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SHORT COMMUNICATION

Kinetics of the acid hydrolysis of isoproturon in the absence and presence of sodium lauryl sulfate micelles

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Abstract Kinetics of the hydrolysis of isoproturon by hydrochloric acid has been studied spectrophotometrically in the absence and the presence of anionic sodium lauryl sulfate (NaLS) micelles. The anionic micelle was found to increase the rate of reaction. The reaction followed first-order kinetics with respect to isoproturon and was linearly dependent upon [HCl]. In both aqueous and micellar pseudophases, the reaction was started with the protonation of the amino group of isoproturon followed by attack of water to yield phenylcarbamic acid and the corresponding amine, thus obeying the addition–elimination mechanism. The surfactant decreased the activation entropy. The binding constant in consistence with the rate constants was evaluated on the basis of pseudophase ion-exchange model. The added salts (NaCl and KCl) decreased the rate of reaction due to the exclusion of H^+ from micellar surfaces.

Keywords Surfactant · Sodium lauryl sulfate · Isoproturon · Hydrolysis

Introduction

Micelles and other association colloids, such as reverse micelles and microemulsions, are dynamic aggregates of non-ionic, ionic or zwitterionic surfactants that form transparent and thermodynamically stable solutions [1, 2]. These aggregates find a variety of important commercial applications like tertiary oil recovery [3], formulations in cleaning products [4], solubilization and stabilization of oils and flavours in food products [5]. Association colloids are also commonly used in the formulations of pesticides and herbicides in agriculture [6]. Micellar media are regarded as model systems for the compartmentalizing and organizing ability of biological membranes and the catalytic activity of enzymes [7–9]. Micelles act as microreactors and influence chemical reactivity primarily by binding or excluding reactants and secondarily by changing the free energy of activation [10–12]. In bimolecular reactions, aggregate effects on chemical reactivity are generally interpreted by using pseudophase models, which treat micelles and water as separate reaction media. The enhancement in the rate of reactions is attributed to the binding and concentrating the reactants in the very much smaller volume of micellar pseudophase, i.e. within the Stern layer's region. Inhibition is explained on the basis of the compartmentalization of reactants.

The hydrolysis of isoproturon and other phenylureas [13–15] has been a subject of increasing interest. These molecules are used as efficient herbicides in agriculture and possess distinctive aspects of reaction mechanism. Isoproturon is a hydrophobic substrate slightly soluble in water and has a polar reactive group. It is hydrolysed in both acidic and basic media. In acidic media, the reaction proceeds through the protonation of isoproturon followed by rate-determining attack by water, giving a tetrahedral intermediate. The intermediate then decomposes to yield amine and phenylcarbamic acid. Finally, phenylcarbamic acid decarboxylates under acidic condition to form the corresponding aniline (Scheme 1). The multi-step protonation and hydrolysis of isoproturon provide an interesting case to study in micellar medium.

In the present work, a detailed kinetic study on the hydrolysis of isoproturon in acidic medium in the absence

