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Micellar effects upon the rate of alkaline hydrolysis of triflusal

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ABSTRACT

The rate of hydrolysis for triflusal was measured at varying concentrations of NaOH at four different temperatures (i.e. 25, 35, 45 and 55 °C). The micelles of cetyltrimethylammonium bromide (CTABr), cetyltrimethylammonium chloride (CTACl), cetyltrimethylammonium hydroxide (CTAOH) and dodecyltrimethyl-ammonium bromide (DTABr) had catalytic effect on the rate of hydrolysis. CTABr, CTACl and DTABr gave maxima like curve for the rate–[surfactant] plot while CTAOH gave plateau like curve. The anionic sodium dodecyl sulfate (SDS) did not influence the rate of alkaline hydrolysis of triflusal. The non-ionic Brij-35 inhibited the rate of the hydrolytic reaction. The catalytic effect by cationic micelles was treated by applying the pseudophase ion exchange model while the inhibitive effect by non-ionic micelles has been described by using the Poisson–Boltzmann pseudophase model. The variation in k_ψ with the change in [surfactant] was used to determined various kinetic parameters e.g., binding constant (K_s), and micellar rate constant (k_m). The addition of electrolytes decreased the reaction rate in CTABr and CTAOH micelles.

1. Introduction

The surfactant molecules above its critical micellar concentration (cmc) in polar solvents like water aggregate together to form micelles. Micelles have the tendency to influence the rate of reaction through aggregating the reactants in smaller volumes causing catalysis or partitioning the reactants in different localities, thereby, resulting into the inhibitive effect [1–4]. The magnitude of catalysis or inhibition largely depends upon the nature of interaction between the surfactant and reactants. However, the factors like orientation of substrate in the micelles, concentration of reactants in the interfacial region, local charge, polarity, water content, and ionic environment around the micelles also play key role on the ability of micelles to influence the reaction rates [5–10]. The rates of reaction are altered in the presence of micelles through the localization, delocalization or dispersion of charges on the substrates' ground state or activated states. The use of surfactants is increasing in the pharmaceutical formulations owing to its ability to lower the surface tension of a liquid, allowing easier spreading, and possessing the tendency to lower the interfacial tension between two liquids [10–12]. Thus, the surfactants enhance the permeability of drugs across biological membranes. Two primary considerations arise in using surfactants to enhance drug transport across biological membranes. The surfactants in the pharmaceutical preparations are also used to solubilize the drugs and to provide stability. However, the surfactants are not the inert additives and may lead to significant changes in the biological activity of the active agents. The kinetics method is among the important tools to study and predict the physico-chemical interactions between drug molecules and surfactants in solution. The surfactant molecules possess both the hydrophilic and hydrophobic parts. The nature of interactions between the drug molecules and the surfactant molecules (through the hydrophilic and hydrophobic parts) is important with the perspective of the solubilization and stabilization of drugs against degradation during its transportations in the biological systems [13–15].

The surfactant aggregates behave like biological fluids and enzymes structurally and functionally. Therefore, the kinetics studies on the alkaline hydrolysis of triflusal in the absence and presence of micelles of cationic, anionic and nonionic surfactants will be helpful in understanding the nature of interaction between triflusal and surfactant molecules. Triflusal, chemically known as 2-acetyloxy-4-trifluoromethyl benzoic acid, is structurally related to acetylsalicylic acid, but, it is not derived from aspirin (acetylsalicylic acid). Triflusal inhibits cycloxygenase-1 in platelets and also favors the production of NO and increases the concentration of cyclic nucleotides [16,17]. It is administered orally and gets absorbed in the small intestine. It binds to plasma proteins (99%) and crosses organic barriers readily [18,19]. Keeping in views of these properties, the present work was undertaken to explore the nature physico-chemical interaction between triflusal and surfactant molecules kinetically. The enhancement in the rate of hydrolysis by cationic micelles was explained on the basis of pseudophase ion exchange model while for the inhibitive effect by non-ionic Brij-35 was explained on the basis of Poisson–Boltzmann pseudophase model [20–23].

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2. Experimental

2.1. Materials

Triflusal was obtained from Inquiry Chemical International with purity higher than 99%. Cetyltrimethylammonium bromide (CTABr, 99%, Aldrich), sodium dodecyl sulfate (SDS, 99%, BDH, England), sodium bromide (99%, BDH, England) and sodium chloride (99%, BDH, England), and polyoxyethylenlaurylether (Brij-35, 97%, MERCK-Schuchardt, Germany) were used without further purification. Cetyltrimethylammonium sulfate (CTAOH) and cetyltrimethylammonium chloride (CTACl) were synthesized and crystallized in the laboratory as described earlier [24]. Dodecyltrimethyl ammonium bromide (DTABr) was synthesized in the laboratory by adding 1-bromododecane (0.1 mol) to trimethylamine (0.1 mol) dissolved in 100 ml isopropyl alcohol. The mixture was refluxed for 48 h. Isopropyl alcohol was removed by distillation and the remaining solvent was evaporated by using rotary evaporator. The dried product was recrystallized from absolute alcohol–dry ethyl ether (M.P. = 248 °C). Sodium hydroxide of Anal R grade was used during the experiments. Deionized double-distilled water (specific conductance: $1–2 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$) was used throughout the experimental work.

