

# Effects of anionic micelles on the intramolecular general base-catalyzed hydrolysis of phenyl and methyl salicylates

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## Abstract

The effects of micelles of sodium dodecyl sulphate (SDS) on hydrolytic cleavage of phenyl salicylate (PS) have been studied at 30 and 37°C under [NaOH] range 0.003–0.060 M. The total concentration of SDS,  $[SDS]_T$ , was varied from 0.02 to 0.40 M. The observed pseudo first-order rate constants,  $k_{obs}$ , reveal decrease with increase in  $[SDS]_T$  at a constant [NaOH] and temperature. These observed data have been treated with pseudophase model of the micelle. The rate of hydrolysis of micellized PS turns out to be insignificant compared to the rate of hydrolysis of non-micellized PS under the entire [NaOH] range of the study. This is rationalized in terms of a proposal that micellized anionic PS molecules exist in the specific micellar region where water concentration,  $[H_2O]$ , is much lower than the  $[H_2O]$  of aqueous pseudophase. The kinetic data have been used to obtain the micellar binding constants,  $K_1$  for ionized and  $K_2$  for non-ionized PS and the respective values of  $K_1$  and  $K_2$  are  $3.0 M^{-1}$  and  $1887 M^{-1}$  at 30°C and  $3.1 M^{-1}$  and  $986 M^{-1}$  at 37°C. The observed pseudo first-order rate constants,  $k_{obs}$ , for hydrolysis of methyl salicylate, MS, remain unchanged with change in  $[SDS]_T$  from 0.0 to 0.4 M at 0.03 M NaOH and 37°C. These observations are concluded to be the consequence of the location of the micellized MS molecules at the junctural region of the Gouy–Chapman and Stern layers where  $[H_2O]$  is similar to  $[H_2O]$  of aqueous pseudophase.

**Keywords:** Anionic micelles; Base; Hydrolysis; Micelles; Salicylate derivatives

## 1. Introduction

Intramolecular general acid, GA, and general base, GB, catalysis have been found to occur in many enzyme-catalyzed reactions [1]. The occurrence of intramolecular GB catalysis in the pH-independent hydrolysis [2–4], alkanolysis [5] and aminolysis [6] of phenyl salicylate has been ascertained. It is widely believed that the medium properties of microenvironment where the actual enzyme-catalyzed reactions occur are quite different from those of the bulk aqueous solvents.

Normal micelles are regarded to have some of the characteristic medium properties of biological membrane and active sites of many enzymes [7]. In an earlier report [8], we described the results of the studies on the effects of sodium dodecyl sulphate, SDS, micelles upon the rate of hydrolysis of ionized phenyl salicylate,  $PS^-$ , at 0.0075 and 0.060 M NaOH and 30°C. The apparent binding constant,  $K_S^{app}$ , for  $PS^-$  with SDS micelles obtained kinetically at 0.0075 M NaOH was nearly 1.5 times higher than  $K_S^{app}$  at 0.060 M NaOH. The observed data at only two different

[NaOH] were not sufficient to carry out a detailed analysis on the variation of  $K_S^{app}$  with [NaOH]. We extended this study by carrying out kinetic runs at several [NaOH] and at 30° as well 37°C in order to perform the data analysis in some more detail. A few kinetic runs have been also carried out in order to find out the effects of SDS micelles on the rate of hydrolysis of methyl salicylate at 0.03 M NaOH. The observed results and probable explanations are described in this paper.

## 2. Experimental section

### 2.1. Materials

Reagent grade chemicals such as phenyl salicylate and sodium dodecyl sulphate, SDS, were obtained from BDH and Aldrich, respectively. Methyl salicylate was prepared from salicylic acid and methanol with a standard procedure. All other chemicals used were also of reagent grade. Stock solutions of phenyl and methyl salicylates were

prepared in acetonitrile and were always stored at low temperature whenever they were not in use.

