ORIGINAL ARTICLE

Micellar effect upon the rate of alkaline hydrolysis of carboxylic and carbonate esters

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Abstract The alkaline hydrolysis of carboxylate (1-naphthylbutyrate) and carbonate esters (2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate) in the presence of different surfactants has been studied. The rate of hydrolysis of these esters was determined under pseudo first order condition in which the concentration of NaOH was kept in large excess over the [ester]. The cationic micelles of cetyltrimethylammonium bromide (CTABr) and cetyltrimethylammonium sulfate ($(CTA)_2SO_4$) 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) inhibited the rate of the hydrolysis. The reaction proceeds through the attack of OH^- 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 variation in the rate of hydrolysis by micelles was treated by considering the pseudophase ion-exchange model and Menger–Portnoy model. The added salts *viz*. NaBr, NaCl, and LiCl inhibited the rate of the reaction in the presence of cationic and anionic micelles. The kinetic parameters i.e. k_m and K_s were determined from the rate–[surfactant] profile.

1. Introduction

Hydrolysis is among the most important reactions of organic molecules with water in aqueous environments that plays a significant environmental fate process for many organic compounds. Many classes of organic compounds like alkyl halides, carboxylic acid esters, phosphate esters, carbamates, epoxides, nitriles, amides, amines, etc. undergo hydrolysis in the medium of acidic, alkaline or neutral [17,18]. The determination of rate

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constants for the hydrolysis reaction can be significant for the identification of the chemical formed or species present in the ecosystem and to determine the possibility of the parent compounds. The hydrolysis of carboxylic acid esters involves bimolecular nucleophilic attack analogous to the SN_2 mechanism on the saturated carbon [2,14,21]. Ester functional groups are among the most common acid derivatives present in natural and man-made chemicals. Carboxylic acid esters are used industrially to make flavors, soaps, herbicides etc. The base-catalyzed or alkaline hydrolysis of esters generally takes place via SN_2 reaction [3]. The presence of water as solvent changes the rate and mechanism of hydrolysis reactions in many ways such as nucleophilic reagent, as a high dielectric-constant; and as a specific solvating agent for organic reactants and products [16,25]. The modifications in the reaction medium i.e. by adding organic solvents or by adding surfactant molecules also affect the solvating power and thus alter the hydrolytic rate [4,23]. The variation in the values of rate constant with the alteration in the medium may involve the interaction of the solvent medium with the reactants, transition states and/or products. The rate of hydrolysis of ester increases when the transition state is better solvated or stabilized by the H-bonding than the initial state [15]. The negatively charged transition states of base and general base-catalyzed ester hydrolysis are strongly stabilized by solvent alpha sites, while the solvent beta sites play a minor role [19].

Surfactants are the amphiphilic molecules consisting of the polar or charged headgroup and non-polar hydrocarbon chain [11]. The surfactant molecules aggregate at concentrations above critical micellar concentrations (cmc) to form micelles [24]. The micelles have a tendency to influence the reaction rates by enhancing it or by retarding the rates of reaction [5]. The influence of cationic cetyltrimethylammonium bromide (CTABr), cetyltrimethylammonium sulfate ((CTA)$_2$SO$_4$), and anionic sodium dodecyl sulfonate (SDS) was investigated on the rate of alkaline hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitro-phenylcarbonate to elaborate the medium role on the rate of hydrolysis. The effects of salts e.g. NaCl, LiCl, NaBr, trimethyl ammonium bromide (TMABr), tetraethyl ammonium bromide (TEABr) etc. on the reactivity of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitro-phenylcarbonate in the presence of surfactant molecules were also studied and are described in this paper.

2. Experimental

2.1. Materials

1-Naphthylbutyrate (98%, Merck, Germany), 2-(methylsulfonyl)-ethyl-4-nitro-phenylcarbonate (98%, Merck, Germany), sodium dodecyl sulfate (SDS, 99%, BDH, England), and cetyltrimethylammonium bromide (CTABr, 99%, BDH, England) were used during the experiment. Sodium bromide (NaBr, 99%, BDH, England), lithium chloride (LiCl, 99%, BDH, England), sodium chloride (NaCl, 99%, BDH, England), tetramethylammonium bromide (TMABr, 99%, Sigma, USA), and tetraethylammonium bromide (TEABr, 99%, Sigma, USA) were used as supplied. Anal R grade sodium hydroxide was used during the experimental work. Deionized double-distilled water with specific conductance; $1-2 \times 10^{-6} \, \Omega^{-1} \, cm^{-1}$ was used as a solvent throughout the experiment. Cetyltri-

methylammonium sulfate, (CTA)$_2$SO$_4$ was synthesized in the laboratory by mixing 50% excess of Ag$_2$SO$_4$ with CTABr in absolute alcohol. The reaction mixture was sonicated for 1.5 h and then AgBr was removed by filtration. The product was then recrystallized three times from the mixture of absolute methanol-diethyl ether. The purity of the synthesized surfactant was checked by determining the melting point. The melting point of the final product was 215 °C.