2.2. Kinetic measurements

The kinetics of the hydrolysis of triflusal was carried out under varying experimental conditions by monitoring the change in absorbance using a Lambda 45 double beam UV–visible spectrophotometer. The temperature was maintained constant (±0.1 °C) by using L.K.B. 2209 multi-temperature water bath. The required amounts of the triflusal and sodium hydroxide (and surfactant, salt) solutions were taken into 3 ml quartz cuvette having the path length of 1 cm. The reaction was started with the addition of calculated amount of triflusal dissolved in CH_3CN in the pre-equilibrated solution containing sodium hydroxide, surfactant, salt etc. at the desired temperature. The increase in absorbance was measured at $\lambda_{max} = 308$ nm and the reaction was followed until its completion to 3–4 half-lives period. All the kinetic runs were performed under the pseudo first order reaction condition in which the concentration of sodium hydroxide was kept large excess over [triflusal]. The values of pseudo first order rate constant (k_{obs}, s^{-1}; for aqueous and k_{ψ}, s^{-1}; for micelles) were calculated from the slopes of plots of ln (A_∞–A_t) versus time with average linear regression coefficient, $r^2 \geq 0.98$. The kinetic runs were repeated at least thrice and the observed results were reproducible within ±5%.

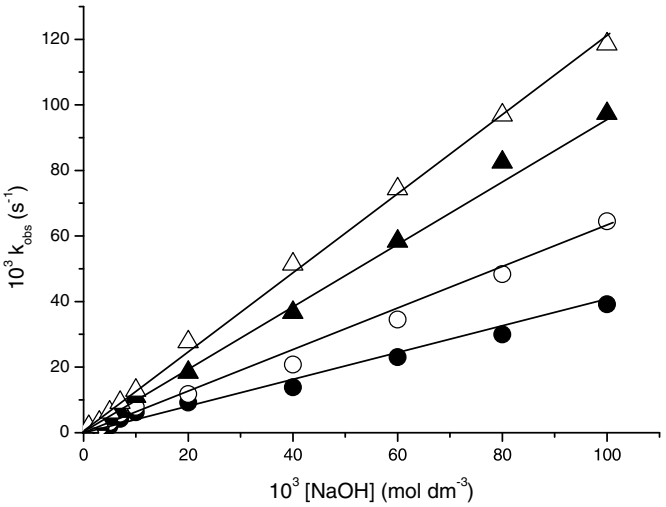


Fig. 2. Plot of k_{obs} vs. [NaOH] for the hydrolysis of triflusal at different temperatures (●; 25.0 ± 0.1 °C, ○; 35.0 ± 0.1 °C, ▲; 45.0 ± 0.1 °C; Δ; 55.0 ± 0.1 °C). Reaction conditions: [triflusal] = 8.0×10^{-5} mol dm^{-3}.

3. Results and discussion

3.1. Hydrolysis of triflusal in aqueous media

Fig. 1 depicts the repetitive scans of hydrolysis of triflusal (= 8.0×10^{-5} mol dm^{-3}) by 5.0×10^{-2} mol dm^{-3} sodium hydroxide at 25.0 ± 0.1 °C. The spectra were recorded at the interval of 2 min. The peak value of absorbance increased with the progress of hydrolysis at 308 nm. The spectra had two well-defined isobestic points at 256 nm and 275 nm. The dependence of rate of reaction on [NaOH] was

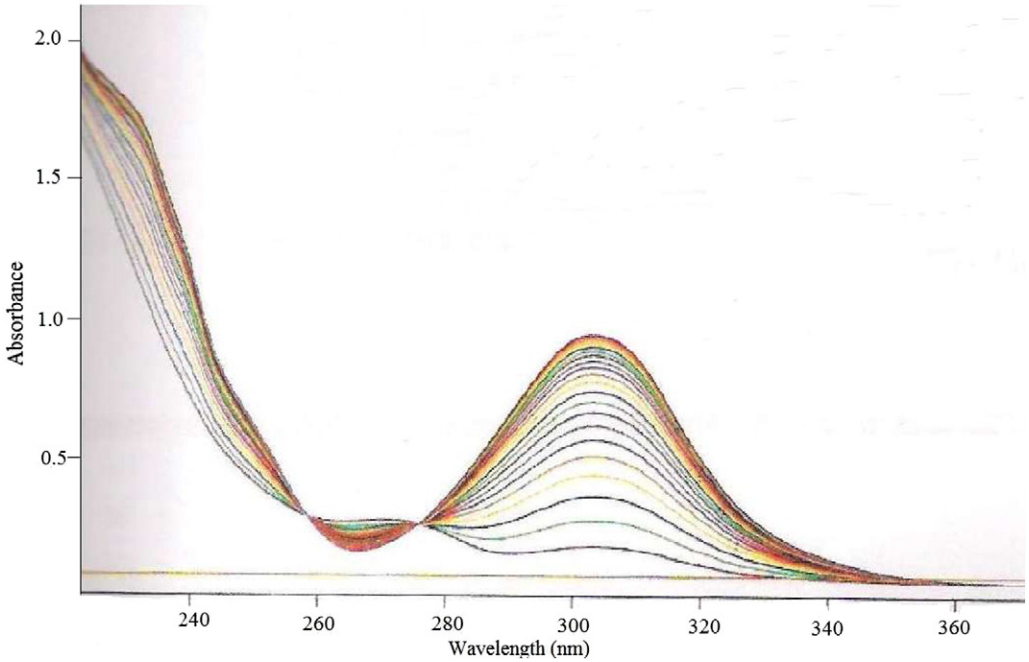
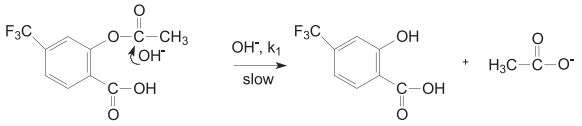


