iii. Effect of $[H^+]$
The observed kinetics depend on the value of equilibrium constant for the formation of substrate-proton complex and the relative concentration of H^+ and therefore, the rate enhancement due to increase in $[H^+]$ (Fig. 4) is justified (Table 5). This is an example of specific hydrogen-ion catalysis [11]. To investigate the effect of carbon chain length of ester on reactivity, the length of the carbon chain has been varied in alkoxy end of ester and the rate constant for hydrolysis are determined at constant concentration of acid. The order of the reactivity is methyl acetate > ethyl acetate > n-propyl acetate > n-butyl acetate. These observation are also explicable in terms of the extent of incorporation of the esters into the micellar core due to hydrophobic interactions and destabilization of the transition state due to increase in bulkiness in the alkoxy part. The longer is the hydrophobic chain length, the larger is the incorporation into the micelle and hence less is the probability of the contact of the ester with the catalytic proton.

The micellar medium provides a multi-pocket environment to the substrate where the polarity of the pockets varies from highly non-polar hexane type medium to polar aqueous medium. Mishra et al. [12] have quantitatively evaluated the polarity of various pockets of the medium by investigating the photo physical processes of some tailor made dyes in cationic and anionic micelles. With increasing hydrophobic group, the substrate finds a suitable polar pocket for its residence.

The polarity (dielectric constants) has an asymmetric trend around the micelle. In the present study, CTAB constitutes the cationic micelles providing a cationic interface devoid of protons. Due to the repulsion between cationic micelle and H^+, hydrolysis will take place on micelle environment, and all the H^+ ion moves to bulk region where reaction takes place. The decrease in the rate constants of the substrate in the presence of CTAB micelles indicates the partitioning of some substrates into the micelle. To discuss the rate dependence on surfactant, a mathematical model (Scheme II) proposed by Bruice et al. [13] is applicable. For the kinetics of unimolecular and bimolecular reactions, consider substrate R, and n number of surfactant molecules (S) aggregates to form catalytic micelles S_nR, which may further gives the products.

Scheme II
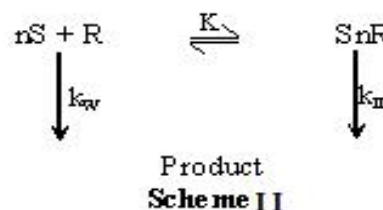
where K is the binding constant of the micelle, k_m and k_w are the rate constant in presence and absence of micelle, respectively. Taking the kinetic steps involved into consideration, Menger and Portnoy have derived an expression (i.e., Eqn. 2), which has been successfully applied to micelle catalyzed unimolecular and bimolecular reactions [14].

$$1/k_{obs}-k_w = 1/k_m-k_w + [N/k_s (k_m-k_w)] \, 1/ (c_D-CMC) \text{------ (2)}$$

where k_{obs} is observed rate constant; c_D is concentration of surfactant; N, aggregation number of surfactant molecules; k_w and k_m are mentioned in scheme II and k_s is association constant related with K as $k_s/N = K$.

The kinetic data of all the reactions with varying concentration of SLS up to 0.04M are fitted to the above equation. Plots of $1/k_{obs}-k_w$ vs. $1/c_D$-CMC are linear in four reaction kinetics with SLS at two temperatures. From the intercept and slope of each of the plot, the value of k_s/N is calculated. Using the value of N for SLS to be 62[11], the association constant (k_s) and k_m for the four reaction kinetics in SLS are calculated and are given in Table 6.