2.2. Kinetic measurements

The repetitive scans for the alkaline hydrolysis of 2.0×10^{-5} mol dm^{-3} 1-naphthylbutyrate in 1.0×10^{-4} mol dm^{-3} NaOH were recorded at 25.0 ± 0.1 °C at the intervals of 2 min. Similarly, the scans for the hydrolysis of 2-(methylsulfonyl)-ethyl-4-nitro-phenylcarbonate (1.0×10^{-5} mol dm^{-3}) in 1.0×10^{-4} mol dm^{-3} NaOH were recorded at 25.0 ± 0.1 °C. The spectra are given in Figs. 1 and 2, respectively. It is observed that the values of absorbance increase with the progress in reaction in both the cases. The values of λ_{max} for 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate were observed at 248 nm and 400 nm, respectively. Therefore, all the kinetics studies were followed by monitoring the absorbance at 248 nm (for 1-naphthylbutyrate) and 400 nm (for 2-(methylsulfonyl)-ethyl-4-nitro-phenylcarbonate). The absorbance was recorded on Perkin-Elmer 330 UV–visible spectrophotometer. The constant temperature was maintained at 25.0 ± 0.1 °C using the L.K.B. 2209 multi-temperature water bath. The values of first-order rate constants (k_{obs}, s^{-1}) were obtained from slopes of plots of ln $(A_\infty - A_t)$ versus time with an average linear regression coefficient, $r^2 \geqslant 0.98$. The rate of reaction was studied until the reaction completed to 3–4 half-lives. Each kinetic run was repeated at least 3 times and the results were found to be reproducible within $\pm 5\%$. The concentration of sodium hydroxide was kept large excess over the carboxylic and carbonate esters.

3. Results

3.1. Hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate in the aqueous medium

The rate of hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate was determined at different concentrations of sodium hydroxide. The concentration of NaOH was taken in the range from 1.0×10^{-3} mol dm^{-3} to 1.0×10^{-1} mol dm^{-3} for 1-naphthylbutyrate. The concentration of NaOH varied from 1.0×10^{-4} mol dm^{-3} to 1.0×10^{-3} mol dm^{-3} for the hydrolysis of 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate. The concentrations of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitro-phenylcarbonate were kept constant at 2.0×10^{-5} mol dm^{-3} and 1.0×10^{-5} mol dm^{-3}, respectively. The observed values of rate constant (k_{obs}) increased linearly with the increase in [NaOH] (Fig. 3 and inset: 3a). The slope of the plot of log (k_{obs}) versus log [NaOH] was found to be 0.948 (with $r^2 \geqslant 0.999$) and 0.825 (with $r^2 \geqslant 0.995$), for hydrolyzes of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate, respectively, indicating that the order of the reaction is close to unity. Little influence of [salt] on the values of first order rate constant was observed indicating that the reaction occurs between the
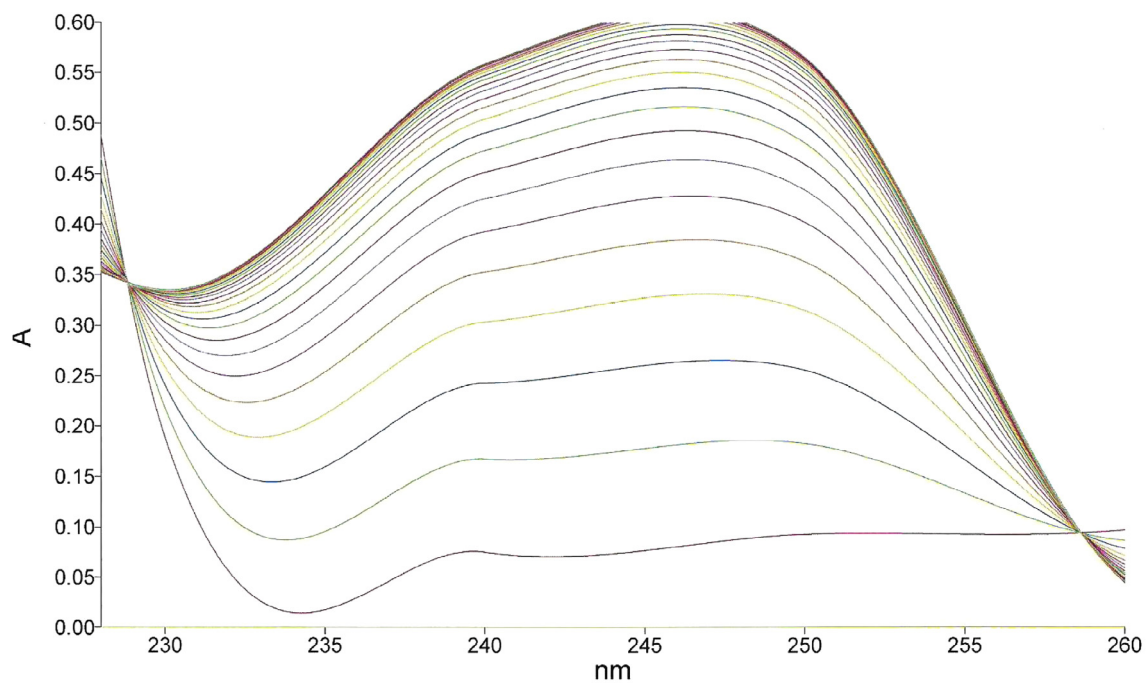
Figure 1 Repetitive scans for the hydrolysis of 1-naphthylbutyrate $(2.0 \times 10^{-5} \, \text{mol dm}^{-3})$ in $1.0 \times 10^{-4} \, \text{mol dm}^{-3}$ NaOH at $25.0 \pm 0.1 \, °\text{C}$. Scans were recorded at the intervals of 2 min.
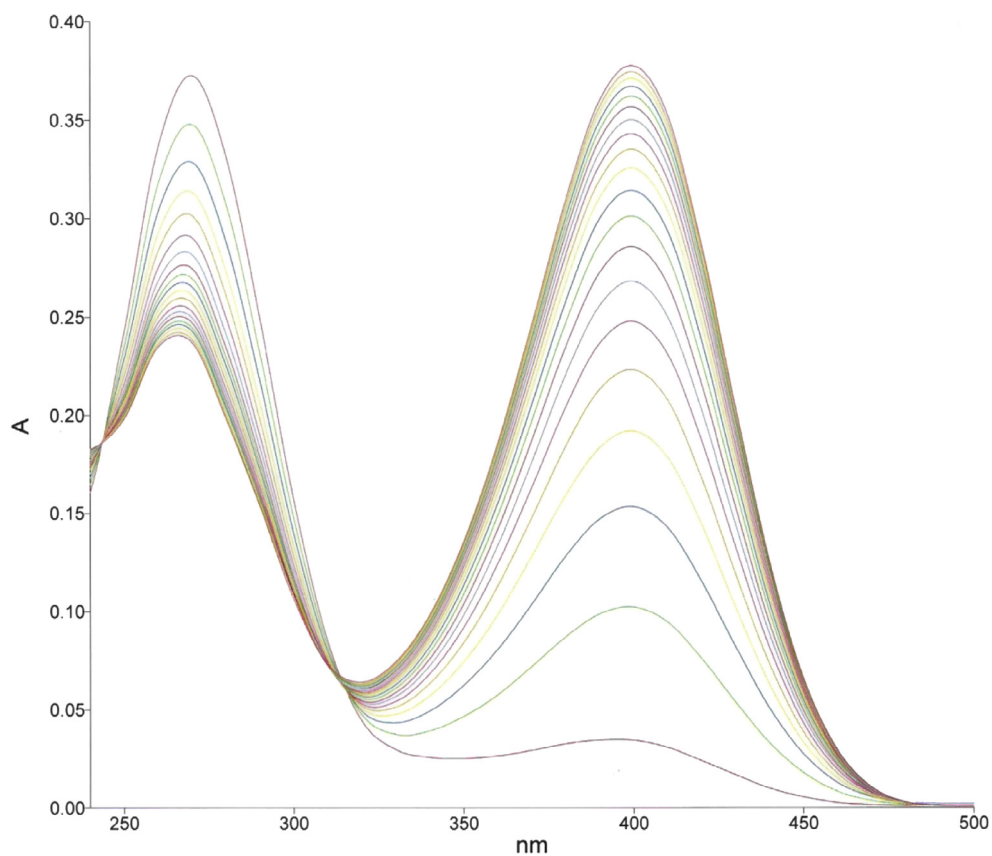

