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Evidence of co-operativity in the pre-micellar region in the hydrolytic cleavage of phenyl salicylate in the presence of cationic surfactants of CTAB, TTAB and CPC

Pratik K. Sen[a,*], Piyali Chatterjee[a], Biswajit Pal[b]

[a] Department of Chemistry, Jadavpur University, Kolkata 700032, India
[b] Department of Chemistry, St. Paul's C.M. College, 33/1 Raja Rammohan Roy Sarani, Kolkata 700009, India

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ABSTRACT

The effects of cationic surfactants of cetyl trimethyl ammonium bromide (CTAB), tetradecyl trimethyl ammonium bromide (TTAB) and cetyl pyridinium chloride (CPC) on the kinetics of intramolecular general base catalyzed hydrolysis ($[OH^-]$ range 0.05–0.1 mol L^{-1}) of phenyl salicylate have been studied at different temperatures. The rate is independent of $[OH^-]$ in the studied range. The anionic surfactant sodium dodecyl sulphate (SDS) has no effect on the rate. The presence of small amount of any of these cationic surfactants well below its critical micelle concentration markedly inhibits the rate of reaction suggesting a pre-micellar aggregation between the substrate and surfactant monomers. The kinetic data have been analyzed in terms of earlier reported models (Piszkiewicz's co-operativity model and Raghavan and Srinivasan's model) for micellar catalysis. The binding constants between the substrate and the surfactants evaluated from the two models are in good agreement. Three dimensional structure of the pre-micellar aggregate controls the approach of the nucleophile water molecule to the reaction center. The planar structure of the pyridinium head group of CPC provides less steric hindrance to the attacking water molecule that leads to the least enthalpy of activation for CPC among the three surfactants. The association between the negatively charged substrate and the cationic surfactant is favored owing to electrostatic as well as hydrophobic interactions. The binding between the substrate and pre-micelles follows the order: CPC > TTAB > CTAB.

1. Introduction

Organized assemblies like micelles are being used extensively in different fields such as cosmetics, preparation of photofunctional dyes and sensors, targeted drug delivery, *etc.* [1–3]. Micelles can act as microreactors where the reactants are partitioned by means of electrostatic and/or hydrophobic interactions and thus modify the reaction rates and equilibria [4–9]. Micellar catalyzed reactions may be compared to those catalyzed by enzymes since the hydrophobic interactions within the micelle have some similarities with the complex reactions occurring in biological assemblies [10,11]. Both micelles and enzymes bind substrates in a non-covalent manner. Micellization takes place at the critical micelle concentration, which in some systems shows the onset of the increase in rate. Micellar effects on the rates are sensitive to the nature of the counterions and the head group bulk [12]. The micelles play a critical role in the localization and/or dispersion of charges on reactants and their activated states, and thus can easily influence reaction rates, equilibrium and concentration or depletion of reactants in the interfacial region [13–16]. However, in some cases it has been found that the surfactants show accelerating or inhibiting effect on reaction rates even at concentrations much lower than CMC where normal micelles are not formed at all. The decarboxylation of alkoxynitrobenzisoxazole-3-carboxylate ions was found to be strongly accelerated [17] in the presence of a few cationic surfactants even at very low amphiphile concentrations (much below CMC). The oxidation of a few amino acids by chloramine-T in $HClO_4$ medium [18] was found to be markedly catalyzed by the presence of a small amount of surfactant much below the CMC of surfactant. These effects may be either due to complexation of the substrate with monomeric surfactant or pre-micelles or to substrate induced formation of pre-micelles [18–20]. In view of the widespread domestic as well as industrial use of detergents, the influence of such amphiphiles even in very dilute solution

* Corresponding author. Tel.: +91 33 2414 6666 2329.
E-mail addresses: senpk@yahoo.com (P.K. Sen), palbiswajit@yahoo.com (B. Pal).

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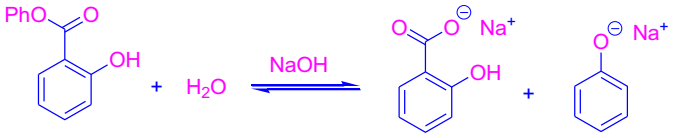
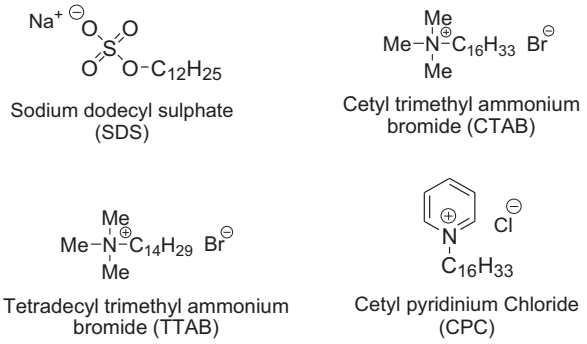


Scheme 1. Alkaline hydrolysis of phenyl salicylate.

on the reactivity of substances should be of environmental concern.