Fig. 1. Repetitive scans of triflusal (= 8.0×10^{-5} mol dm^{-3}) in 5.0×10^{-2} mol dm^{-3} sodium hydroxide at 25.0 ± 0.1 °C. The scans were recorded at the gap of 2 min.



Scheme 1. Proposed mechanism for the alkaline hydrolysis of Triflusal.

determined by carrying out kinetic experiments at different concentrations of NaOH varied from 1.0×10^{-3} mol dm^{-3} to 1.0×10^{-1} mol dm^{-3} keeping the concentration of triflusal constant at 8.0×10^{-5} mol dm^{-3} at 25.0 ± 0.1 °C. The dependence of pseudo first order rate constant on [NaOH] was determined at four different temperatures viz. 25, 35, 45 and 55 ± 0.1 °C. It was observed that the values of rate constant were linearly dependent upon [NaOH] at these temperatures as shown in Fig. 2.

The hydrolysis of ester by OH^- ions is a nucleophilic acyl substitution reaction. The acyl substitution reaction starts with the nucleophilic attack of OH^- ions on the carbonyl carbon atom with the formation of a tetrahedral intermediate. Thus, formed tetrahedral intermediate is highly unstable and collapses immediately to yield final product with the loss of an acetate ion. Therefore, the attack of OH^- ions on the carbonyl carbon atom of triflusal is considered to be the rate determining step. The mechanism of hydrolysis of triflusal by sodium hydroxide is presented in Scheme 1.

The following rate equation was used to relate the rate of reaction with concentration of triflusal and hydroxide ion:

$$\text{Rate} = -\frac{d[\text{triflusal}]}{dt} = k_1\,[\text{triflusal}][OH-] \quad (1)$$

Where, k_1 is the first order rate constant. Eq. (1) can be rewritten as:

$$\frac{dP}{dt} = k_{obs}[A]_T \quad (2)$$

Where,

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

The reaction is bimolecular in nature and the second order rate constant (k_2) was determined from the slope of k_{obs} versus [NaOH].

$$k_{obs} = k_2\,[\text{NaOH}] \quad (4)$$

The plots of k_{obs} versus [NaOH] at different temperatures are given in Fig. 2. The values of the second-order rate constants (k_2) are given in Table 1.

3.2. Hydrolysis of triflusal in micellar media of CTABr, CTACl and DTABr

Fig. 3 depicts the variation in the values of the observed rate constant with the variation in concentrations of CTABr, CTACl and DTABr. In the presence of these surfactants, the plots of k_ψ–[surfactant] gave a maxima like curve indicating the bimolecular nature of alkaline hydrolysis of triflusal. The rate of hydrolysis increases with the increase in concentration of CTABr/CTACl/DTABr, reaches to a maximum value and, then decreases on further increasing the concentration of

Table 1
Values of the second order rate constant for the alkaline hydrolysis of triflusal at different temperatures.

Temperature (°C)	k_2 ($mol^{-1}\,dm^3\,s^{-1}$)
25.0	0.374
35.0	0.615
45.0	0.991
55.0	1.194

[Triflusal] = 8.0×10^{-5} mol dm^{-3}.

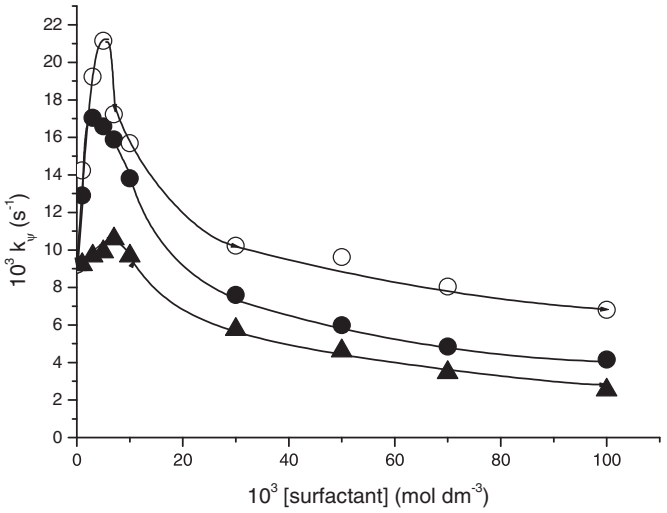


Fig. 3. Plot of k_ψ vs. [surfactant] for the alkaline hydrolysis of triflusal in surfactant media (●; CTABr, ○; CTACl, ▲; DTABr). Reaction conditions: [triflusal] = 8.0×10^{-5} mol dm^{-3}, [NaOH] = 2.0×10^{-2} mol dm^{-3}, Temperature = 25.0 ± 0.1 °C.