Figure 2 Repetitive scans for the hydrolysis of 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate $(1.0 \times 10^{-5} \, \text{mol dm}^{-3})$ in 1.0×10^{-4} - mol dm^{-3} NaOH at $25.0 \pm 0.1 \, °\text{C}$. Scans were recorded at the intervals of 2 min.
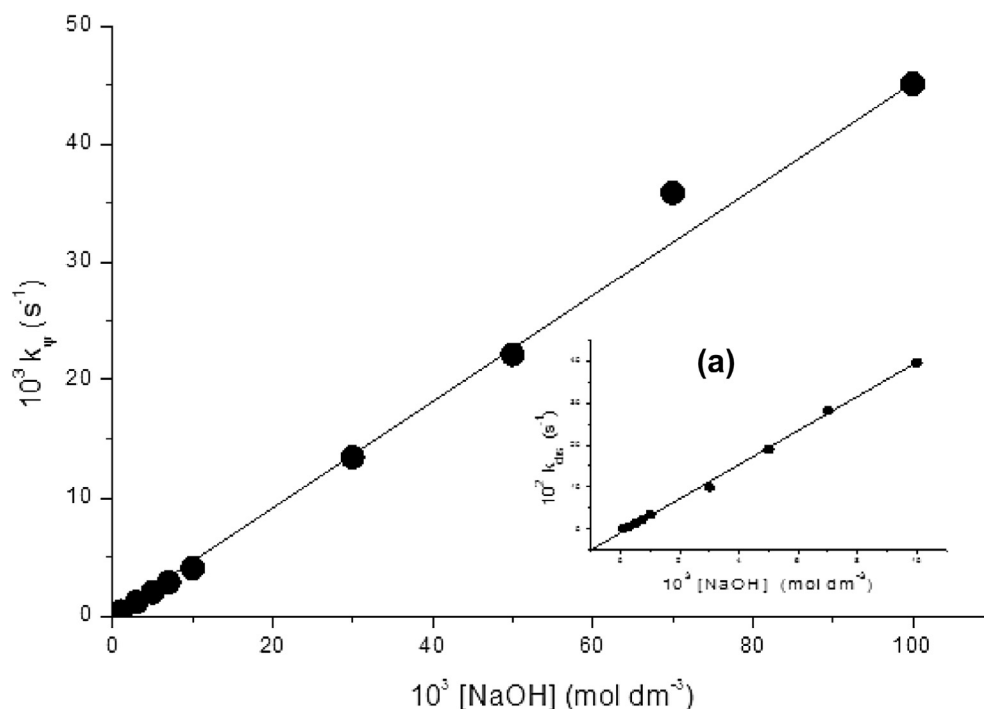
Figure 3 k_{obs} *versus* [NaOH] for the hydrolysis of 1-naphthylbutyrate $(2.0 \times 10^{-5} \text{ mol dm}^{-3})$ and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate (inset (a); $1.0 \times 10^{-5} \text{ mol dm}^{-3}$) at temperature = 25.0 ± 0.1 °C.