Phenyl salicylate finds use as an antiseptic owing to its antibacterial activity upon hydrolysis in the small intestine [21]. That is why the mechanism of the hydrolytic cleavage of the ester moiety followed by further biochemical reaction is of great importance [22]. A number of studies have been carried out on the hydrolysis of methyl salicylate, methyl o-methoxybenzoate [23], phenyl salicylate and its derivatives [24,25] in neutral and alkaline medium. The effects of both cationic and anionic micelles on the intramolecular general base catalyzed hydrolysis, alkanolysis, aminolysis and hydrazinolysis of phenyl salicylate have already been investigated [26–30]. It may be mentioned that all such studies were carried out in the post-micellar region. Nevertheless the substrate–surfactant interaction in the pre-micellar region may also be an important area of research which requires detailed investigations. However, no such studies on the reactions of phenyl salicylate in the pre-micellar region are found in the literature. The submicellar assemblies of surfactant monomers either formed spontaneously or produced by interactions with reactants are generally known as "premicelles". However, it is not always easy to distinguish between reactant induced micellization and formation of premicelles [31]. Since phenyl salicylate exists as anion in alkaline medium, an electrostatic interaction between the anionic substrate and a cationic surfactant monomer is expected and thus there is a possibility that the rate of hydrolysis may be influenced even in the pre-micellar region. This prompted us to study the kinetics of alkaline hydrolysis of phenyl salicylate (Scheme 1) in the presence of different cationic surfactants like CTAB, TTAB and CPC at concentrations much lower than their respective CMC's in order to see whether there is any evidence of co-operativity between the substrate and the surfactant which may influence the reaction rate.

The chemical structures of the cationic surfactants used in this study are shown in Scheme 2. The effect of surfactants on the hydrolysis reaction in the pre-micellar region has been analyzed using Piszkiewicz's model [19] and Raghavan and Srinivasan's model [32] and an attempt has been made to find out the binding constants between the substrate and the surfactants as well as to account for the thermodynamic parameters in terms of the electrostatic and hydrophobic interactions between the substrate and the surfactant monomers.



Scheme 2. The chemical structures of different anionic and cationic surfactants.

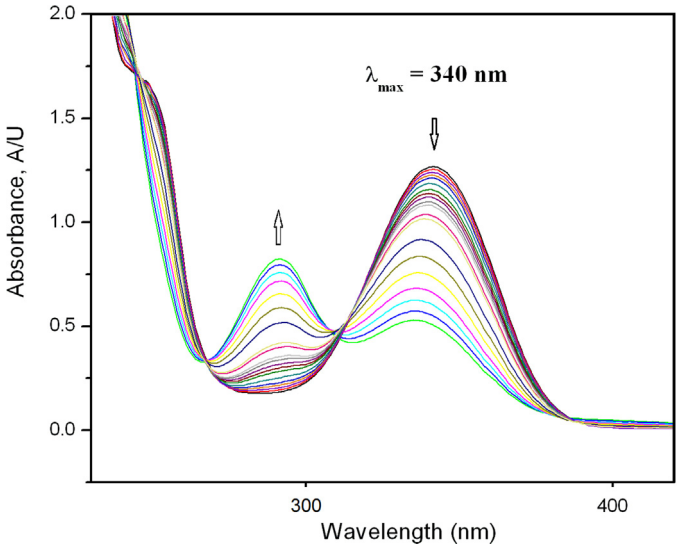


Fig. 1. UV–vis spectra of the reaction mixture at different time intervals; [PhS] = 2.0×10^{-4} mol L^{-1}, [OH^-] = 0.01 mol L^{-1}, 4% aqueous ethanol (v/v), T = 298 K and scanning time interval: 150 s.

2. Materials and methods

2.1. Materials

Phenyl salicylate (PhS) (AR, CDH, India), absolute ethanol (Merck, Germany), sodium hydroxide (AR, SRL, India) and surfactants SDS (extrapure, SRL, India), CTAB (extrapure AR, SRL, India), TTAB (extrapure, SRL, India) and CPC (extrapure, SRL, India) were used without purification. For kinetic measurements, stock solutions of PhS in 50% ethanol–water solvent and sodium hydroxide in water were freshly prepared. The sodium hydroxide solution was standardized against standard oxalic acid solution frequently. Water obtained from Millipore Synergy was used throughout the experiments.

2.2. Kinetic measurements

The kinetics of the hydrolytic cleavage of phenyl salicylate under weakly alkaline medium (0.005–0.1 mol L^{-1} NaOH) in 4% aqueous ethanol solvent in the presence and in the absence of surfactants were studied spectrophotometrically by using UV–visible Shimadzu 1800 spectrophotometer with thermostatted cell compartments and quartz cells with 1.0 cm path lengths. Appropriate quantities of solutions of PhS, aqueous ethanol and Millipore water were placed in the cuvette. After ensuring thorough mixing and temperature equilibration, the reaction was initiated by adding requisite amount of NaOH solution. The time-resolved spectra (scanning time interval: 150 s) of the reaction mixture ([PhS] = 2.0×10^{-4} mol L^{-1}, [OH^-] = 0.01 mol L^{-1}, 4% (v/v) aqueous ethanol) show maximum absorbance at 340 nm (Fig. 1). There is no apparent shift of the absorption peak near λ_{max}, indicating that the concentration of any reaction intermediate during the reaction course would be very low. The absorbance at the λ_{max} decreases gradually with time indicating the progress of the reaction.