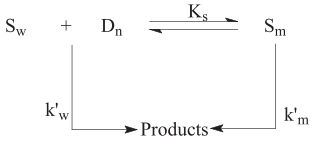
surfactant. The variation in the rate of hydrolysis with the change in surfactant concentration is contributed by two major factors. Firstly, the hydrolysis of triflusal occurs into both the aqueous and micellar pseudophases with different rates and, secondly, the amounts of the reactants (triflusal and OH^- ions) distributed in the aqueous and micellar pseudophases. The distribution of triflusal and OH^- ions in the aqueous and micellar pseudophases depends upon the binding constant and the concentration of surfactant. Therefore, for the quantitative analysis of the plot of k_ψ versus [surfactant], it is needed to (i) evaluate the values of rate constants in each aqueous and micellar pseudophases, and (ii) estimate the quantities of reactants in the aqueous and micellar pseudophases. In the presence of surfactant, the organic and inorganic substrates are distributed in the micellar and aqueous pseudophases according to their hydrophilic and hydrophobic affinities. The partitioning of triflusal into the aqueous and micellar pseudophases can be represented by the following equation.

$$S_w + D_n \overset{K_s}{\rightleftharpoons} S_m \quad (5)$$

In this equation, K_S is called binding constant, S_m is the amounts of triflusal associated with the micellar pseudophase and S_w is unbound triflusal existing in the aqueous pseudophase. D_n is the equilibrium concentration of surfactants aggregated in the form of micelles (i.e. D_n = [Surfactant] − cmc). K_S is related to S_m and S_w as follows:

$$K_s = \frac{[S_m]}{[S_w][D_n]}. \quad (6)$$

The mechanism of the hydrolysis of triflusal occurring in the presence of micelles is shown in Scheme 2. The representative mechanism demonstrate that the hydrolysis of triflusal is occurring in the aqueous and in micellar pseudophases with the values of rate constants k_w' and k_m', respectively.



Scheme 2. Mechanism of alkaline hydrolysis of Triflusal in the presence of surfactant.

Corresponding to Scheme 2, the overall observed value of rate constant is given by;

$$k_\psi = \frac{k'_w + k'_m K_s\,[D_n]}{1 + K_s[D_n]}. \quad (7)$$

The values of first order rate constant in terms of concentration of OH^- ions in the aqueous pseudophase can be expressed by Eq. (8).

$$k'_w = k_2\,[OH^-_w] \quad (8)$$

k_2 is the second order rate constant in the aqueous pseudophase. In micellar pseudophase, the first order micellar rate constant (k'_m) is related to the concentration of OH^- ions bound with the micellar head group through Eq. (9) in which k_m represents the second order micellar rate constant.

$$k'_m = \frac{k_m\,[OH^-_m]}{[D_n]} \quad (9)$$

Thus, putting the values of k'_w and k'_m from Eqs. (8) and (9), respectively, in Eq. (7), we get Eq. (10). This equation mathematically relates the overall values of observed rate constant with the surfactant concentration, concentration of reactants in each pseudophases and the values of rate constant in the aqueous and micellar pseudophases.

$$k_\psi = \frac{k_2\,[OH^-_T] + (k_m K_s - k_2)m_{OH}[D_n]}{1 + K_s[D_n]} \quad (10)$$

The distribution of OH^- ions in the aqueous and micellar pseudophases can be estimated by using the ion exchange equations. It is assumed that an ion exchange process takes place between the reactive OH^- ions and the micellar counter ions (Br^- or Cl^-) at the micellar surface, an analogy with the exchange reaction at ion exchange resin surface. CTABr, CTACl and DTABr are cationic surfactant with positively charged micellar surface. Both, the reactive OH^- ions and the non-reactive counterions of the surfactant (Br^- or Cl^- ions) compete for binding to the micellar surface. The amount of OH^- ions and Br^-/Cl^- ions in the Stern layer of CTA^+ micelles can be estimated by using the following ion exchange reaction [25,26].

$$X^-_w + OH^-_m \underset{}{\overset{K_X^{OH}}{\rightleftharpoons}} X^-_m + OH^-_w \quad (11)$$

The equilibrium constant, K_X^{OH} predicts the distribution of surfactant counterions (X = Br^- or Cl^- ions) and the reactive OH^- ions in the aqueous and micellar pseudophases by,

$$K_X^{OH} = \frac{[X^-_m][OH^-_w]}{[X^-_w][OH^-_m]}. \quad (12)$$

The micellar surfaces of ionic micelles are not fully neutralized. Most of the counterions/co-ions lie in and around micellar surface in the Stern layer and Gouy–Chapman layer. The total fractions of the micelle surface that are neutralized with the counterions or reactive ions

Table 2
Fitted parameters of the kinetic results for the alkaline hydrolysis of triflusal in CTABr, CTACl and DTABr.