### 2.2. Kinetics

Non-ionized phenyl and methyl salicylates, ionized salicylic acid and phenol do not show detectable absorption at 350 nm. But ionized phenyl ( $PS^-$ ) and methyl ( $MS^-$ ) salicylates show strong absorption at 350 nm. The rates of hydrolysis of  $PS^-$  and  $MS^-$  were studied spectrophotometrically by monitoring the decrease in absorbance at 350 nm. The details of the kinetic procedure and data analysis were same as described elsewhere [6]. The absorbance values obtained at  $t = \infty$  were in agreement with the products formed as salicylate and phenolate ions.

## 3. Results

### 3.1. Effect of $[SDS]_T$ upon hydrolysis of phenyl salicylate at a constant [NaOH]

The effects of total concentration of SDS ( $[SDS]_T$ ) upon the rates of hydrolysis of phenyl

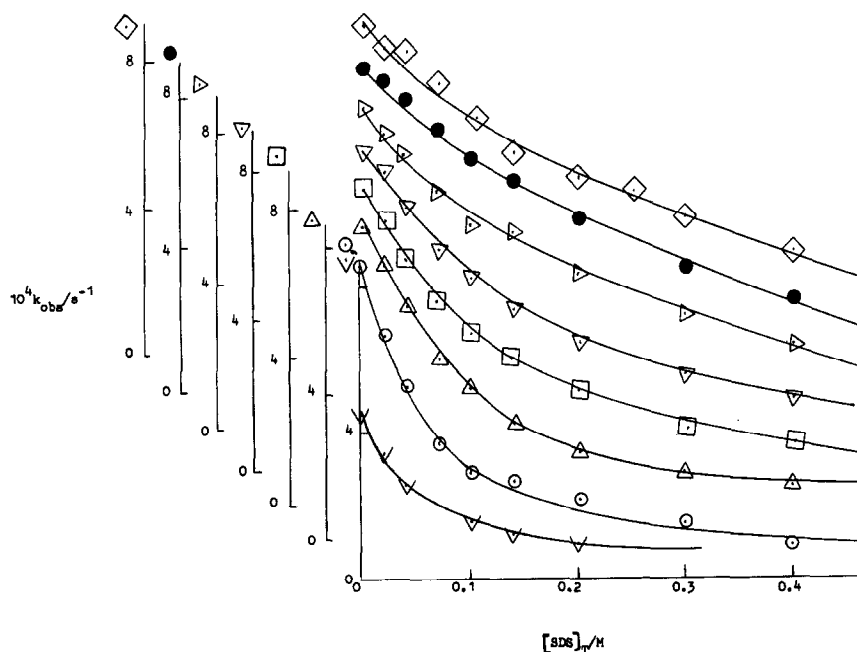


Fig. 1. Plots showing the dependence of the observed pseudo first-order rate constants,  $k_{obs}$ , upon total concentration of SDS,  $[SDS]_T$ , for hydrolysis of phenyl salicylate at 30°C and 0.003 M NaOH ( $\nabla$ ), 37°C and 0.003 M NaOH ( $\bullet$ ), 0.005 M NaOH ( $\Delta$ ), 0.0075 M NaOH ( $\square$ ), 0.0095 M NaOH ( $\nabla$ ), 0.020 M NaOH ( $\triangleleft$ ), 0.040 M NaOH ( $\circ$ ), and 0.060 M NaOH ( $\diamond$ ).