Thus, the kinetics of the reaction was followed by monitoring the absorbance of the reaction mixture at 340 nm [33]. The reaction was studied under pseudo-first order conditions, where [OH^-] ≫ [PhS]. Under such conditions, the observed pseudo-first order rate constant (k_{obs}) was calculated from Eq. (1) using the non-linear least-square technique.

$$A_t = A_\infty + \varepsilon S_0 \exp(-k_{obs} t) \quad (1)$$

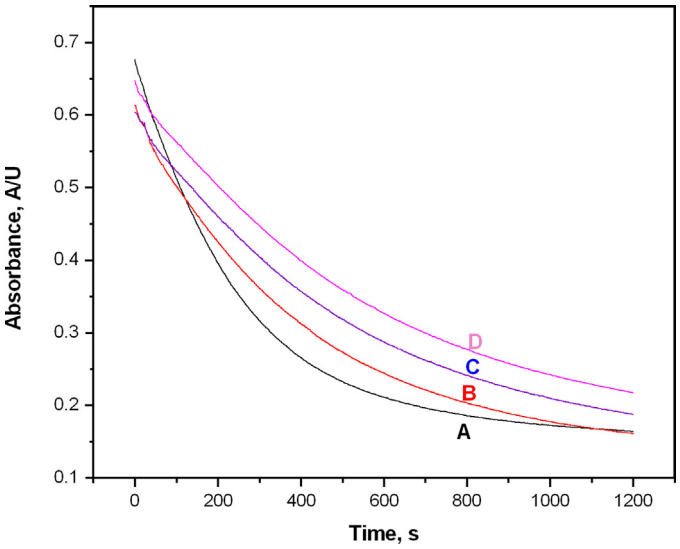


Fig. 2. Typical pseudo-first order exponential decay curves in the presence of different concentrations of CTAB at 315 K. Plots of absorbance *versus* time; [PhS] = 0.75×10^{-4} mol L^{-1}, [OH^-] = 0.05 mol L^{-1}, [CTAB] = (A) 0.0, (B) 2.0×10^{-4}, (C) 4.0×10^{-4} and (D) 7.0×10^{-4} mol L^{-1}.

A_t and A_∞ are the absorbance values at time t and at infinite time respectively. S_0 is the initial concentration of PhS and ε is the apparent molar extinction coefficient. The fitting of the observed data points to Eq. (1) was found to be reasonably good for all kinetic runs. The k_{obs} values were reproducible to within ±5%. Typical pseudo-first order plots for the reaction in the presence of different concentrations of CTAB [$(0.0–7.0) \times 10^{-4}$ mol L^{-1}] are shown in Fig. 2.

2.3. Tensiometric measurements of CMC

In order to find out the critical micelle concentration of CTAB, TTAB and CPC, tensiometric measurements were performed in the presence of 0.01 mol L^{-1} NaOH and 0.0002 mol L^{-1} PhS separately. A plot of surface tension (γ) *versus* log [surfactant] was drawn for each of the surfactants. The intersection of two straight lines indicated the value of CMC.

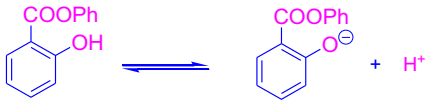
3. Results and discussion

3.1. Hydrolysis reaction in the absence of surfactants

The hydrolysis of phenyl salicylate in the absence of surfactants was studied at various hydroxyl ion concentrations in the range (0.05–0.1) mol L^{-1} keeping [PhS] and temperature constant at 7.5×10^{-5} mol L^{-1} and 305 K, respectively. No attempt was made to keep the ionic strength constant since the reaction was found to be independent of ionic strength as studied by the variation of [$NaClO_4$] in the range (0.01–0.5) mol L^{-1}. In this range of alkali concentration, the rate was found to be independent of [OH^-]. The observed pseudo-first order rate constant (k_{obs}) values are presented in Table 1.

The hydrolysis reaction under the experimental condition was studied at three different temperatures *viz.*, 305, 310 and 315 K and the activation parameters for the uncatalyzed reaction in the absence of surfactants have been determined using the Eyring equation. The enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were found to be 68.60 ± 6.21 kJ mol^{-1} and -73.21 ± 5.84 J K^{-1} mol^{-1}, respectively.

The pK_a value of phenol is 9.89 [34]. However, in case of salicylic acid, due to the intra molecular H-bonding between —COO^- and the —OH group as well as +R effect of the —COO^- group, the pK_a for the phenolic—OH (13.6) in salicylic acid [34] becomes much higher compared to that of phenol. But in phenyl salicylate the —R effect of —COOPh group will increase the acidity of the phenolic —OH group and the pK_a value should be much lower than that of salicylic acid (mentioned above) and it is expected to be slightly less than that of phenol. Literature report [35] shows that the pK_a of phenyl salicylate is 9.25. Therefore, under the condition of the experiments ([OH^-] = 0.05–0.1 mol L^{-1}), salicylate ion happens to be the predominating reactive species of the ester molecule according to the following dissociation taking place:



(2)

The pH-independent hydrolytic cleavage of the reaction is suggested to take place through the participation of the neighboring hydroxyl group which acts as a general base catalyst [23]. The preferred mechanism is shown in Scheme 3, where a water molecule is presumed to be involved in the rate determining step.

Thus when phenyl salicylate undergoes hydrolytic cleavage, the rate determining step involves the nucleophilic attack by a water molecule which is assisted by the neighboring O^- group of the phenolate ion. Since water (nucleophile) is present in large excess compared to PhS, the rate law may be expressed as:

$$v = -\frac{d[PhS]}{dt} = k_{obs}[PhS] \quad (3)$$

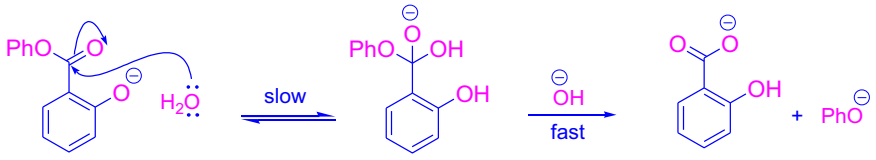
where k_{obs} is the pseudo-first order rate constant.