Surfactant	β	K_X^{OH}	$10^2\,k_m$ ($mol^{-1}\,dm^3\,s^{-1}$)	K_s
CTABr	0.80	18	11.32 ± 0.11	184
CTACl	0.80	11	13.78 ± 0.26	106
DTABr	0.80	16	2.29 ± 0.03	66

Reaction conditions: [Triflusal] = 8.0×10^{-5} mol dm^{-3}, [NaOH] = 2.0×10^{-2} mol dm^{-3}, Temperature = 25.0 ± 0.1 °C.

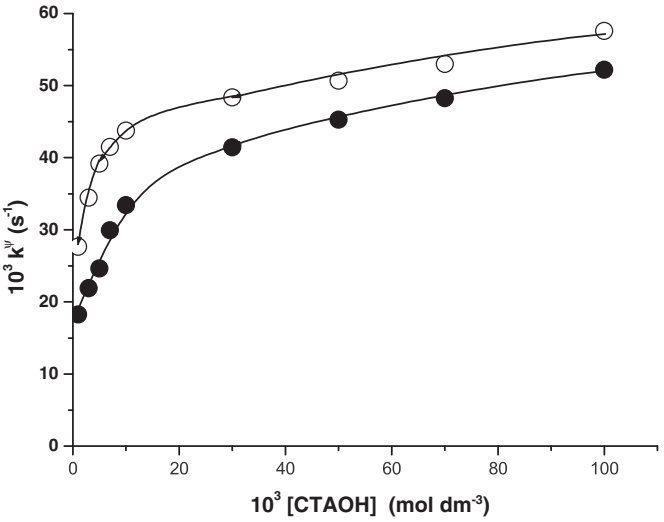


Fig. 4. Plot of k_ψ vs. [CTAOH] for the hydrolysis of triflusal without added NaOH(●) and with NaOH (○; 2.0×10^{-2} mol dm^{-3}). Reaction conditions: [triflusal] = 8.0×10^{-5} mol dm^{-3}, Temperature = 25.0 ± 0.1 °C.

depend upon the charge density on the ions and on the ionic environment around the micelles. But, in most of the cases ~80% of the ionic micellar headgroups are neutralized by the counterions of surfactants and reactive ions. The total fraction of the headgroup neutralized by the opposite ions, β, is the sum of the fractions of the micellar headgroup neutralized by the reactive OH^- ions (m_{OH}) and non-reactive surfactant counterions Br^- or Cl^- (m_X).

$$\beta = m_{OH} + m_X \quad (13)$$

The micelles bound total OH^- ions is related to the fractions of the OH^- ions that neutralizes headgroup of the ionic micelles is given by;

$$m_{OH} = \frac{[OH^-_m]}{[D_n]}. \quad (14)$$

Similarly, the micelles bound total X^- ions can be given by

$$m_X = \frac{[X^-_m]}{[D_n]}. \quad (15)$$

The following mass balance Eqs. (16) and (17) give the total concentrations of reactive OH^- ions and non-reactive counterions (Br^- or Cl^-) dispersed in the aqueous and micellar pseudophases are;

$$[OH^-_T] = [OH^-_w] + [OH^-_m] \quad (16)$$

$$[X^-_T] = [X^-_w] + [X^-_m]. \quad (17)$$

Putting the values of m_{OH} and m_X in Eq. (13), we get:

$$\beta = \frac{[OH^-_m]}{[D_n]} + \frac{[X^-_m]}{[D_n]} = \frac{[X^-_m] + [OH^-_m]}{[D_n]}. \quad (18)$$

On putting the values of $[X^-_m]$ and $[OH^-_m]$ in terms of their total concentrations as presented in Eqs. (16)–(17) in Eq. (12), we get the

$$S + D_n \underset{}{\overset{K_{CTAOH}}{\rightleftharpoons}} SD_n$$

$$SD_n \xrightarrow{k_{ctaoh}} \text{Products}$$

Scheme 3. Mechanism of hydrolysis in the presence of CTAOH.

Table 3
values of k_{ctaoh} and K_{CTAOH} obtained from the intercept and slope using Eq. (21).

[NaOH] (mol dm^{-3})	$10^2 k_{ctaoh}$	K_{CTAOH}
0	5.05	11.42
0.2	5.37	31.45

Reaction conditions: [Triflusal] = 8.0×10^{-5} mol dm^{-3}, Temperature = 25.0 ± 0.1 °C.

following quadratic equation. On solving Eq. (19), the value of m_{OH} corresponding to each surfactant concentration can be obtained.

$$m_{OH}^2 + m_{OH}\left\{\frac{[OH_T^-] + K_X^{OH}[X_T^-]}{(K_X^{OH}-1)[D_n]} - \beta\right\} - \frac{\beta[OH_T^-]}{(K_X^{OH}-1)[D_n]} \quad (19)$$

The values of m_{OH} at different surfactant concentrations were used to obtain the values of k_m and K_s (from Eq. (10)) for minimum deviation by varying the values of K_{Br}^{OH} in the range between 2 and 40 [27,28]. The values of these parameters obtained in the presence of CTABr, CTACl and DTABr micelles at different temperatures are given in Table 2. The maxima like curves for CTABr, CTACl and DTABr micelles catalyzed reactions imply that the rate increases with the increase in [surfactant] due to increase in the local molalities of reactants. After reaching maxima, the rate of hydrolysis decreases with the further increase in [surfactant] because the added micelles dilute the concentration of reactants in the micellar pseudophase.