molecular forms of 1-naphthylbutyrate/2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate and negatively charged OH⁻ ions. The concentrations of salts (LiCl, NaCl, NaBr, and TMABr/TEABr) varied from $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ to $20.0 \times 10^{-2} \text{ mol dm}^{-3}$ at fixed concentrations of reactants ($2.0 \times 10^{-5} \text{ mol dm}^{-3}$ 1-naphthylbutyrate and $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ NaOH; and $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate and $3.0 \times 10^{-4} \text{ mol dm}^{-3}$ NaOH).

3.2. Hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate in the micellar medium

CTABr and (CTA)$_2$SO$_4$ influenced the rate of alkaline hydrolysis of esters like a typical bimolecular reaction in which the increase in [CTABr]/[(CTA)$_2$SO$_4$] increased the values of first order rate constant in the lower concentration range. The values of rate constant attained maximum values and then started to decrease on further increasing the cationic [surfactant]. Fig. 4 (and 4a) graphically depicts the dependence of rate constant on [CTABr] and [(CTA)$_2$SO$_4$] for the hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate in the micellar medium. The anionic micelles of SDS inhibited the rate of hydrolysis of the carboxylate and carbonate esters (Fig. 5). The concentration of SDS was changed from $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ to $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ and the observed values of rate constants were decreased with the increase in [SDS]. The values of rate constant become almost negligible at [SDS] > 10 mM for the hydrolysis of 1-naphthylbutyrate.

The addition of 0.10 mol dm^{-3} of NaBr, NaCl and LiCl to the different [CTABr] decreased the rate of reaction. Also, the addition of 0.10 mol dm^{-3} NaBr to the reactant solution containing (CTA)$_2$SO$_4$ and SDS lowered the rate of hydrolysis

of 1-naphthylbutyrate (Table 1). The rate of hydrolysis of 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate slightly increased with increasing concentration of CTABr and reached a maximum value and then decreased on increasing [CTABr] in the presence of 0.10 mol dm^{-3} NaBr, NaCl and TEABr (Table 1). An increase in the amount of salts to the fixed concentration of surfactant decreased the rate of the reaction.

4. Discussion

4.1. Hydrolysis in aqueous medium

The hydrolysis of carboxylic and carbonate esters may proceed through various mechanisms depending upon the nature of substrate, the pH and the presence of catalyzing species (Jencks and Carriuolo, 1960; [18]. Under the alkaline condition, the reaction starts through the addition of hydroxyl anion to the carbonyl carbon to produce a tetrahedral intermediate. The tetrahedral intermediate is highly unstable and collapses immediately to yield the respective acid and alcohol. An increase in [OH⁻] increases the chance of attack of the hydroxyl ions on the carbonyl carbon and equilibrium shifts toward the formation of the tetrahedral intermediate. The following mechanism in Scheme 1 has been proposed for the alkaline hydrolysis of 1-naphthylbutyrate. Like 1-naphthylbutyrate, the hydrolysis of 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate follows the similar reaction path. Therefore, the same rate equation represents the hydrolysis of both 1-naphthylbutyrate and 2-(methylsulfonyl)-4-nitrophenylcarbonate.

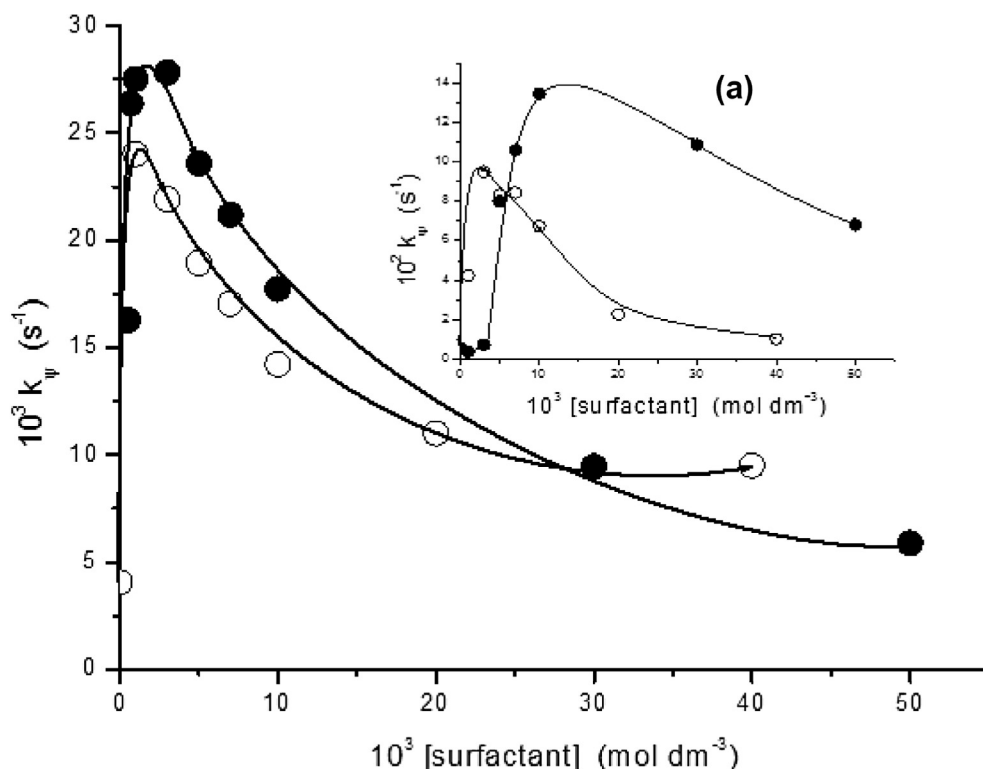Corresponding to the mechanism in Scheme 1, the following general rate equation has been used to represent the rate