3.2. Hydrolysis reaction in the presence of surfactants

From tensiometric measurements the CMC values of CTAB were found to be 0.81×10^{-3} mol L^{-1} and 0.95×10^{-3} mol L^{-1} respectively in the presence of 0.01 mol L^{-1} NaOH and 2.0×10^{-4} mol L^{-1} PhS separately. Similar CMC values are 0.32×10^{-3} mol L^{-1} and 0.40×10^{-3} mol L^{-1} for TTAB and 1.10×10^{-3} mol L^{-1} and 1.31×10^{-3} mol L^{-1} for CPC respectively in the presence of NaOH and PhS. Thus, it will be evident that our kinetic experiments were carried out at detergent concentrations much below the respective CMC's.

The reaction was investigated in the presence of an anionic surfactant SDS. The rate was studied at varying concentrations of SDS ($(2.0–20.0) \times 10^{-4}$ mol L^{-1}) keeping [PhS], [OH^-] and temperature constant at 7.5×10^{-5} mol L^{-1}, 0.05 mol L^{-1} and 305 K, respectively. The rate was found to remain unaffected by SDS (Table S1).

The influence of three cationic surfactants, *viz.*, CTAB, TTAB and CPC on the reaction rate was then studied by varying surfactant



Scheme 3. Mechanism of the hydrolytic cleavage of phenyl salicylate in the absence of surfactant.

Table 1
Observed pseudo-first order rate constants for the alkaline hydrolysis of phenyl salicylate in the absence and presence of cationic and anionic surfactants at 305 K; [PhS] = 7.5×10^{-5} mol L^{-1}.

[NaOH] (mol L^{-1})	Aqueous medium, $10^4\ k_{obs}$ (s^{-1})	Micellar medium			
		$10^4\ k_\psi$ (s^{-1}) (SDS)[a]	$10^4\ k_\psi$ (s^{-1}) (CTAB)[b]	$10^4\ k_\psi$ (s^{-1}) (TTAB)[c]	$10^4\ k_\psi$ (s^{-1})* (CPC)[d]
0.05	16.8 ± 0.7	17.4 ± 0.8	10.8 ± 0.5	13.7 ± 0.6	13.9 ± 0.7
0.07	17.0 ± 0.8	17.1 ± 0.7	11.0 ± 0.5	13.4 ± 0.7	14.0 ± 0.8
0.10	16.7 ± 0.7	17.2 ± 0.6	10.7 ± 0.4	13.6 ± 0.6	14.2 ± 0.7

[a] [SDS] = 4.0×10^{-4} mol L^{-1}.
[b] [CTAB] = 1.0×10^{-4} mol L^{-1}.
[c] [TTAB] = 3.33×10^{-5} mol L^{-1}.
[d] [CPC] = 1.0×10^{-4} mol L^{-1}.
* [PhS] = 1.12×10^{-4} mol L^{-1}.

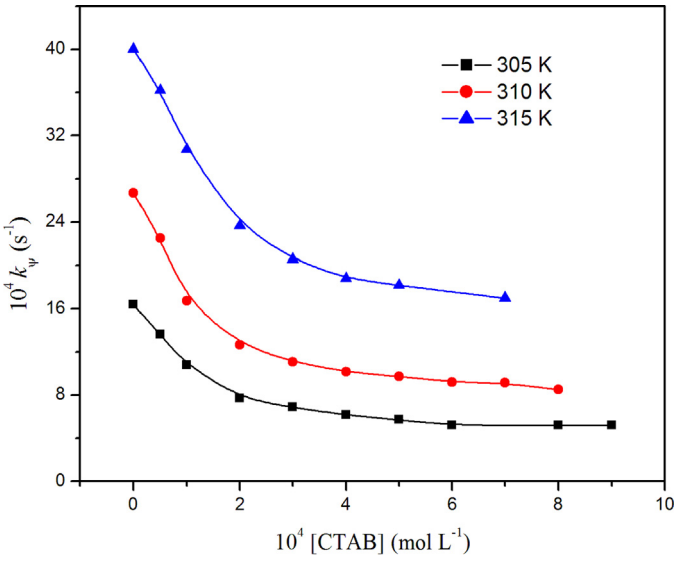


Fig. 3. Dependence of pseudo-first order rate constant on [CTAB]. Plots of k_ψ *versus* [CTAB] at different temperatures; [PhS] = 7.5×10^{-5} mol L^{-1}, [OH^-] = 0.05 mol L^{-1}.

concentrations (below their respective CMC's) while [PhS] and [OH^-] were kept constant at 7.5×10^{-5} mol L^{-1} and 0.05 mol L^{-1} respectively at a constant temperature (Table S1). It has been observed that in each case the rate constant (k_ψ) decreases with an increase in [surfactant] at lower concentration range (below CMC) and tends to reach a limiting value (Fig. 3 and Figs. S1, S2).

The alkaline hydrolysis of phenyl salicylate in the presence of surfactant was also studied at different NaOH concentrations ((0.05–0.1) mol L^{-1}) keeping [PhS], [surfactant] and temperature constant. The pseudo-first order rate constant (k_ψ) was found to remain more or less unchanged with change of alkali concentration (Table 1). The effect of variation of surfactant concentrations on the reaction rate was studied for all the three cationic surfactants at three different temperatures. The activation parameters for the reaction in the presence of cationic surfactants have been determined using the Eyring equation and the values are presented in Table 2.