3.3. Hydrolysis of triflusal in CTAOH micelles

The values of observed rate constant, k_ψ increased with increase in [CTAOH] and gave plateau like curve (Fig. 4). The OH^- ions of the reactive surfactant are distributed in aqueous and micellar pseudophases and the hydrolysis of triflusal occurs in these pseudophases. The variation of k_ψ with the change in [CTAOH] in the absence and the presence of NaOH can be treated similar to the enzyme catalyzed reactions following the mechanism proposed in Scheme 3.

Corresponding to Scheme 3, we get the following rate equation

$$k_\psi = \frac{k_{ctaoh} K_{CTAOH}[D_n]}{1 + K_{CTAOH}[D_n]}. \quad (20)$$

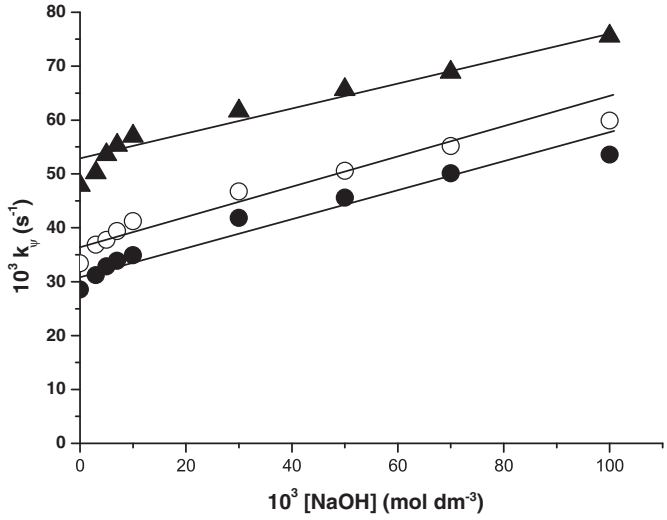


Fig. 5. Plot of k_ψ vs. [NaOH] for the hydrolysis of triflusal at different [CTAOH] (●; 5.0×10^{-3} mol dm^{-3}, ○; 1.0×10^{-2} mol dm^{-3}, ▲; 5.0×10^{-2} mol dm^{-3}). Reaction conditions: [triflusal] = 8.0×10^{-5} mol dm^{-3}, Temperature = 25.0 ± 0.1 °C.

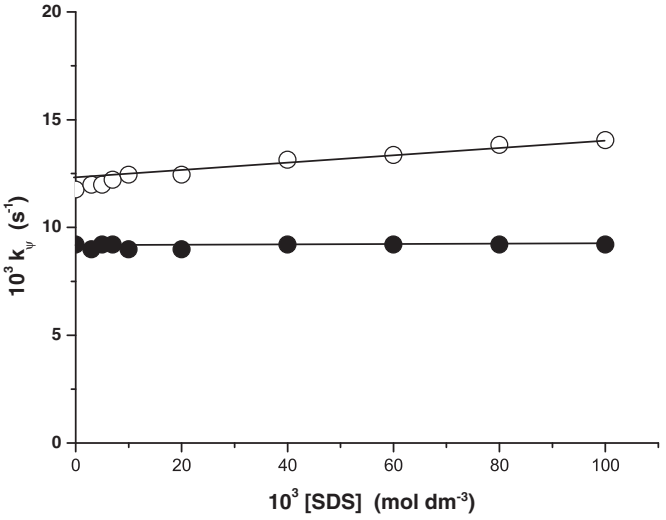


Fig. 6. Plot of k_ψ vs. [SDS] for the alkaline hydrolysis of triflusal in SDS at 25.0 ± 0.1 °C (●) and 35.0 ± 0.1 °C (○). Reaction conditions: [triflusal] = 8.0×10^{-5} mol dm^{-3}, [NaOH] = 2.0×10^{-2} mol dm^{-3}.

On inverting Eq. (20), we get Eq. (21):

$$\frac{1}{k_\varphi} = \frac{1}{k_{ctaoh}} + \frac{1}{K_{CTAOH}[D_n]}. \quad (21)$$

The plot of $\frac{1}{k_\varphi}$ versus $\frac{1}{[D_n]}$ gave straight line in accordance with Eq. (21) and the values of k_{ctaoh} and K_{CTAOH} were obtained from the intercept and slope, respectively. The values are given in Table 3. The addition of NaOH increased the rate of reaction due to increase in the concentration of reactive OH^- ions (Fig. 5).