Figure 4 k_ψ *versus* [surfactant] for the hydrolysis of 1-naphthylbutyrate $(=2.0 \times 10^{-5} \text{ mol dm}^{-3}$ and $[\text{NaOH}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3})$ and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate $(=1.0 \times 10^{-5} \text{ mol dm}^{-3}$ and $[\text{NaOH}] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$, inset (a)) in the presence of CTABr (●) and (CTA)$_2$SO$_4$ (○). Temperature = 25.0 ± 0.1 °C.
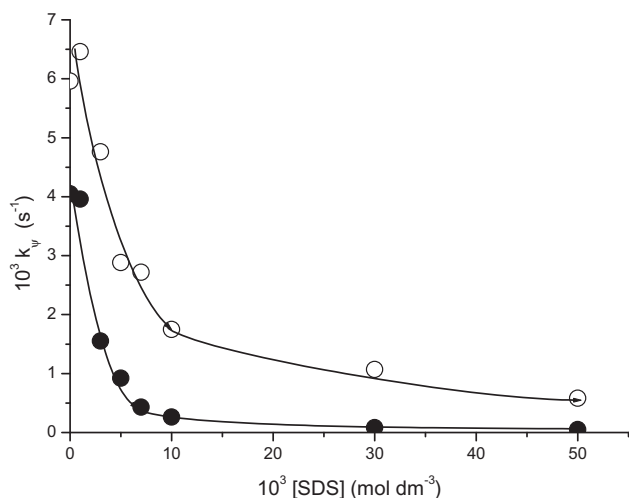

Figure 5 k_ψ *versus* [SDS] for the hydrolysis of 1-naphthylbutyrate (○) and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate (●) at temperature = 25.0 ± 0.1 °C. [1-naphthylbutyrate] = 2.0 × 10^{-5} mol dm^{-3} and [NaOH] = 1.0 × 10^{-2} mol dm^{-3}; [2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate] = 1.0 × 10^{-5} mol dm^{-3} and [NaOH] = 3.0 × 10^{-4} mol dm^{-3}.

of hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate:

$$\frac{d\text{P}}{dt} = k_1[\text{NaOH}][A]_\text{T} \qquad (1)$$

Here, $[A]_\text{T}$ represents the total concentration of 1-naphthylbutyrate (and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate). The rate of reaction is related to the observed value of rate constant for pseudo first order reaction, k_obs through the following relationship:

$$\frac{d\text{P}}{dt} = k_\text{obs}[A]_\text{T} \qquad (2)$$

Or,

$$k_\text{obs} = k_1[\text{NaOH}] \qquad (3)$$

Thus, according to Eq. (3), a plot of k_obs *versus* [NaOH] should give a straight line passing through the origin with slope equal to k_1 (Fig. 3a). The second order rate constant (k_2) was obtained from the slope of the plots of Fig. 3.

4.2. Hydrolysis in micellar medium

The cationic micelles of CTABr and (CTA)$_2$SO$_4$ catalyzed the rate of hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate giving a maxima like curve for the k_ψ–[surfactant] plot. The anionic micelles of SDS inhibited the rate of reaction. The catalytic or inhibitive effect of micelles on the values of rate constant can be explained in terms of the partitioning of the reactants in the aqueous and micellar pseudophases. The pseudophase model [10,12] and pseudophase ion exchange model [13,22] are used to explain the quantitative treatment of the data for the k_ψ–[surfactant] profile. The variation in the values of rate constant with the variation in [surfactant] is attributed to (i) variation in the local concen-

Table 1 Influence of [CTABr], [(CTA)₂SO₄] and [SDS] on the observed value of rate constant for the alkaline hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate in the presence of 0.10 mol dm^{-3} salt at 25.0 ± 0.1 °C.

10^3 [surfactant] (mol dm^{-3})	$10^3 \, k_\psi$ (s^{-1}) for 1-naphthylbutyrate[a]					$10^3 \, k_\psi$ (s^{-1}) for 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate[b]					
	CTABr			(CTA)₂SO₄	SDS	CTABr			(CTA)₂SO₄		
	NaBr	NaCl	LiCl	NaBr	NaBr	NaBr	NaCl	TEABr	NaBr	NaCl	TEABr
0	3.97	4.20	3.96	3.97	3.97	–	–	–	–	–	–
1.0	1.23	3.37	3.79	1.16	2.49	0.58	0.81	0.42	6.93	11.08	4.03
3.0	1.03	3.05	3.30	1.09	0.90	0.68	1.21	0.51	8.94	14.50	5.33
5.0	0.80	2.82	3.05	0.96	0.50	0.81	1.40	0.56	9.12	17.88	5.57
7.0	0.76	2.73	3.18	0.93	0.38	0.91	1.51	0.64	7.85	18.87	4.98
10.0	0.78	2.51	2.79	1.00	0.23	1.04	1.58	0.67	5.95	17.68	4.02
20.0	–	–	–	–	–	1.12	1.61	0.71	3.07	14.09	1.64
30.0	0.88	1.98	2.06	–	0.09	1.11	1.67	0.68	2.97	13.12	0.94
50.0	0.78	1.80	1.79	–	0.06	–	–	–	–	–	–