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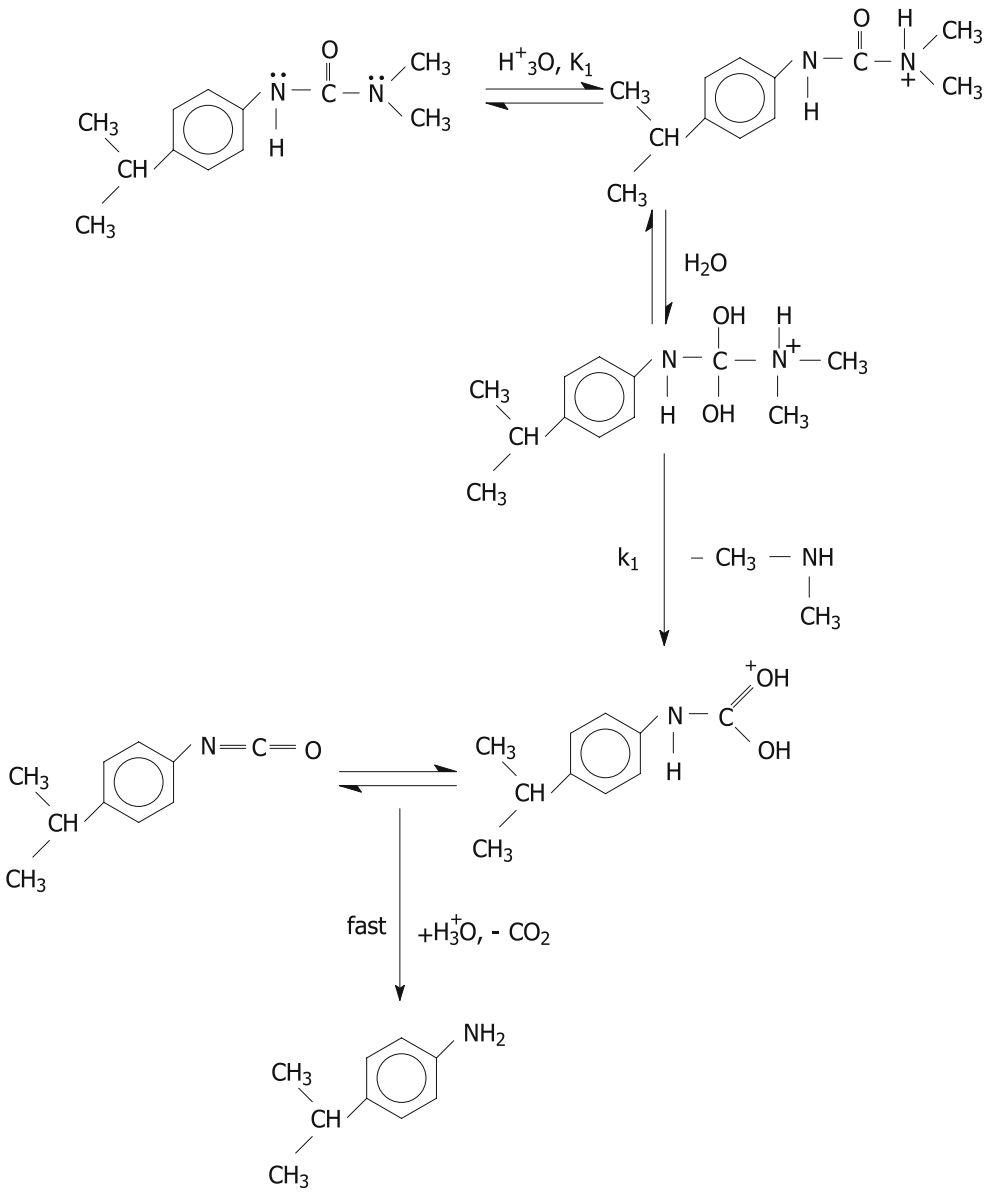
Scheme 1 Hydrolysis of isoproturon in acidic media through an addition–elimination mechanism



and presence of sodium lauryl sulfate has been carried out to study the influence of surfactant on the rate of reaction. The aim of the work also includes the understanding of the mechanism of the reaction in the presence of surfactant. The results were treated using pseudophase ion-exchange (PPIE) model [16–19], and the kinetic parameters obtained gave a good fit to the kinetic data.

Experimental

Materials

Isoproturon 3-(4-isopropyl phenyl)-1, 1-dimethyl urea (Siris Crop Sciences Limited, New Delhi, India), hydrochloric acid (E. Merck, India), methanol (Qualigens, India), sodium lauryl sulfate (CDH, India) and sodium chloride (BDH, India) were used as received. All the other salts used were of analytical reagent grade. Double-distilled and deionised water was used throughout.

Stock solutions of hydrochloric acid (1.0 mol dm^{-3}) and sodium lauryl sulfate (1.0×10^{-1} mol dm^{-3}) were prepared in distilled water and that of isoproturon (1×10^{-2} mol dm^{-3}) in methanol.