The values of k_s indicate that there is a substantial binding of all substrate molecules with SLS micelles. For n-propyl and n-butyl acetate, the hydrolysis was studied in 0.4 M HCl medium, since the rate constant values are very low in 0.1M HCl. So, the rate constant of ester hydrolysis is a function of H^+ ion but is not proportion to H^+ concentration. From the Table 7, it is observed that reactivity of aliphatic esters in SLS media with n-propyl acetate > methyl acetate > n-butyl acetate > ethyl acetate. But in the case of n-propyl acetate, k_s will be lower than ethyl acetate considering H^+ concentration 0.1 M instead of 0.4 M, in the case of n-butyl acetate, k_s value is lower than n-propyl acetate even at 0.4 M HCl, so it will be further lower than n-propyl acetate considering the hydrolysis in 0.1M HCl media. So, the reactivity order will be methyl acetate > ethyl acetate > n-propyl acetate > n-butyl acetate at both 35ºC and 45ºC temperatures. The k_m values are remarkably larger due to increase in the effective concentration of both reactants in a small volume of micellar phase. Since, rate constants of ester hydrolysis in CTAB and TX-100 (i.e. k_{obs}) and k_m are lower compared to K_w of aqueous media. So, Menger and Portnoy's equation (2) is modified for CTAB media as

$$1/k_w-k_{obs} = 1/k_w-k_m + [N/k_s (k_w-k_m)] \, 1/ (c_D-CMC) ----- (3)$$

The k_s and k_m of acidic hydrolysis of esters in CTAB micellar phase is calculated using modified equation (3) and N is equal to 78 (Table 7) which exhibits that the binding ability of CTAB is 2-8 fold lower than compared to SLS with substrates.
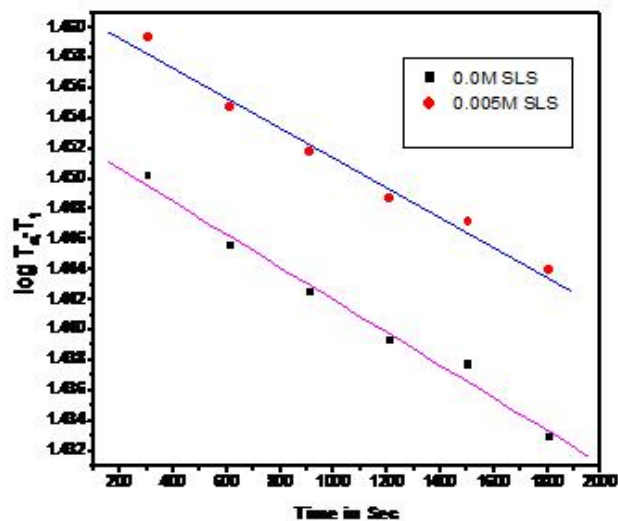
Figure 1: Effect of surfactant, SLS and its concentration on the rate constant of acidic hydrolysis of methyl acetate at 35ºC.
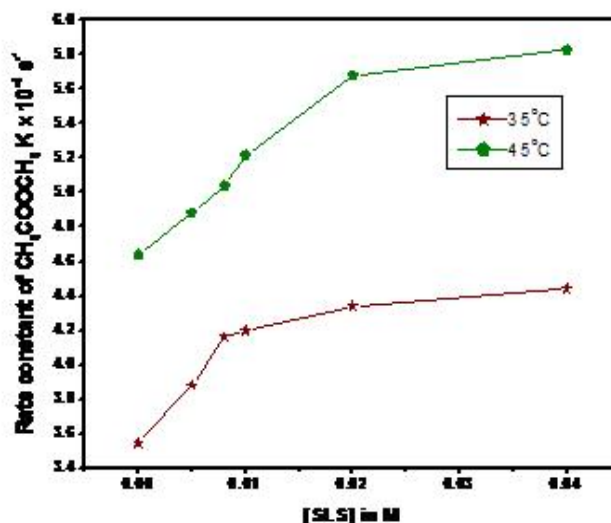
Figure 2: Variation of rate constant of methyl acetate with increase in concentration of SLS at both 35ºC and 45ºC.
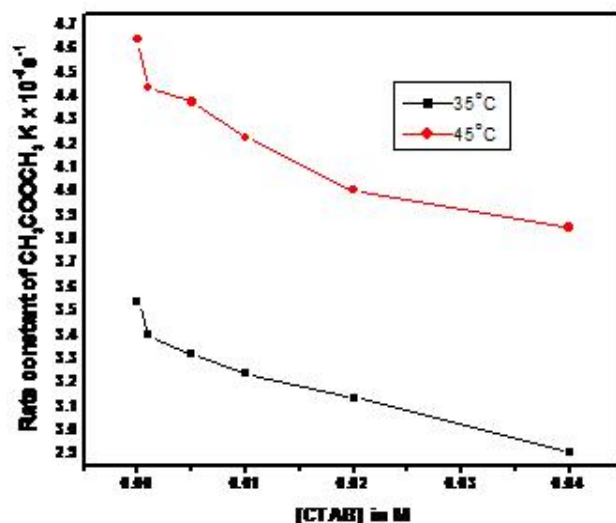
Figure 3: Variation of rate constant of methyl acetate with increase in concentration of CTAB atboth 35ºC and 45ºC.