[a] [1-Naphthylbutyrate] = 2.0 × 10–5 mol dm^{-3}, [NaOH] = 1.0 × 10^{-2} mol dm^{-3}.
[b] [2-(Methylsulfonyl)-ethyl-4-nitrophenylcarbonate] = 1.0 × 10^{-5} mol dm^{-3}; [NaOH] = 3.0 × 10^{-4} mol dm^{-3}.

tration of the reactants in the aqueous and micellar pseudo-phases; (ii) variation in the polarity of the media (aqueous and micellar pseudophases); (iii) different rates of reaction in the aqueous and micellar pseudophases. The reactive organic molecules of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate are considered to be distributed in both the aqueous and micellar phases in accordance with their hydrophilic or hydrophobic characteristics [7,9]. The molecules are oriented with the micelles in a manner that suits their polarity. The reactive anion OH$^-$ is also distributed in the aqueous and Stern layer of the micellar region. Its concentration in the micellar pseudophase can be optimized on the basis of ion exchange model. The mechanism of hydrolysis occurring in the presence of micelles can be presented as follows (Scheme 2).

In this Scheme, the subscript w and m denote the substrate and hydroxide ions in the aqueous and micellar pseudophases, respectively. D_n is the micellized surfactant (D_n = [D] – cmc, where D is the total surfactant concentration). K_s is the binding constant for the esters with micelles and K_X^{OH} is equilibrium constant for the binding of bromide and hydroxide ions to the micellar surface. Mathematically, K_s and K_X^{OH} are given by Eqs. (4) and (5)

$$K_s = \frac{[S_m]}{[S_w][D_n]} \quad (4)$$

$$K_X^{OH} = \frac{[OH_w^-][X_m^-]}{[OH_m^-][X_w^-]} \quad (5)$$

In this expression, X_m^- and X_w^- are surfactant counterions existing in the micellar and aqueous phases, respectively. The values of K_X^{OH} can be obtained experimentally by employing some physical methods e.g. electrochemistry, ultrafiltration, using indicator etc. or by simulating the variation in rate (or equilibrium concentration) with surfactant concentration by taking the ion exchange constant as an adjustable parameter [6,23,25].

In accordance with the Scheme 2, the overall rate of reaction in terms of second order equation is given by:

$$k_\psi = \frac{k_2[OH_T^-](k_m K_s - k_2)m_{OH[D_n]}}{1 + K_s[D_n]} \quad (6)$$

Here, in Eq. (6), k_2 is the second order rate constant in the aqueous pseudophase and k_m is the second order rate constant in micellar pseudophase. k_m is usually expressed in terms of the molar ratio of OH$^-$ ions bound to the micellar head-groups and m$_{OH}$ is the micellar head group neutralized by the hydroxide ions. The reactions occurring in the presence of cationic micelles of CTABr or (CTA)₂SO₄, the reactive OH$^-$ ions bind with the micellar surface by replacing some of the counter Br$^-$ and SO$_4^{2-}$ ions. It results into increased local concentrations of OH$^-$ ions around the CTABr and (CTA)₂SO₄ micelles in the Stern's and Gouy–Chapman region. The distribution of OH$^-$ ions in the Stern region of micelles can be quantitatively estimated by using ion-exchange model. According to this model, it is assumed that; (a) the fraction of neutralized micellar head-group (β) (by the reactive OH$^-$ ions or non-reactive Br$^-$/SO$_4^{2-}$ ions) is constant when one of the ions in solution bind very strongly in comparison with others to a micellar headgroup, and (b) the reactive and non-reactive ions compete on the charged micellar surface depending upon the nature, charge density and their respective concentrations [20,23,25]. The values of m$_{OH}$ at different concentrations of micelles ([D_n]) in terms of total surfactant concentration, total OH$^-$ concentrations, and equilibrium constant (K_X^{OH}) can be expressed by the following quadratic Eq. (7)

$$m_{OH}^2 + m_{OH} = \left\{ \frac{[OH_T^-]K_X^{OH}[X_T^-]}{(K_X^{OH} - 1)[D_n]} - \beta \right\} - \frac{\beta[OH_T^-]}{(K_X^{OH} - 1),[D_n]}$$

$$= 0 \quad (7)$$

Here, β is the fraction of the micellar headgroup neutralized by surfactant counter ions and reactive OH$^-$ ions.