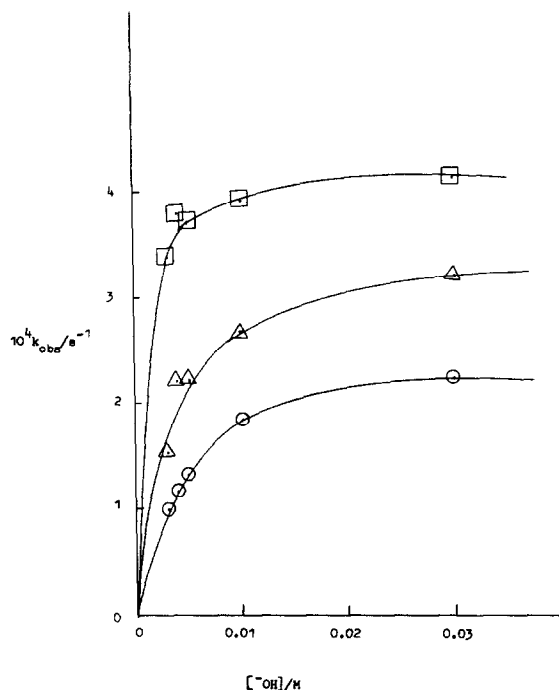


Fig. 2. Effects of  $[\text{NaOH}]$  on observed pseudo first-order rate constants,  $k_{\text{obs}}$ , for hydrolysis of phenyl salicylate at  $30^\circ\text{C}$  and in the presence of  $0.20\text{ M}$  SDS ( $\circ$ ),  $0.10\text{ M}$  SDS ( $\Delta$ ), and  $0.02\text{ M}$  SDS ( $\square$ ).

salicylate were studied at a constant  $[\text{NaOH}]$  and  $37^\circ\text{C}$ . The observed pseudo first-order rate constants,  $k_{\text{obs}}$ , are shown graphically in Fig. 1 as a function of  $[\text{SDS}]_{\text{T}}$  ( $[\text{SDS}]_{\text{T}}$  range  $0.02\text{--}0.40\text{ M}$ ) at different  $[\text{NaOH}]$ . The observed data reveal nearly 9- to 3-fold decrease in  $k_{\text{obs}}$  with increase in  $[\text{SDS}]_{\text{T}}$  from  $0.0$  to  $0.4\text{ M}$  at  $[\text{NaOH}]$  range of  $0.003$  to  $0.060\text{ M}$ . A few kinetic runs were also carried out within the  $[\text{SDS}]_{\text{T}}$  range  $0.0$  to  $0.2\text{ M}$  at  $0.003\text{ M}$   $\text{NaOH}$  and  $30^\circ\text{C}$  (Fig. 1).

### 3.2. Effect of $[\text{NaOH}]$ upon hydrolysis of phenyl salicylate at a constant $[\text{SDS}]_{\text{T}}$

The rates of hydrolysis of phenyl salicylate were studied within the  $[\text{NaOH}]$  range  $0.003\text{--}0.030\text{ M}$  at different  $[\text{SDS}]_{\text{T}}$  and  $30^\circ\text{C}$ . The observed data are shown in Fig. 2 as the plot of  $k_{\text{obs}}$  versus  $[\text{^-OH}]$ .

### 3.3. Effect of $[\text{SDS}]_{\text{T}}$ upon hydrolytic cleavage of methyl salicylate

A few kinetic runs were carried out to study the effect of  $[\text{SDS}]_{\text{T}}$  upon the rate of hydrolytic cleav-

Table 1  
Effect of  $[\text{SDS}]_{\text{T}}$  on observed pseudo first-order rate constants,  $k_{\text{obs}}$ , for hydrolysis of methyl salicylate at  $0.03\text{ M}$   $\text{NaOH}$ <sup>a</sup>

$[\text{SDS}]_{\text{T}}$ M	$10^4 \cdot k_{\text{obs}}$ <sup>b</sup> $\text{s}^{-1}$	$\epsilon_{\text{app}}$ <sup>b</sup> $\text{M}^{-1}\text{ cm}^{-1}$	$A$ <sup>b</sup>
0.00	$2.47 \pm 0.02$ <sup>c</sup>	$3187 \pm 9$ <sup>c</sup>	$-0.007 \pm 0.002$ <sup>c</sup>
0.02	$2.46 \pm 0.02$	$3231 \pm 9$	$0.001 \pm 0.003$
0.07	$2.39 \pm 0.02$	$3224 \pm 9$	$-0.001 \pm 0.003$
0.10	$2.34 \pm 0.03$	$3071 \pm 13$	$0.019 \pm 0.003$
0.14	$2.28 \pm 0.02$	$3096 \pm 9$	$0.023 \pm 0.003$
0.20	$2.27 \pm 0.02$	$3103 \pm 9$	$0.026 \pm 0.003$
0.30	$2.11 \pm 0.02$	$2996 \pm 10$	$0.037 \pm 0.002$
0.40	$1.97 \pm 0.02$	$2985 \pm 10$	$0.060 \pm 0.003$

<sup>a</sup> Conditions:  $[\text{Methyl salicylate}]_0 = 3 \times 10^{-4}\text{ M}$ ,  $37^\circ\text{C}$ ,  $\lambda = 350\text{ nm}$ , aqueous reaction mixture contained  $1\%$ , v/v, MeCN.