Figure 4: Effect of variation of acid strength on the hydrolysis of methyl acetate in CTAB media at 45 ºC

Table 1: Effect of variation of [CTAB] on the rate of acid catalyzed hydrolysis of different esters.
([methyl acetate] = 0.6308M, [ethyl acetate] = 0.5118M, [n-propyl acetate] = 0.1739M and [n-butyl acetate] = 0.1517M, [HCl] = 0.1M for methyl & ethyl acetate, 0.4M for n-propyl & n-butyl acetate).
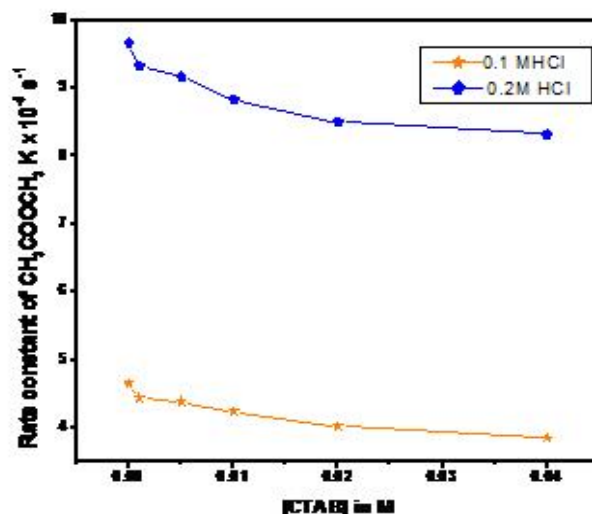
[CTAB] in M	methyl acetate $k \times 10^{-5}$ s^{-1}		ethyl acetate $k \times 10^{-5}$ s^{-1}		n-propyl acetate $k \times 10^{-5}$ s^{-1}		n-butyl acetate $k \times 10^{-5}$ s^{-1}	
	35ºC	45ºC	35ºC	45ºC	35ºC	45ºC	35ºC	45ºC
0.000	3.54	4.65	3.15	4.44	13.34	14.44	2.44	4.96
0.001	3.41	4.45	3.02	4.34	12.33	13.64	2.15	4.56
0.005	3.33	4.38	2.84	4.27	11.56	13.25	2.12	4.03
0.01	3.24	4.24	2.57	4.16	10.48	12.54	1.85	3.74
0.02	3.14	4.02	1.96	3.70	8.92	12.11	1.61	3.35
0.04	2.91	3.85	1.73	3.36	5.66	10.90	1.52	3.19

Table 2: Effect of variation of [SLS] on the rate of acid catalyzed hydrolysis of different esters.
([methyl acetate] = 0.6308M, [ethyl acetate] = 0.5118M, [n-propyl acetate] = 0.1739M and [n-butyl acetate] = 0.1517M, [HCl] = 0.1M for methyl & ethyl acetate, 0.4M for n-propyl & n-butyl acetate).