$$\beta = m_{OH} + m_x \quad (8)$$

The values of m_{OH} were calculated corresponding to different [surfactants] by simulating the values of K_X^{OH} in the range from 2 to 40 by using the quadratic Eq. (7) from the k_ψ–[surfactant] profile. The optimum values of K_X^{OH} was chosen for the minimum observed deviation. The values of k_m, K_s and K_X^{OH} from the k_ψ–[surfactant] profile were obtained and are given in Table 2. The observed results supported the validity of pseudophase ion exchange model for the alkaline hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitro-
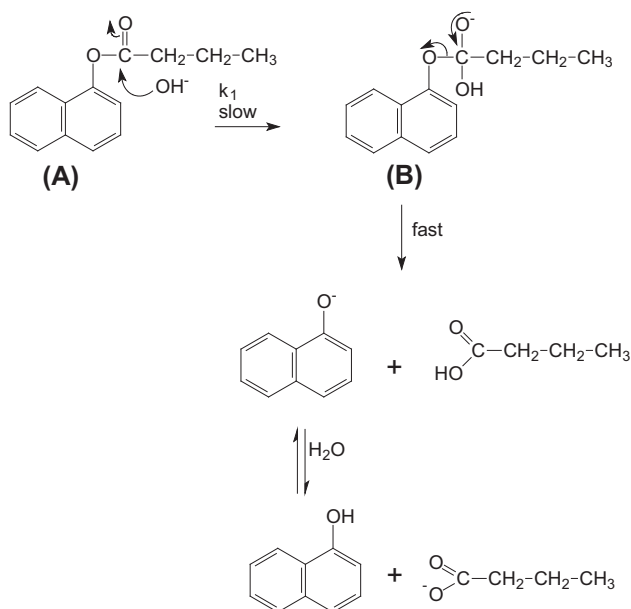
Scheme 1   Mechanism of hydrolysis of 1-naphthylbutyrate.

phenyl-carbonate in CTABr and (CTA)$_2$SO$_4$ micelles. The value of the equilibrium constant K_X^{OH} is dependent upon the microenvironment around the micelles e.g. surface potential, charge density of the reactive and counterions, ionic/molecular species present near the Stern layer etc. The obtained values of K_X^{OH} (= 16 for CTABr and = 22 for (CTA)$_2$SO$_4$) are found to be in the similar order of range as have been determined by earlier workers [1,23,25]. The higher values of K_X^{OH} for (CTA)$_2$-SO$_4$ may be due to the stronger binding of OH$^-$ ions with the micellar surface in comparison with the SO$_4^{2-}$ ions. The value of β was taken constant (0.81 for CTABr and 0.80 for (CTA)$_2$-SO$_4$) for the determination of the values of micellar rate constant k_m and binding constant K_s.

The rate of reaction decreases at higher surfactant concentrations in most of the micelle catalyzed bimolecular reactions. It may be due to the dilution of the reactant molecules in the micellar medium. Thus, at higher [surfactants], the total number of micelles is increased and the local molalities of the organic substrate and OH$^-$ ions in and around Stern layer of micellar surface are decreased. As a result, the net concentrations of reactant are diluted with the increase in the concentrations of surfactants and, thereby, causing a decrease in the reaction rate.

The inhibitive effect of SDS micelles on the reaction rate can be explained by applying the Berezin's pseudophase model
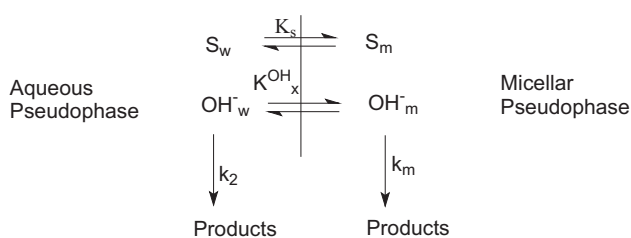
Scheme 2   Pseudophase ion exchange model for the reaction in aqueous and micellar media.

[8]. The inhibition in the observed reaction rate is attributed to the selective partitioning of reactant in the micellar region. According to it, one of the reactants (usually organic) is preferentially bound with the micelles while the other is repelled due to bearing the similar charges as on the micellar surface. The hydrophobic molecules or ions having dissimilar or opposite charges are attracted to the micellar surface while the highly hydrophilic molecules or ions having the similar charges are repelled. Thus, the inhibition in the rate of alkaline hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate is may be due to preferential binding of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitro-phenyl-carbonate with the SDS micelles. Also, at the same time the negatively charged OH$^-$ ions are being repelled by the negatively charged surface of DS$^-$ micelles. Thus, the distribution of the two reactive species in the different localities provides less chance for interaction between them and therefore, causes decrease in the reaction rate. The following Eq. (9) was used to determine the binding constant and the micellar rate constant from the rate-[SDS] profile.

$$\frac{1}{(k_w' - k_\psi)} = \frac{1}{(k_w' - k_m')} + \frac{1}{(k_w' - k_m')K_s[D_n]} \tag{9}$$

The values of K_s for the hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate were obtained from the slope using Eq. (9) and are given in Table 2.

The addition of salt to the reactant solution decreased the values of rate constant. The observed data were treated in accordance with Eq. (9) to determine the values of K_s and k_m in the presence of the added salt. The influence of salt on the values of rate constant provides an insight regarding the binding nature of organic substrate to the micelles. The plot of $\frac{1}{(k_w' - k_\psi)}$ *versus* $\frac{1}{[D_n]}$ was used to obtain the values of micellar rate constant and binding constant. Addition of salt of NaBr inhibited the rate of hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate in the presence of SDS, CTABr and (CTA)$_2$SO$_4$. The values of rate constant reached to almost negligible at [surfactant] $> 3.0 \times 10^{-3}$ mol dm^{-3} in the presence of 0.10 mol dm^{-3} NaBr. In surfactant solution, most of the ionic and polar species remain concentrated in the Stern and/or Gouy–Chapman region of micelles as counter ions or co-ions. Most of the ions compete for binding to the ionic micellar surface and cause accumulation of some ions preferentially over the other ions. As a result, partitioning and dilution of reactants including the OH$^-$ ions occur and an inhibition in reaction rates is observed (Table 3).

