Journal of Molecular Liquids 206 (2015) 321–327

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Micellar effects upon the rate of alkaline hydrolysis of triflusal

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ARTICLE INFO

Article history:
Received 11 January 2015
Received in revised form 15 February 2015
Accepted 1 March 2015
Available online 4 March 2015

Keywords:
Triflusal
Alkaline hydrolysis
Micellar effects
CTABr
CTACl
SDS
Brij-35

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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http://dx.doi.org/10.1016/j.molliq.2015.03.006
0167-7322/

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%.

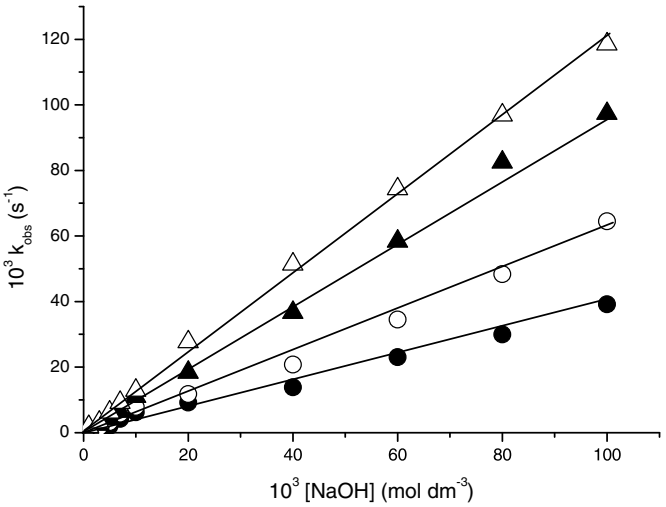
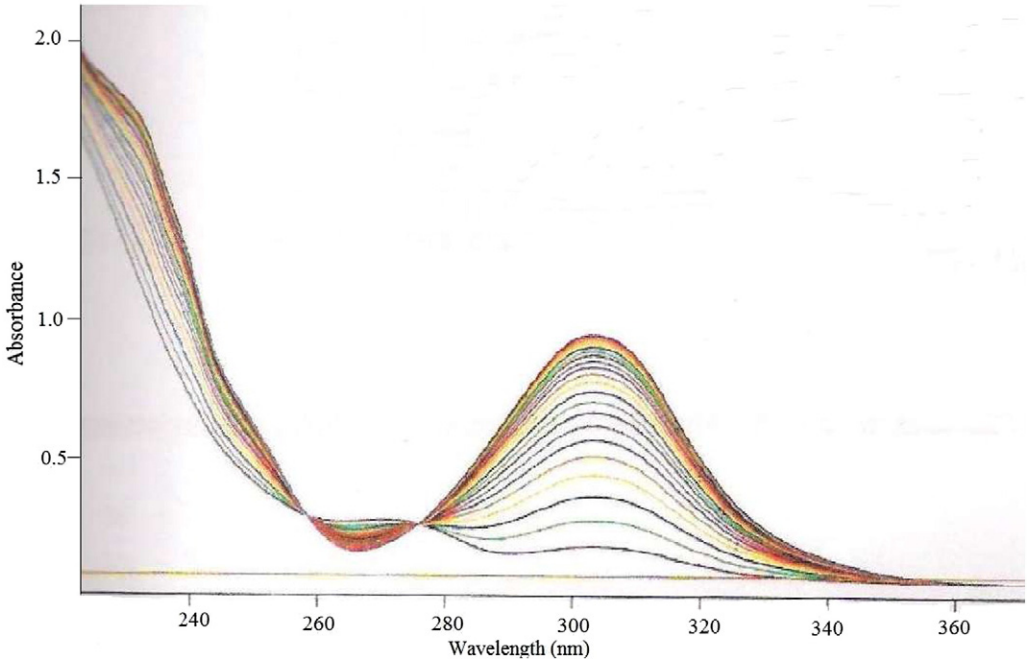


Fig. 2. Plot of k_{obs} vs. [NaOH] for the hydrolysis of triflusal at different temperatures (●; 25.0 ± 0.1 °C, ○; 35.0 ± 0.1 °C, ▲; 45.0 ± 0.1 °C; Δ; 55.0 ± 0.1 °C). Reaction conditions: [triflusal] = 8.0×10^{-5} mol dm^{-3}.

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



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