[SLS] in M	methyl acetate $k \times 10^{-5}$ s^{-1}		ethyl acetate $k \times 10^{-5}$ s^{-1}		n-propyl acetate $k \times 10^{-5}$ s^{-1}		n-butyl acetate $k \times 10^{-5}$ s^{-1}	
	35ºC	45ºC	35ºC	45ºC	35ºC	45ºC	35ºC	45ºC
0.000	3.54	4.65	3.15	4.44	13.34	14.44	2.44	4.96
0.005	3.89	4.88	3.24	4.53	13.95	14.56	4.03	6.38
0.008	4.16	5.05	3.32	4.65	14.26	14.81	6.93	8.52
0.01	4.21	5.23	3.42	4.75	14.39	16.12	8.38	12.71
0.02	4.34	5.68	3.51	4.81	14.55	18.03	11.21	15.70
0.04	4.45	5.83	3.75	5.02	14.70	20.48	13.80	16.80

Table 3: Effect of variation of [TX-100] on the rate of acid catalyzed hydrolysis of different esters.
([methyl acetate] = 0.6308M, [ethyl acetate] = 0.5118M, [n-propyl acetate] = 0.1739M and [n-butyl acetate] = 0.1517M [HCl] = 0.1M for methyl & ethyl acetate, 0.4M for n-propyl & n-butyl acetate).

[TX-100] in M	methyl acetate $k \times 10^{-5}$ s^{-1}		ethyl acetate $k \times 10^{-5}$ s^{-1}		n-propyl acetate $k \times 10^{-5}$ s^{-1}		n-butyl acetate $k \times 10^{-5}$ s^{-1}	
	35ºC	45ºC	35ºC	45ºC	35ºC	45ºC	35ºC	45ºC
0.000	3.54	4.65	3.15	4.44	13.34	14.44	2.44	4.96
0.001	3.44	4.53	2.88	3.96	10.63	13.18	2.39	4.94
0.002	3.45	4.53	2.93	4.03	10.79	13.30	2.39	4.90
0.01	3.46	4.51	2.94	4.09	10.44	13.39	2.40	4.92
0.02	3.45	4.53	2.96	4.06	10.73	13.49	2.39	4.91
0.04	3.45	4.53	2.93	4.09	10.70	13.41	2.38	4.88

Table 4: Effect of temperature on the rates of acid catalyzed hydrolysis of esters
[HCl]= 0.1M for methyl & ethyl acetate, 0.4M for n-n-propyl & n-butyl acetate

[Esters]	[surfactant] = 0.00M $k \times 10^{-5}$ s^{-1}		H kJ mol^{-1} at 35ºC	- S J mol^{-1} at 35ºC	G kJ mol^{-1} at 35ºC
	35ºC	45ºC			
Methyl acetate	3.54	4.65	67.89	110.01	101.77
Ethyl acetate	3.15	4.44	68.10	110.29	102.07
n-propyl acetate	13.34	14.44	65.11	106.67	98.37
n-butyl acetate	2.44	4.96	68.58	110.86	102.74
	[CTAB] = 0.01M				
Methyl acetate	3.24	4.24	68.05	110.24	102.00
Ethyl acetate	2.57	4.16	68.47	110.78	102.59
n-propyl acetate	10.48	12.54	65.98	107.26	98.99
n-butyl acetate	1.85	3.74	69.06	111.56	103.43
	[SLS] = 0.02M				
Methyl acetate	4.34	5.68	67.52	109.49	101.25
Ethyl acetate	3.51	4.81	67.91	110.02	101.79
n-propyl acetate	14.55	18.03	65.38	106.38	98.15
n-butyl acetate	11.21	15.70	65.87	107.05	98.82

[TX-100] = 0.04M

Methyl acetate	3.45	4.53	67.93	110.08	101.84
Ethyl acetate	2.93	4.03	68.22	110.48	102.25
n-propyl acetate	10.79	13.30	65.92	107.19	98.94
n-butyl acetate	2.39	4.90	68.64	110.92	102.80

Table 5: Effect of variation of [acid] on the rate of acid catalyzed hydrolysis of different esters. ([methyl acetate] = 0.6308 M, [ethyl acetate] = 0.5118 M, [n-propyl acetate] = 0.1739 M and [n-butyl acetate] = 0.1517 M, [HCl] = 0.1 & 0.2M for methyl & ethyl acetate, 0.4 & 0.5M for   n-propyl & n-butyl acetate at 45ºC).