Surfactants are often found to accelerate or inhibit the reaction rates either by changing the reaction environments or by modifying the reaction scheme [17–20]. If the reaction scheme remains unaltered the variation of rate may arise owing to partitioning of the reactants between the bulk aqueous phase and the micellar pseudo-phase which may either increase or decrease the local concentration of the reactants thereby enhancing or diminishing the reaction rate [20]. Actually electrostatic and/or hydrophobic interaction between the reactants and the surfactant aggregates are responsible for the change of reaction rates [5]. Sometimes change in reaction rate is attributed to a change in the dielectric constant or the pH of the medium at the micellar surface [36,37].

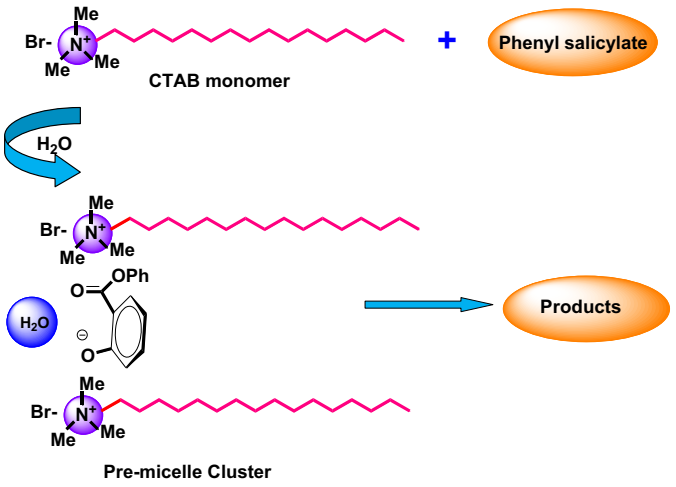
Table 2
Activation parameters for the alkaline hydrolysis of phenyl salicylate in the absence and presence of different surfactants.

In presence of	$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (J K^{-1} mol^{-1})
No surfactant	68.60 ± 6.21	73.21 ± 5.84
CTAB	91.93 ± 10.23	6.85 ± 2.75
TTAB	78.91 ± 2.09	42.35 ± 6.70
CPC	67.50 ± 7.44	82.58 ± 9.67

In the present case the reactions were studied at surfactant concentrations much below the CMC region. Hence the effect of micellar aggregates on the reaction rate is not applicable in our present study. The decrease in reaction rate in the presence of cationic surfactants in this region of surfactant concentration may be attributed to the formation of pre-micelles. The negatively charged salicylate ion possibly aggregates with a small number ($n \approx 2$–4) of positively charged surfactant monomers to form pre-micelles which are different from normal micelles (formed by the aggregation of a large number of surfactant molecules only). A number of different studies have been reported where the reaction rates are found to be accelerated by the surfactants in the pre-micellar region [20,38,39] and this enhancement of reaction rate has been explained by the formation of a catalytic micelle by the surfactant monomers with the substrate. It has been proposed by Piszkiewicz [19] that this small number, n (approx. 1–6) of detergent monomers which aggregate with the substrate molecule, may be viewed as an index of positive co-operativity. However, there are instances [17,40] where the inhibition of reaction rates also are attributed to the formation of such small assemblies of substrate and surfactant monomers known as pre-micelles.

The interesting feature observed for the hydrolytic cleavage of phenyl salicylate in the presence of three cationic surfactants is the decrease of rate of reaction at low surfactant concentrations (well below CMC of respective surfactant). This observation indicates either substrate induced micellization or premicellar aggregates [17]. The decrease in rate in the presence of cationic surfactants may be explained in the following manner. In the absence of any surfactant the hydrolysis of phenyl salicylate takes place through nucleophilic attack by a water molecule in the slow step. In the pre-micellar aggregates, since the substrate is surrounded by/bound to surfactant monomers, the entry of water molecule to the reaction site gets restricted and the reaction rate becomes slower. A possible reaction mechanism for the hydrolytic cleavage of phenyl salicylate in the presence of surfactant occurring through pre-micellar cluster is shown in Scheme 4.

In earlier investigations [19,32,41] several models have been proposed to account for such enhancement or inhibition of reaction rate in the presence of surfactant at concentrations much below the CMC. In the present case, the data of rate constant (k_ψ) *vs.* [surfactant] plots at various temperatures have been analyzed in terms of those models of pre-micellar aggregates reported earlier.



Scheme 4. Schematic representation of hydrolysis of phenyl salicylate in the presence of cationic surfactant in the pre-micellar region.

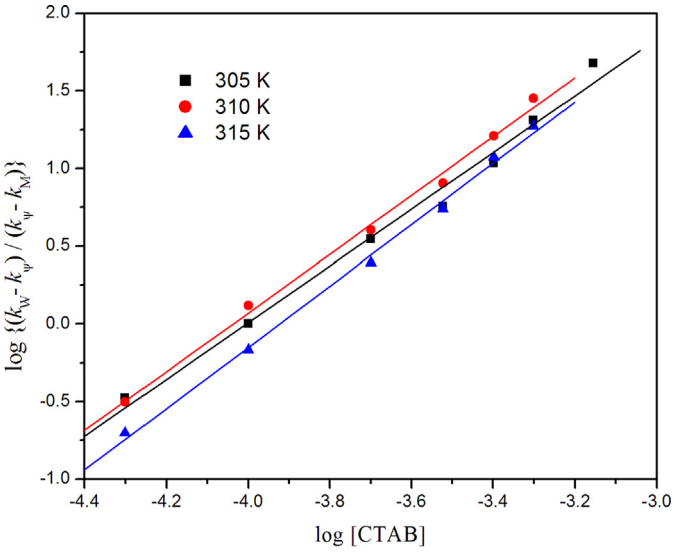


Fig. 4. Plot of $\log\{(k_w - k_\psi)/(k_\psi - k_m)\}$ *versus* log[CTAB] at different temperatures; [PhS] = 7.5×10^{-5} mol L^{-1}, [OH^-] = 0.05 mol L^{-1}.