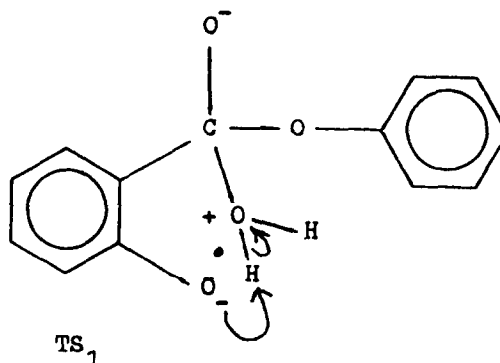
<sup>b</sup> Calculated from the relationship:  $A_{\text{obs}} = \epsilon_{\text{app}}[\text{Methyl salicylate}]_0 \exp(-k_{\text{obs}}t) + A_{\infty}$  where  $A_{\text{obs}}$  represents observed absorbance at time  $t$ ,  $\epsilon_{\text{app}}$  is the apparent molar extinction coefficient and  $A_{\infty}$  is absorbance at  $t = \infty$ .

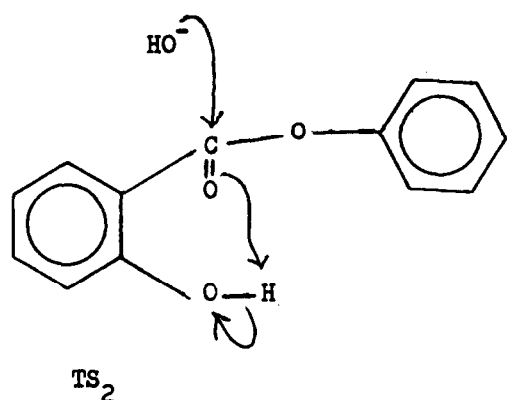
<sup>c</sup> Error limits are standard deviations.

age of methyl salicylate in the presence of  $0.03\text{ M}$   $\text{NaOH}$  at  $37^\circ\text{C}$ . The observed data are summarized in Table 1.

## 4. Discussion

The rate of hydrolysis of phenyl salicylate has been found to be unchanged with change in  $[\text{^-OH}]$  from nearly  $0.001$  to  $0.070\text{ M}$ . This pH-independent rate of hydrolysis of phenyl salicylate has been unequivocally ascertained to involve ionized phenyl salicylate,  $\text{PS}^-$ , and  $\text{H}_2\text{O}$  as the reactants [2–4]. The detailed mechanism which involves intramolecular general base catalysis,  $\text{TS}_1$ , has been discussed elsewhere [9]. The probable occurrence of intramolecular general acid catalysis,  $\text{TS}_2$ , has been ruled out [2–4,9].