Kinetic measurements

Kinetic experiments were carried out by taking the requisite amount of isoproturon, surfactants and salts in a three-necked reaction vessel. The reaction vessel was fitted with a double-surface condenser to check any evaporation. The reaction vessel was kept in a thermostated water bath at the

desired temperature (±0.1 °C). The zero time was taken when half of the required volume of thermally equilibrated hydrochloric acid was added to the reaction vessel. Progress of the reaction was followed by measuring the absorbance at constant intervals of time on an Elico SL-164 UV–Vis Spectrophotometer using 1-cm path length quartz cuvettes. All the kinetic experiments were run under the first-order condition in which the concentrations of H^+ and surfactant were kept largely in excess over [isoproturon]. The pseudo-first-order rate constants were determined from the slope of $\ln(A-A\alpha)$ vs time, where A is the absorbance of isoproturon at λ_{max} (240 nm). The hydrolytic reaction was followed for the completion of 80% of the reaction. A non-linear least-square technique was used for the treatment of data to obtain values of the binding constant of isoproturon with sodium lauryl sulfate micelles, K_s, and second-order rate constant with sodium lauryl sulfate micelles, k_m. The best values that fit the curves were obtained from the computer program. The critical micelle concentration (CMC) of sodium lauryl sulfate containing isoproturon and hydrochloric acid were determined conductometrically at 70 °C, and its value was 8.3×10^{-3} mol dm^{-3}.

Results

Reaction in the absence of micelles

The kinetic experiments were performed at different initial concentrations of isoproturon ranging from 4.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} at fixed [HCl] (1.0×10^{-1} mol dm^{-3}) at 70 °C, and the ionic strength was kept constant at 1.0 mol dm^{-3}. The values of pseudo-first-order rate constants obtained remained the same with the increase in initial concentrations of isoproturon, indicating that the order of hydrolysis is unity with respect to it. The order with respect to hydrochloric acid was deduced from the values of the rate constants obtained at several [HCl] (0.5×10^{-1}–1.5 mol dm^{-3}) at fixed ionic strength (1.0 mol dm^{-3}) and [isoproturon] (5.0×10^{-5} mol dm^{-3}). The results are given in Fig. 1. The rate of reaction was found to increase with the increase in [HCl] linearly. The rate constants were found to be independent of the ionic strength, showing that one of the reactants taking part in the hydrolysis is an uncharged molecule. The kinetic runs were also performed within the temperature range of 40–70 °C. The concentrations of HCl (1.0×10^{-1} mol dm^{-3}) and isoproturon (5.0×10^{-5} mol dm^{-3}) were kept constant, and the ionic strength was maintained at 1.0 mol dm^{-3}. The energy of activation was determined from the plot of log k_{obs} vs $1/T$. The values of other activation parameters were calculated using Arrhenius and Eyring equation and are given in Table 1.

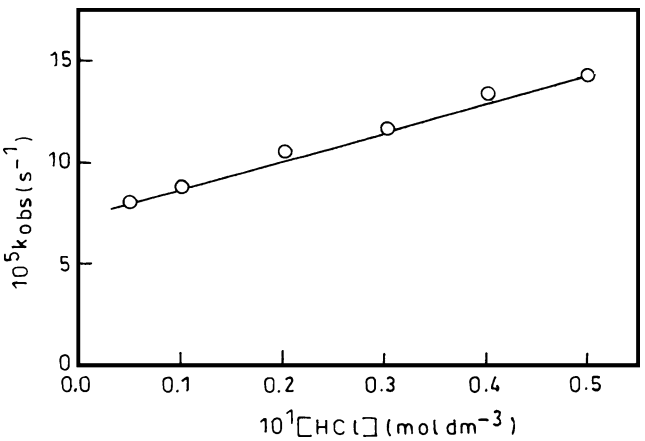


Fig. 1 Effects of [HCl] on the k_{obs}. Reaction conditions: isoproturon (5.0×10^{-5} mol dm^{-3}) at 70 °C