3.3. Piszkiewicz's model

A kinetic model, which is very much similar to the Hill model [42] for enzymatic reactions, was developed by Piszkiewicz [19]. This model accounts for the dependence of the rate constants on the surfactant concentration especially at low surfactant concentration and the data may be treated without reference to CMC. According to this model, a small number (n) of detergent molecules (D) aggregates/associates with the substrate (S) to form a pre-micelle (D_nS) which may react at a different rate to yield the product in addition to the normal reaction occurring in the aqueous phase as given in Scheme 5.

Here, K_D is the dissociation constant of the pre-micelle (D_nS) [19] back to its free components and k_m and k_w are the rate constants in micellar medium and aqueous phase respectively.

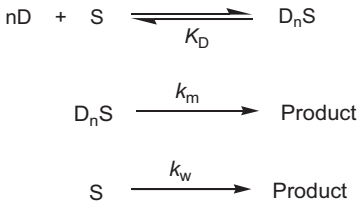
Following this model the observed rate constant (k_ψ) comes out to be:

$$k_\psi = \frac{k_m[D]^n + k_w K_D}{K_D + [D]^n} \quad (4)$$

On rearranging, the above equation takes the form:

$$\log\left\{\frac{k_w - k_\psi}{k_\psi - k_m}\right\} = n\log[D] - \log K_D \quad (5)$$

Thus, according to the above scheme of reaction, a plot of $\log\{(k_w - k_\psi)/(k_\psi - k_m)\}$ *versus* log[D] is expected to be linear. The linear plot will have a slope value of 'n' which is also known as co-operativity index. At $\log\{(k_w - k_\psi)/(k_\psi - k_m)\} = 0$, k_ψ becomes equal to the average of k_w and k_m. Thus at this point the effect of surfactant shows one half of its maximum effect on rate constant. The value of log[D] at this point has been designed as $\log[D]_{50}$ [19]. The $\log\{(k_w - k_\psi)/(k_\psi - k_m)\}$ *versus* log [surfactant] plots are shown in Fig. 4 and Figs. S3, S4.



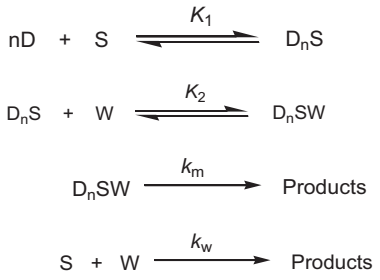
Scheme 5. Reaction steps involved in the Piszkiewicz model.

The k_m was taken as the limiting or minimum rate constant in the presence of surfactant (*i.e.* constant value of rate constant at higher surfactant concentration but below CMC) in the plot of k_ψ *vs.* [surfactant] (Fig. 3). The plots at three different temperatures were fairly linear. The values of co-operativity index (n), $\log[D]_{50}$, $[D]_{50}$ and K_D at three different temperatures have been determined with the help of these plots and are summarized in Table 3.

It appears that for a given reaction the nature of the surfactant produces an effect on both $[D]_{50}$ and 'n'. In the present investigation, the observed values of 'n' greater than one ($1 < n < 4$) are in agreement with earlier observations of Piszkiewicz and are viewed as indices of co-operativity. These values are far less than the number of surfactant molecules found in the normal micelle and previously been interpreted as indicative of pre-micellar aggregates. $[D]_{50}$ values for the three surfactants are also in good agreement with the experimental observations. The K_D values are very small indicating that dissociation of the pre-micelle (D_nS) back to its free components is negligible. Such small K_D values were also obtained in earlier studies [18]. It may be plausible that before the formation of pre-micelles, both phenyl salicylate and the surfactant monomer remain in hydrated forms. Again in the pre-micelle these molecules are bound through hydrophobic as well as electrostatic interactions which are possibly stronger than the hydration interactions of the individual species. This may account for the small values of K_D for all the three surfactants.

Table 3
Piskiewicz's co-operativity values.

Temperature	Surfactant	n	$\log[D]_{50}$	$[D]_{50}$ (mol L^{-1})	K_D
305 K	CTAB	1.83	−4.0	1.0×10^{-4}	4.90×10^{-8}
	TTAB	2.29	−4.54	2.88×10^{-5}	4.28×10^{-11}
	CPC	3.26	−3.80	1.58×10^{-4}	4.22×10^{-13}
310 K	CTAB	1.89	−4.03	0.93×10^{-4}	2.32×10^{-8}
	TTAB	2.52	−4.53	2.95×10^{-5}	3.68×10^{-12}
	CPC	3.42	−3.71	1.94×10^{-4}	2.01×10^{-13}
315 K	CTAB	1.97	−3.92	1.20×10^{-4}	1.82×10^{-8}
	TTAB	2.60	−4.48	3.31×10^{-5}	2.21×10^{-12}
	CPC	3.62	−3.72	1.91×10^{-4}	0.34×10^{-13}



Scheme 6. Reaction steps involved in the Raghavan and Srinivasan's model.