3.4. Hydrolysis of triflusal in SDS and Brij-35 micelles

No significant variation in the values of rate constant was observed with the variation in concentration of SDS micelles as shown in Fig. 6. The micelles of non-ionic surfactant Brij-35 inhibited the rate of hydrolysis of triflusal (Fig. 7). The inhibitive effect by Brij-35 on the rate of hydrolysis of triflusal can be due to the partitioning of triflusal and OH^- ions in the different localities i.e. aqueous and micellar

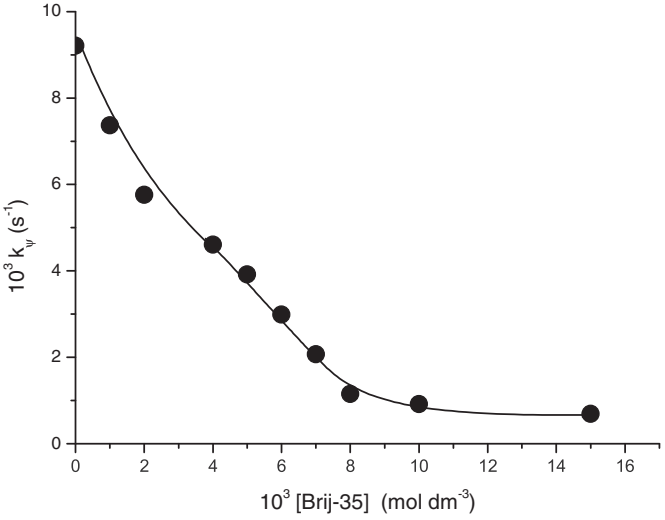


Fig. 7. Plot of k_ψ vs. [Brij-35] for the alkaline hydrolysis of triflusal. Reaction conditions: [triflusal] = 8.0×10^{-5} mol dm^{-3}, [NaOH] = 2.0×10^{-2} mol dm^{-3}, Temperature = 25.0 ± 0.1 °C.

pseudophases. The increase in concentration of Brij-35 incorporates more and more amount of triflusal molecules into the Brij-35 micelles and, thereby, decreasing the amount to triflusal in aqueous pseudophases. At the same time, the negatively charged OH^- ions are repelled by the electronegative polyoxyethylenated alcohol group of the Brij-35 micelles and its major proportions exist in the aqueous phase. As a result, triflusal and OH^- ions are predominantly distributed in the retroactive micellar and aqueous pseudophases. The chance of interaction between triflusal and OH^- ions is decreased and thus, causing the inhibition in the rate of hydrolysis with the increase in Brij-35 micelles. Additionally, the other factors like lower water activity in the Stern layer, the stabilization of substrate by the micelles, destabilization of the transition state, and unfavorable orientation of the substrate may also contribute in lowering the rate of reaction. The rearrangement of Eq. (7), gives Eq. (23):

$$\frac{1}{k'_w - k_\psi} = \frac{1}{k'_w - k'_m} + \frac{1}{(k'_w - k'_m)\, K_s\, [D_n]}. \quad (23)$$

The k_ψ–[Brij-35] profile shows that the rate of hydrolysis of triflusal decreases and becomes extremely slow at [Brij-35] > 8.0×10^{-3} mol dm^{-3}. From the analysis of these data, it can be inferred that with the increase in concentration of Brij-35 the observed rate constant decreases progressively, because more and more triflusal molecules are incorporated inside the micelles. The observed rate constant in the presence of micelles is due to the reaction of aqueous triflusal molecules with OH^- ions and so, the value of micellar rate constant can be neglected in the above equation (Bunton and Cerichelli [29]). Eq. (23) can be rewritten in the form of Eq. (24) after eliminating the term 'k_m' in the above equation:

$$\frac{1}{k'_w - k_\psi} = \frac{1}{k'_w} + \frac{1}{k'_w\, K_s\, [D_n]}. \quad (24)$$

Thus, according to Eq. (24), a plot of $\frac{1}{k'_w - k_\psi}$ versus $\frac{1}{[D_n]}$ should give a straight line with intercept at $\frac{1}{k'_w}$ and slope $= \frac{1}{k'_w\, K_s}$. The value of K_s was calculated from this plot and the values are given in Table 4.

3.5. Hydrolysis of triflusal in the presence of salt

The rate of hydrolysis of triflusal decreased with the increasing concentrations of NaBr, $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$ in the presence of 6.0×10^{-3} mol dm^{-3} CTABr (Fig. 8). Similarly, the salts of NaBr, NaCl, and CH_3COONa decreased the rate of hydrolysis in the presence of CTAOH micelles (Fig. 9). The inhibitive effect by CTABr and CTAOH micelles may be attributed to the substitution of the reactive OH^- ions by the nonreactive ions from the Stern layer. The addition of salts alter the polarity of the micellar surface potential and thereby, altering the rate of reactivity. After, certain concentrations of salt the hydroxide ions are almost completely excluded from the micellar surface by the nonreactive anions and results into the decrease in the reaction rate. The k_ψ–[CTABr] and k_ψ–[CTAOH] profiles for the hydrolysis of triflusal were treated in terms of pseudophase model and the kinetic parameters were determined using Eq. (20). Besides the partitioning of the reactants in the different pseudophases, the added salt may increase the aggregation number of micelles or modify the micelle structure by extending the hydrocarbon chain. The size of micelles increases, resulting into the entrance of more and more organic substrate into the interior of micelles.