	methyl acetate $k \times 10^{-5}$ s^{-1}		ethyl acetate $k \times 10^{-5}$ s^{-1}		n-propyl acetate $k \times 10^{-5}$ s^{-1}		n-butyl acetate $k \times 10^{-5}$ s^{-1}	
	0.1M	0.2M	0.1M	0.2M	0.4M	0.5M	0.4M	0.5M
[CTAB] in M								
0.000	4.65	9.67	4.44	9.30	14.44	21.44	4.96	10.85
0.001	4.45	9.33	4.34	9.19	13.64	18.61	4.56	8.57
0.005	4.38	9.17	4.27	8.87	13.25	17.49	4.03	7.04
0.01	4.24	8.83	4.16	8.33	12.54	16.60	3.74	6.50
0.02	4.02	8.50	3.70	8.19	12.11	15.12	3.35	5.28
0.04	3.85	8.33	3.36	8.02	10.90	14.82	3.19	3.85
[SLS] in M								
0.000	4.65	9.67	4.44	9.30	14.44	21.44	4.96	10.85
0.005	4.88	9.83	4.53	9.45	14.56	22.10	6.38	11.62
0.008	5.05	10.07	4.65	9.52	14.81	24.49	8.52	13.14
0.01	5.23	10.25	4.75	9.68	16.12	25.70	12.71	15.49
0.02	5.68	10.46	4.81	9.89	18.03	26.91	15.70	18.03
0.04	5.83	10.51	5.02	10.03	20.48	27.32	16.80	20.17
[TX-100] in M								
0.000	4.65	9.67	4.44	9.30	14.44	21.44	4.96	10.85
0.001	4.53	9.54	3.96	9.18	13.18	20.16	4.94	10.78
0.002	4.53	9.57	4.03	9.19	13.30	20.32	4.90	10.80
0.01	4.51	9.52	4.09	9.17	13.39	20.45	4.92	10.82
0.02	4.53	9.56	4.06	9.18	13.49	20.66	4.91	10.79
0.04	4.53	9.55	4.09	9.19	13.41	20.31	4.88	10.82

Table 6: Association constants (k_s) and rate constants (k_m) for acid hydrolysis of esters in SLS micellar pseudo phase at 35ºC and 45ºC, respectively.

	Association constant, k_s		Rate constant in Micellar phase $k_m \times 10^{-5}$ s^{-1}	
System	35ºC	45ºC	35ºC	45ºC
Methyl acetate	79.51×10^3	26.24×10^3	4.4592	5.8977
Ethyl acetate	22.47×10^3	32.94×10^3	3.7833	5.033
n-propyl acetate	10.09×10^4	15.5 ×10^3	14.7687	19.4446
n-butyl acetate	32.09×10^3	52.08×10^3	13.7987	16.862

Table 7: Association constants (k_s) and rate constants (k_m) for acid hydrolysis of esters in CTAB micellar pseudo phase at 35ºC and 45ºC, respectively.

	Association constant, k_s		Rate constant in Micellar phase, $k_m \times 10^{-5}$ s^{-1}	
System	35^{0}C	45^{0}C	35^{0}C	45^{0}C
Methyl acetate	12.1×10^3	8.25×10^3	2.9863	3.7386
Ethyl acetate	3.86×10^3	2.29×10^3	1.1504	2.7782
n-propyl acetate	4.11×10^3	3.4×10^3	3.3401	8.5622
n-butyl acetate	6.54×10^3	16.25×10^3	1.153	2.9572

4. Conclusion

The rate constant of acidic hydrolysis of different aliphatic esters is enhanced in anionic surfactant, SLS media compared to cationic and non- ionic surfactants. It is a two phase kinetics compared to traditional one phase reaction. The effect of surfactant media can be extended in bio-molecular kinetic reaction in vitro.

5. Acknowledgement

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