Reaction in the presence of sodium lauryl sulfate

It was observed that the rate of reaction was increased with the increase in [sodium lauryl sulfate, NaLS]. The effect of varying [NaLS] (1.0×10^{-3}–5.0×10^{-2} mol dm^{-3}) was studied at constant [isoproturon] (5.0×10^{-5} mol dm^{-3}) and [HCl] (1.0×10^{-1} mol dm^{-3}) at 70 °C. The values of the pseudo-first-order rate constants (k_ψ) were determined in the presence of NaLS. The plot of k_ψ vs [NaLS] is given in Fig. 2. The kinetic experiments performed in the presence of NaLS micelles show that the pseudo-first-order rate constants are independent of the initial concentrations of isoproturon. The values of rate constants increased rapidly with increase in [HCl] at lower concentrations, but it increased gradually on further increase in [HCl], as shown in Fig. 3.

Discussion

At surfactant concentrations above the CMC, k_ψ is assumed to depend upon the reactants' concentrations in each of aqueous and micellar pseudophases. The reaction occurring in each of the pseudophases is presented in Scheme 2.

Table 1 Activation parameters in absence and presence of NaLS micelles for the hydrolysis of isoproturon by hydrochloric acid

Activation parameter	In the absence of surfactant	In the presence of NaLS
E_a (kJ mol^{-1})	14.0±1.2	30.1±1.6
$\Delta H^{\neq}$ (kJ mol^{-1})	11.5±1.6	27.6±1.7
$-\Delta S^{\neq}$ (J mol^{-1} K^{-1})	284±4	225±6

[Isoproturon]=5.0×10^{-5} mol dm^{-3}, [HCl]=1.0×10^{-1} mol dm^{-3}; [NaLS]=2.0×10^{-2} mol dm^{-3}, temperature=70 °C

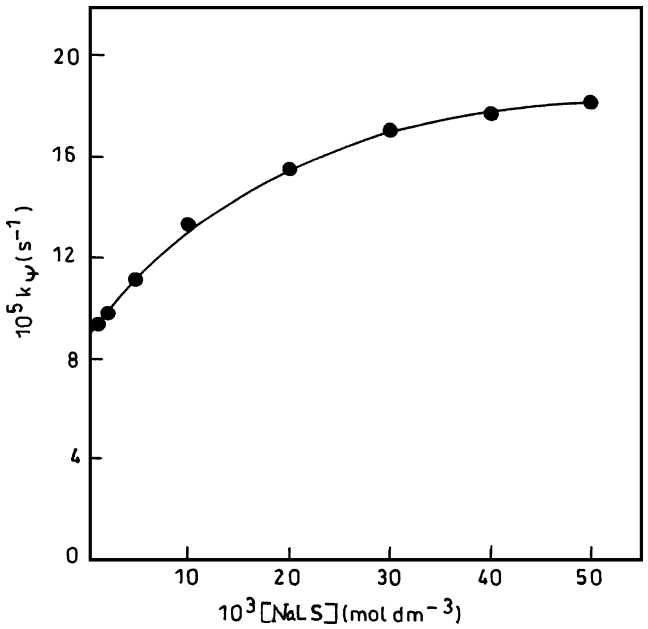


Fig. 2 Effects of surfactant [NaLS] (*filled circle*) on k_ψ. Reaction conditions: isoproturon (5.0×10^{-5} mol dm^{-3}), HCl (1.0×10^{-1} mol dm^{-3}) at 70 °C

The rate equation corresponding to Scheme 2 in terms of pseudo-first-order rate constants is given by

$$k_\psi = \frac{k_w^{'} + k_m^{'} K_s [D_n]}{1 + K_s [D_n]} \tag{1}$$

In this scheme and rate equation, S denotes isoproturon, D_n the micellized surfactant and K_s the binding constant of isoproturon with micelles. Subscripts w and m denote, respectively, the aqueous and the micellar pseudophases. The pseudo-first-order rate constants in aqueous and micellar pseudophases are given by:

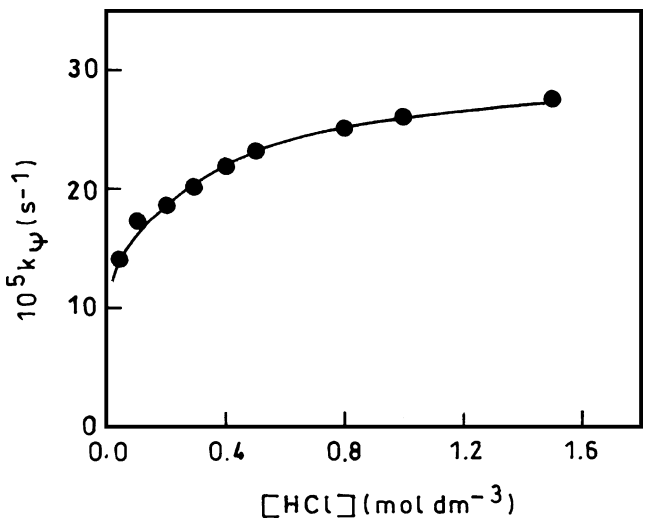
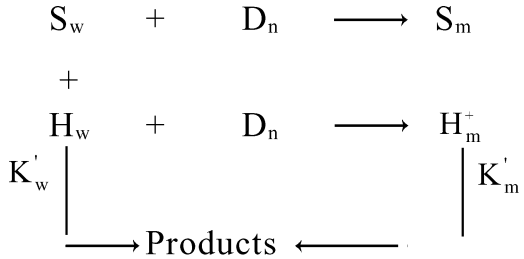


Fig. 3 Effects of [HCl] on the k_ψ. Reaction conditions: isoproturon (5.0×10^{-5} mol dm^{-3}), NaLS (2.0×10^{-2} mol dm^{-3}) at 70 °C



Scheme 2 The reaction occurring in aqueous and micellar pseudophases

$$k_w^{'} = k_w [H^+] \text{ and } k_m^{'} = k_m m_{H^+}^s \tag{2}$$

$m_{H^+}^s$ is the molarity of hydrogen ions in micellar pseudophase,

$$m_{H^+}^s = \left[H_m^+\right] / [D_n] \tag{3}$$

According to the PPIE model, the micellar surface is treated as a selective ion exchanger. The distribution of Na^+ and H^+ in aqueous and micellar pseudophases is given by considering the following equilibrium:

$$H_m^+ + Na_w^+ \overset{K_H \backslash Na}{\Leftrightarrow} H_w^+ + Na_m^+ \tag{4}$$

and the equilibrium constant,

$$K_{H/Na} = \left[Na_m^+\right]\left[H_w^+\right] / \left[Na_w^+\right]\left[H_m^+\right]. \tag{5}$$

The reactants exist in dynamic equilibrium between the aqueous and micellar pseudophases. The entrance and exit rates of isoproturon and H^+ from micelles are an order-of-magnitude faster than the rates of its hydrolysis. The distributions of surfactants, substrate, H^+ and counterions Na^+ are at thermodynamic equilibrium throughout the time course of reaction. On applying the mass balance for isoproturon, Na^+, H^+ and surfactant, the following quadratic equation was obtained for $m_{H^+}^s$:

$$m_{H^+}^{s\,2} + \left(\frac{[Na^+t] + \left[H_w^+\right]}{[D_n]} - \beta\right) m_{H^+}^s - \frac{\beta\left[H_w^+\right]}{[D_n]} = 0 \tag{6}$$

where β is the degree of binding of counterion by the micellar surface, and $[H_w^+]$ was obtained from the measured pH ($pH = -\log\left[H_w^+\right]$).