3.4. Raghavan and Srinivasan's model

Further attempt has been made to explain the inhibition effect of the surfactant monomers on the reaction kinetics with the help of another kinetic model known as Raghavan and Srinivasan's model [32]. This model describes the distribution of the reactant and the nucleophile in both the aqueous and pre-micellar pseudo phases. It predicts the formation of a ternary complex involving substrate, nucleophile and surfactant monomers. This ternary complex is assumed to be the pre-micelle. Similar to Piszkiewicz model, this model also predicts the constancy in pseudo-first order rate constant (k_Ψ) at high surfactant concentrations (below CMC) and may be used for evaluating the binding constants of reactants. The model is represented in Scheme 6.In Scheme 6, *D*, *S* and *W* represent the surfactant monomer, the substrate and water, respectively. Here water is the attacking reagent and thus has been considered as the nucleophile. D_nS and D_nSW are the binary and ternary complexes, respectively. The reaction occurs in both the aqueous and pre-micellar pseudo phases. Following the above scheme, the pseudo-first order rate constant comes out to be:

$$k_\psi = \frac{k_w + k_m K_1 K_2 [D]^n}{1 + K_1 [D]^n \{1 + K_2 [S]_T\}} \tag{6}$$

Similar type of rate equation has also been reported in earlier studies (Martinek et al. [43], Berezin [44] and Bunton et al. [36]). On rearranging the equation takes the form:

$$\left[\frac{k_w - k_\psi}{k_\psi}\right] \frac{1}{[D]^n} = K_1\{1 + K_2[S]_T\} - (K_1 K_2)\left[\frac{k_m}{k_\psi}\right] \tag{7}$$

Thus, if a plot of $\{(k_w - k_\psi)/k_\psi\}(1/[D]^n)$ *versus* (k_m/k_ψ) is drawn at a particular temperature a straight line with a negative slope is expected. Actually such linear plots were obtained at three different temperatures for all the three surfactants (Fig. 5 and Figs. S5, S6).

The value of the co-operativity index (n) applied in this model has been obtained from Piszkiewicz's co-operativity model (Table 3). From the intercepts and slopes of these linear plots, the values of the binding constants (K_1 and K_2) and K_D (reciprocal of K_1) have been evaluated. It is evident that K_D, the dissociation constant of the binary complex (D_nS) in the Piszkiewicz model is actually the reciprocal of the value of K_1 in Raghavan and Srinivasan's Model. The evaluated K_D values from this model corroborate with those obtained from the Piszkiewicz's model. The values of the binding constants and K_D for all the three surfactants at three different temperatures are shown in Table 4.

The high values of K_1 indicate that the equilibrium favors the formation of the binary complex. Initially phenyl salicylate and the surfactant monomers are in the environment of water molecules, but stronger electrostatic and hydrophobic interactions between them play a role such that the substrate, in a co-operative manner, binds to a small number (n) of surfactant monomers forming binary complex or the catalytic micelle (D_nS). Again the low values of K_2 indicate that the nucleophile, *i.e.*, the water molecule

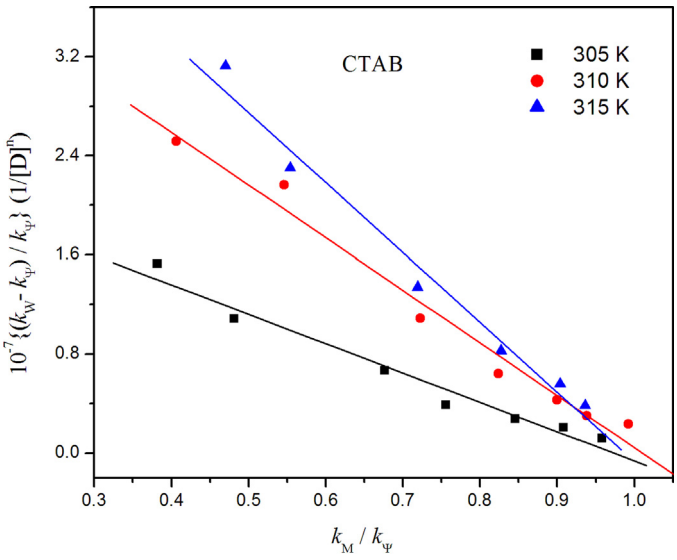


Fig. 5. Plots of $\{(k_w - k_\psi)/\ k_\psi\}(1/[D]^n)$ *versus* (k_M/k_ψ) for CTAB at different temperatures.

remains mostly in the bulk phase. Thus one may suggest that the reaction takes place between the substrate solubilized into a catalytic micelle and the nucleophile water residing at the interface.

Since SDS is an anionic surfactant, the electrostatic repulsion between the anionic substrate (Phenyl salicylate) and SDS possibly does not favor the co-operative binding between the substrate and SDS and thus SDS has no effect on the reaction rate. The binding between the negatively charged substrate and the cationic surfactant may arise due to both electrostatic and hydrophobic interactions. In case of CPC, possibly the similar nature of aromatic rings in both the substrate and the surfactant favors the binding more because of better hydrophobic interactions. Hence the values of the binding constant K_1 are highest for CPC among the three surfactants.