Table 4
Values of k'_w and K_s obtained from the intercept and slope using Eq. (24) for the hydrolysis of triflusal in Brij-35.

$10^2 k'_w (s^{-1})$	9.05
K_s	916.43

Reaction conditions: [Triflusal] = 8.0×10^{-5} mol dm^{-3}, [NaOH] = 2.0×10^{-2} mol dm^{-3}, Temperature = 25.0 ± 0.1 °C.

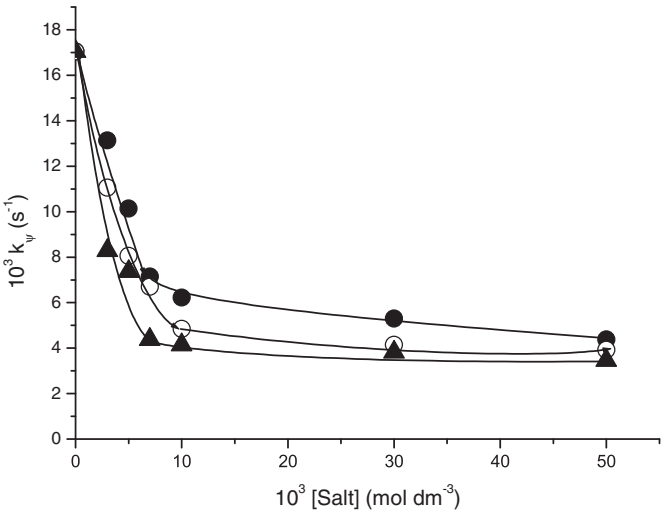


Fig. 8. Plot of k_ψ vs. [salt] for the alkaline hydrolysis of triflusal in the presence of different salt (●; NaBr, ○; $(CH_3)_4NBr$, ▲; $(C_2H_5)_4NBr$) in CTABr. Reaction conditions: [triflusal] = 8.0×10^{-5} mol dm^{-3}, [NaOH] = 2.0×10^{-2} mol dm^{-3}, Temperature = 25.0 ± 0.1 °C.

4. Conclusion

The increase in the concentration of cationic surfactants (CTABr, CTACl, and DTABr) increased the rate of hydrolysis in the lower concentration ranges. The further increase in [surfactant] decreased the values of rate constant, thus, giving maxima like curves for k_ψ–[surfactant] profile. The k_ψ versus [CTAOH] gave plateau like curve in which the rate of reaction increased with the increase in surfactant and then reached to a constant value. The anionic SDS did not influence the rate of reaction while the non-ionic Brij-35 inhibited the rates of alkaline hydrolysis of triflusal. The presence of micelles of CTABr, CTACl and DTABr increased the local molalities of organic substrate and OH^- ions in the interfacial region, thereby, increasing the reaction rate. The amounts of reactants in the micellar region were quantitatively estimated using the pseudophase ion exchange model. The inhibitive

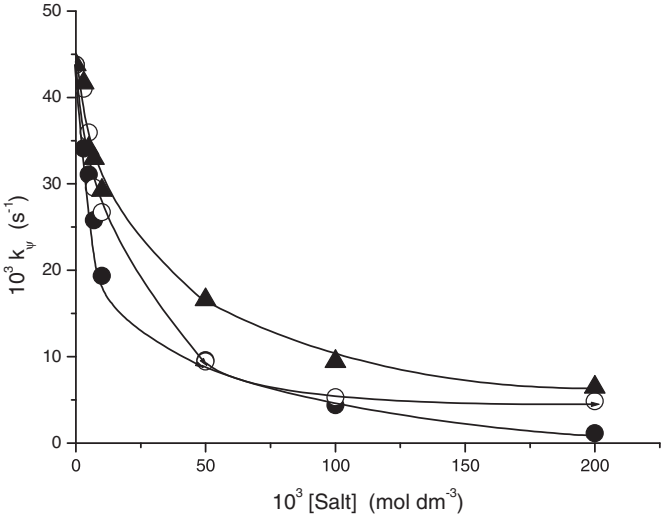


Fig. 9. Plot of k_ψ vs. [salt] for the alkaline hydrolysis of triflusal in the presence of different salt (●; NaBr, ○; NaCl, ▲; CH_3COONa) in CTAOH. Reaction conditions: [triflusal] = 8.0×10^{-5} mol dm^{-3}, [NaOH] = 2.0×10^{-2} mol dm^{-3}, Temperature = 25.0 ± 0.1 °C.

effect by Brij-35 was dealt with the model partitioning the reactants in the micellar and aqueous pseudophases, respectively. The addition of electrolytes like NaBr, $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$ decreased the values of rate constants in the micellar media. The presence of electrolytes excludes the reactive OH^- ions from the vicinity of reactive Stern layer region, and, thus lowers the chance of interaction between the organic molecules and OH^- ions.

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