Table 2 Parameter used to simulate k_ψ–[NaLS] profile

Parameters	Values
K_s (mol^{-1} dm^3)	410
k_m (mol^{-1} dm^3 s^{-1})	$2.4\pm0.19\times10^{-4}$
β	0.75
$K_{H/Na}$	1.00
CMC (mol dm^{-3})	8.3×10^{-3}

[Isoproturon]=5×10^{-5} mol dm^{-3}, [HCl]=1.0×10^{-1} mol dm^{-3}; [NaLS]=2×10^{-2} mol dm^{-3}, temperature=(70 °C) 343 K

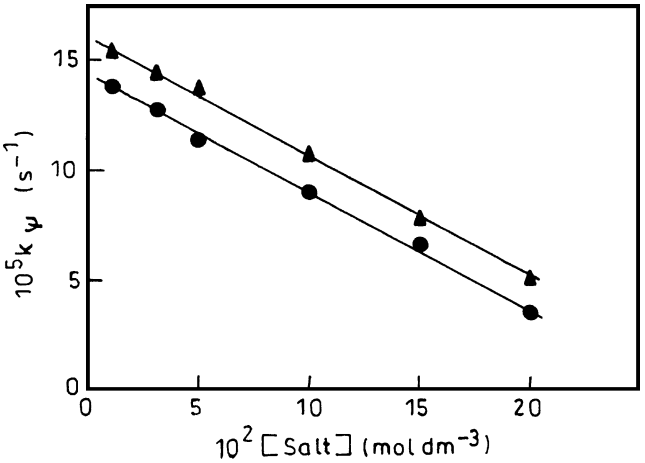


Fig. 4 Effects of [NaCl] (*filled circle*), [KCl] (*filled triangle*) on the k_ψ. Reaction conditions: isoproturon (5.0×10^{-5} mol dm^{-3}), NaLS (2.0×10^{-2} mol dm^{-3}) at 70 °C

On substitution of the values of k_m' and k_w' in Eq. 1, the first-order rate equation can be transformed in terms of second-order rate constants as:

$$k_\psi = \frac{k_w[H_t^+] + (k_m K_s - k_w) m^s_{H^+}[D_n]}{1 + K_s[D_n]} \quad (7)$$

where k_m and k_w are second-order rate constants for reactions in micellar and aqueous pseudophases, respectively. The fitting values of k_m and K_s were obtained from the computer program by minimizing the deviation between the simulation and the observed values for the k_ψ–[NaLS] profile. The values of these parameters are given in Table 2.

The overall increase in the rate of reaction with the increase in NaLS micelles is explained in terms of the binding and concentration of both the reactants, i.e. isoproturon and H^+ within the small vicinity of anionic pseudophase (Stern's layer). The mechanism of the reaction in both the aqueous and micellar pseudophases are similar, as it is evident from the dependence of the rate of reaction on [isoproturon], [HCl] and temperature.

The hydrolysis of isoproturon in acidic media proceeds through an addition–elimination mechanism. At low pH, the reaction is initiated by the protonation of carbonyl oxygen, thereby facilitating the nucleophilic attack of water to form tetrahedral intermediate. The attack by water molecule is the rate-determining step, and the tetrahedral intermediate decomposes to give phenylcarbamic acid and an amine. Under the acidic condition, the phenylcarbamic acid decarboxylates quickly to yield the final product, i.e. 4-isopropyl-aniline (Scheme 1).

The NaLS micelles concentrate both hydrogen ions and isoproturon into a very small volume of Stern's layer. In acidic medium, isoproturon is protonated, and this positively charged isoproturon gets more strongly bonded to anionic NaLS micelles. Thus, the micelle facilitates the extensive buildup of protonated isoproturon in the region of Stern's layer and enhances the rate of hydrolysis. In the presence of micelles, the dependence of rate of hydrolysis on [HCl] is linear at lower concentration but shows a levelling behaviour at higher concentration (Fig. 3). The phenomenon may arise due to the low polarity of Stern's layer of micelles as compared to water. The studies by Giffney and O'Connor [15] demonstrate that the rate of hydrolysis of phenylureas increases with the acid strength at low acidity, whereas it passes through a maximum and decreases again in stronger acid solutions. It elaborates the role of water activity during the hydrolysis of phenylureas. The activity of water is reduced appreciably at higher acidic concentrations. The addition of water to the protonated isoproturon (which is the rate-determining step) becomes slow in Stern's layer.