In the pre-micelle the electrostatic interaction operates between the phenyl salicylate anion and the cationic head group of the surfactant monomers. Also there are hydrophobic interactions present in the pre-micelle between the hydrocarbon tail of the surfactant and the aromatic ring of the substrate. The pre-micelle undergoes nucleophilic attack by the water molecule in the rate determining step which ultimately leads to the reaction products. The entry of the water molecule is controlled by the three dimensional structure of the catalytic micelle at the reaction center. In case of CPC, due to the planner structure of the pyridinium head group, the nucleophile water molecule experiences less steric hindrance and the attack becomes easier. That is why the enthalpy of activation ($\Delta H^{\#}$) is least in case of CPC (Table 2). For CTAB and TTAB the three dimensional structure of the trimethyl ammonium ($-N(CH_3)^+$) head group bound to the salicylate provides greater steric hindrance which makes it more difficult for the entry of the water molecule. As a result the enthalpy of activation ($\Delta H^{\#}$) is higher for these two surfactants (Table 2).

When phenyl salicylate undergoes hydrolytic cleavage, the rate determining step involves the nucleophilic attack by a water molecule which is assisted by the neighboring O^- group of the phenolate ion. The resulting intermediate containing two —OH groups, one oxo anion (O^-) and another phenoxy group (—OPh) is highly polar and thus will be surrounded by a large number of water molecules (Electrostriction). Due to this highly water-structured intermediate compared to salicylate, a moderate decrease in entropy is observed.

Table 4
Binding constants using Raghavan and Srinivasan model and comparison with Piskiewicz's co-operativity values.

Temperature	Surfactant	Piszkiewicz model K_D	Raghavan and Srinivasan model		
			K_D	K_1	K_2
305 K	CTAB	4.90×10^{-8}	4.34×10^{-8}	2.31×10^{7}	1.028
	TTAB	4.28×10^{-11}	4.96×10^{-11}	2.01×10^{10}	0.982
	CPC	4.22×10^{-13}	3.37×10^{-13}	2.97×10^{12}	1.022
310 K	CTAB	2.32×10^{-8}	2.33×10^{-8}	4.28×10^{7}	0.990
	TTAB	3.68×10^{-12}	3.54×10^{-12}	2.83×10^{11}	1.010
	CPC	2.01×10^{-13}	1.83×10^{-13}	5.45×10^{12}	1.020
315 K	CTAB	1.82×10^{-8}	1.80×10^{-8}	5.56×10^{7}	1.012
	TTAB	2.21×10^{-12}	2.08×10^{-12}	4.80×10^{11}	1.009
	CPC	0.34×10^{-13}	0.41×10^{-13}	2.42×10^{13}	0.973

When the hydrolysis takes place in the presence of surfactants, the electrostatic attraction between the substrate and the surfactant monomer in the pre-micelle decreases the polarity of the entity and thus it is much less hydrated. The nucleophilic attack by the water molecule to the pre-micelle in the rate determining step gives rise to the final products which are very much polar. Thus it may be expected that the transition state will be much more polar compared to the pre-micelle cluster. Therefore, the transition state will be appreciably hydrated (Electrostriction) [45], resulting in a decrease in entropy (−ve ΔS). As the reaction proceeds, in the transition state the surfactant monomers tend to become free with the breaking of the pre-micellar structure, there should be an increase in entropy (+ve ΔS), but these monomers will get hydrated again with a decrease in entropy (−ve ΔS). It may be plausible that all these −ve ΔS terms overbalance the +ve ΔS term and the resultant entropy of activation ($\Delta S^{\#}$) becomes negative. But the magnitude is different due to different extent of aggregation in the pre-micelle for different surfactants and different amount of hydration in the transition state. The greater the number of monomers coming out of the pre-micelle cluster, the greater will be their hydration and the larger the decrease in entropy. In case of CTAB, less than two monomers (Table 3) aggregate with the substrate in the pre-micelle and so when they become free and get hydrated, the decrease in entropy is comparatively less resulting in a small negative $\Delta S^{\#}$ (Table 2). But for TTAB more than two surfactant monomers (Table 3) aggregate with the substrate and consequently when they become free, decrease in entropy due to hydration is higher than in case of CTAB leading to a higher negative $\Delta S^{\#}$ (Table 2). In a similar way, the higher negative value of $\Delta S^{\#}$ (Table 2) for CPC compared to TTAB can be explained due to higher co-operativity index (n) value for CPC ($n > 3$) (Table 3). Such type of large difference in $\Delta S^{\#}$ value for a CTAB catalyzed reaction compared to uncatalyzed reaction has been observed for the oxidation of D-fructose by Ce(IV) in sulfuric acid medium [15].

4. Conclusion

The alkaline hydrolysis of Phenyl salicylate is independent of hydroxyl ion concentration in the [OH^-] range 0.05–0.1 (M). In this region of [OH^-], a small number of cationic surfactant molecules (CTAB, TTAB and CPC) bind with Phenyl salicylate to form pre-micelles and show negative co-operativity (*i.e.* retards the reaction rate). The inhibition effect of the cationic surfactants on the hydrolytic cleavage of phenyl salicylate has been explained using Piszkiewicz's co-operativity model and Raghavan and Srinivasan's model. The binding constants evaluated from these two models are found to corroborate with each other. The binding between the negatively charged phenyl salicylate ion and the cationic surfactant monomer occurs due to both electrostatic and hydrophobic interactions. Among these three surfactants, CPC binds in a stronger manner owing to the similar aromatic rings in the substrate and the surfactant.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.09.026.

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