4.3. Comparison of reactions in micellar and aqueous pseudophases

The two sets of rate constants k_m (micellar rate constant) and k_w (aqueous rate constant) for the alkaline hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate cannot be directly compared as they represent them in different dimensions [11]. Apart from their different microenvironments, k_w symbolizes the concentration of organic reactants present in the aqueous pseudophase in moles per liter, whereas k_m signifies the rate constant in terms of concentration of reactants in molar ratio to micellar head groups. To

Table 2 Kinetic parameters obtained for the alkaline hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenyl-carbonate in micellar media.

Kinetic parameters	1-Naphthylbutyrate[a]			2-(Methylsulfonyl)-ethyl-4-nitrophenyl-carbonate[b]		
	SDS	CTABr	$(CTA)_2SO_4$	SDS	CTABr	$(CTA)_2SO_4$
β	–	0.81	0.80	–	0.81	0.80
K_X^{OH}	–	16	22	–	16	22
$k_m\ (s^{-1})$	0.02	19.89 ± 0.44	23.47 ± 0.32	0.022	55.4 ± 4.48	24.97 ± 4.37
K_s	658	680	520	181	120	280
k_2^m	–	2.78	3.29	–	7.756	3.50
k_2^m/k_w	–	6.87	8.12	–	0.39	0.17

Reaction conditions:
[a] [1-Naphthylbutyrate] $= 2.0 \times 10^{-5}$ mol dm^{-3} and [NaOH] $= 1.0 \times 10^{-2}$ mol dm^{-3}.
[b] [2-(Methylsulfonyl)-ethyl-4-nitrophenyl-carbonate] $= 1.0 \times 10^{-5}$ mol dm^{-3} and [NaOH] $= 3.0 \times 10^{-4}$ mol dm^{-3}, temperature $= 25.0 \pm 0.1$ °C.

Table 3 Kinetic parameters obtained for the alkaline hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenyl-carbonate in micellar media in the presence of salt.

[Surfactant] with salt	1-Naphthylbutyrate		2-(Methylsulfonyl)-ethyl-4-nitrophenyl-carbonate	
	$k_m\ (s^{-1})$	K_s	$k_m\ (s^{-1})$	K_s
CTABr + LiCl	–	–	2.20 ± 0.28	239
CTABr + NaBr	3.48 ± 0.48	140	0.57 ± 0.17	2907
CTABr + NaCl	5.37 ± 0.54	410	0.20 ± 0.13	441
CTABr + TEABr	1.89 ± 0.32	370	–	–
$(CTA)_2SO_4$ + NaBr	1.77 ± 0.24	580	0.83 ± 0.22	4892
$(CTA)_2SO_4$ + NaCl	7.05 ± 0.76	620	–	–
$(CTA)_2SO_4$ + TEABr	1.09 ± 0.16	430	–	–
SDS + NaBr	–	–	–	1565

Reaction conditions: [2-(methylsulfonyl)-ethyl-4-nitrophenyl-carbonate] $= 1.0 \times 10^{-5}$ mol dm^{-3}, [NaOH] $= 3.0 \times 10^{-4}$ mol dm^{-3}, [salt] $= 1.0 \times 10^{-1}$ mol dm^{-3}, [1-naphthylbutyrate] $= 2.0 \times 10^{-5}$ mol dm^{-3}, [NaOH] $= 1.0 \times 10^{-2}$ mol dm^{-3}, temperature $= 25.0 \pm 0.1$ °C.

compare the two rate constants, it is needed to include the volume element of the micellar pseudophase region in which reaction occurs (Romsted, 1982; [15]. The volume element of the Stern region is reported to be ~0.14 mol dm^{-3}. On the basis of the consideration of this volume element for the reactions occurring in the Stern layer of CTABr or $(CTA)_2SO_4$, the second order rate constant, k_2^m (mol^{-1} dm^3 s^{-1}) for the hydrolysis can be given by the following relationship (10);

$$k_2^m = 0.14\, k_m \tag{10}$$

The values of k_2^m are given in Table 2. The second order rate constant values for the hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenyl-carbonate in micellar pseudophase are higher than the values in aqueous pseudophase in CTABr and $(CTA)_2SO_4$ micelles.

5. Conclusion

The kinetics of alkaline hydrolysis of carboxylate ester (1-naphthylbutyrate) and carbonate ester (2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate) were studied in aqueous and micellar media. The rate of hydrolysis increased with the increase in [NaOH] and the plot of k_{obs} versus [NaOH] was found linearly dependent upon [NaOH]. The cationic micelles of CTABr and $(CTA)_2SO_4$ catalyzed the rate of reaction while an opposite influence was observed for anionic SDS micelles. The reaction started with the attack of OH$^-$ ions on the carbonyl carbon to form tetrahedral intermediate which collapses

immediately to yield respective acid and alcohol. The observed result for the catalytic effect of [CTABr] and [(CTA)$_2$SO$_4$] micelles was treated by applying pseudophase ion exchange model. The rate–[surfactant] profile was used to determine kinetic parameters like k_m, K_s etc. The observed data were treated on the basis of Menger–Portnoy model for the inhibitive effect of SDS. The added salts viz. NaBr, NaCl, and LiCl inhibited the rate of the reaction in the presence of micelles.

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