The activation parameters were evaluated from the linear regression of log k_{obs} vs $1/T$ (for aqueous medium) and log k_ψ vs $1/T$ (for surfactant medium) by least-squares method. The values are given in Table 1. The enthalpy and entropy of activation were calculated by using Eyring relationship [18]. The decrease in entropy in the presence of micelles suggests that reactants are in greater degree of orders. The interactions with micelles favour the charge dispersion of reactants in the transition state, and its greater degree of orderliness results in the increases in the values of rate constants.

The added salt (NaCl, KCl) inhibited the reaction, and the values of pseudo-first-order rate constants were decreased (Fig. 4). The inhibition effect could be due to a competitive binding of H^+ and Na^+/K^+ with the micelles [19–21]. The increase in concentrations of Na^+/K^+ causes exclusion of H^+ from the micelles. The added salts also cause micelles to grow and change their shapes from spherical to spheroidal or rod-like. It results into change in reaction rate at micellar surfaces [22–25].

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References

1. Fendler JH (1982) Membrane mimetic chemistry. Wiley, New York
2. Rosen MJ (1978) Surfactants and interfacial phenomena. Wiley, New York
3. Shah DO (ed) (1985) Micro- and macroemulsions: theory and practice. ACS Symposium Series 272, American Chemical Society, Washington, DC
4. Cutler WG, Kissa E (1987) Detergency: theory and technology. Marcel Dekker, New York
5. El-Nokaly M, Cornell D (eds) (1991) Microemulsions and emulsions in food. ACS Symposium Series 448, American Chemical Society, Washington, DC
6. Tonellato U (1988) J Chim Phys Phys-Chim Biol 85:1047

7. Tanford C (1980) The hydrophobic effect: formation of micelles and biological membranes, 2nd edn. Wiley, New York
8. Jain MK (1988) Introduction to biological membranes, 2nd edn. Wiley, New York, p 423
9. Bunton CA (1991) In: Gratzel M, Kalyanasundaram K (eds) Kinetics and catalysis in microheterogeneous systems. Marcel Dekker, New York, p 525
10. Bunton CA, Nome F, Quina FH, Romsted LS (1991) Acc Chem Res 24:357
11. Bunton CA, Savelli G (1986) Adv Phys Org Chem 22:213
12. Salvestrini S, Di Cerbo P, Capasso S (2002) J Chem Soc Perkin Trans 2:1893
13. Laudien R, Mitzner R (2001) J Chem Soc Perkin Trans 2:2230–2232
14. O'Connor CJ, Barnett JW (1973) J Chem Soc Perkin Trans 2:1457–1461
15. Giffney JC, O'Connor CJ (1976) J Chem Soc Perkin Trans 2:362–368
16. Vera S, Rodenas E (1986) Tetrahedron 42:143–149
17. Shinoda K, Lindman B (1987) Langmuir 3:135
18. Ruzza AA, Nome F, Zanette D (1995) Langmuir 11:2393
19. Connors KA (1990) Chemical kinetics: the study of reaction rate in solutes. VCH, New York, USA
20. Spindli D, Noto R, Consiglo G, Werber G, Buchheri F (1978) J Org Chem 43:4042
21. Broxton TR, Deady LW, Duddy NW (1978) Aust J Chem 31:1525
22. Gensmental NG, Page MI (1982) J Chem Soc Perkin Trans 147
23. Bunton CA, Robinson L (1969) J Org Chem 34:773
24. Anacker EW, Ghose HM (1968) J Am Chem Soc 90:3161
25. Bunton CA, Wolfe B (1973) J Am Chem Soc 95:3742