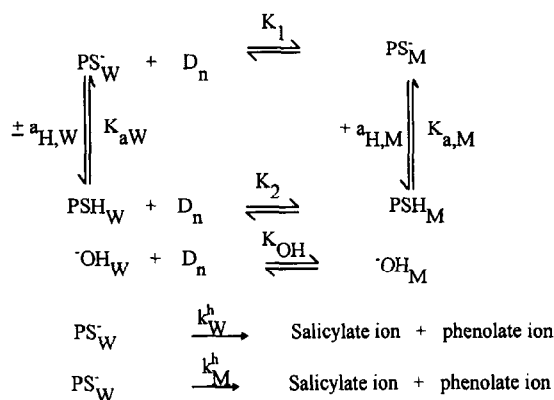




The initial observed absorbance (i.e. absorbance at  $t=0$ )  $A_{\text{obs}(t=0)}$  turned out to be unchanged with change in  $[\text{SDS}]_{\text{T}}$  from 0.0 to 0.4 M at  $[\text{OH}^-] \geq 0.02$  M. But  $A_{\text{obs}(t=0)}$  revealed decrease with increase in  $[\text{SDS}]_{\text{T}}$  at  $[\text{OH}^-] \leq 0.0095$  M and this decrease became more pronounced with decrease in  $[\text{OH}^-]$ . The decrease in  $A_{\text{obs}(t=0)}$  with increase in  $[\text{SDS}]_{\text{T}}$  at a constant  $[\text{NaOH}]$  is the consequence of the increase in the concentration of non-ionized phenyl salicylate, PSH, (PSH molecules do not absorb at 350 nm). Thus, these observations show that phenyl salicylate remains in 100% ionized form,  $\text{PS}^-$ , within the  $[\text{SDS}]_{\text{T}}$  range 0.0–0.4 M at  $[\text{OH}^-] \geq 0.02$  M. Under such conditions, the rate constants,  $k_{\text{obs}}$ , revealed nearly 3-fold decrease with increase in  $[\text{SDS}]_{\text{T}}$  from 0.0 to 0.4 M (Fig. 1). These observations demonstrate the micellar incorporation of  $\text{PS}^-$  molecules and the rate of hydrolysis of micellized  $\text{PS}^-$  is much slower than that of non-micellized  $\text{PS}^-$ . The rate constants,  $k_{\text{obs}}$ , decreased nearly 9-fold with increase in  $[\text{SDS}]_{\text{T}}$  from 0.0 to 0.4 M at the lowest  $[\text{NaOH}]$  ( $=0.003$  M) of the present study (Fig. 1). Under such conditions, the fraction of non-ionized phenyl salicylate,  $f_{\text{PSH}}$ , increased from 0.0 to 0.73. Thus, nearly 9-fold decrease in  $k_{\text{obs}}$  may be attributed to the combined effects of both the lower reactivity of micellized  $\text{PS}^-$  and increase in the concentration of essentially non-reactive PSH under such conditions. The hydroxide ions are expected to have extremely weak

binding affinity towards SDS micelles due to energetically unfavourable electrostatic interaction and highly hydrophilic nature of  $\text{OH}^-$ . But, even an extremely weak binding of  $\text{OH}^-$  with SDS micelles provides enough concentration of micellized hydroxide ions,  $[\text{OH}^-]_{\text{M}}$ , to ionize completely the micellized phenyl salicylate at  $[\text{OH}^-] \geq 0.02$  M. As the  $[\text{OH}^-]$  decreases from 0.02 M, the  $[\text{OH}^-]_{\text{M}}$  becomes less than sufficient to ionize completely the micellized phenyl salicylate molecules.

The hydrolysis of  $\text{PS}^-$  in the presence of SDS micelles may be discussed in terms of micellar pseudophase model [10]. The assumptions involved in this model and its advantages and disadvantages are critically discussed by Bunton [11]. The reaction scheme for hydrolysis of  $\text{PS}^-$  in the presence of micelles,  $\text{D}_n$ , may be given as depicted in Scheme 1. In Scheme 1, the subscripts W and M stand for aqueous pseudophase and micellar pseudophase, respectively. The rate constants,  $k_{\text{W}}^{\text{h}}$  and  $k_{\text{M}}^{\text{h}}$  represent pseudo first-order rate constants for hydrolysis of  $\text{PS}^-$  in aqueous pseudophase and micellar pseudophase, respectively. It has been concluded that the observed pseudo first-order rate constants,  $k_{\text{obs}}$ , for the intramolecular general base-catalyzed hydrolysis of  $\text{PS}^-$  is nearly  $10^6$ -fold higher than  $k_{\text{obs}}$  for hydrolysis of an analogous substrate where such catalysis would not be expected [12]. Intramolecular general base, IGB, catalysis has been shown to occur in the aminolysis of both  $\text{PS}_{\text{W}}^-$  and  $\text{PS}_{\text{M}}^-$  under the presence of SDS micelles [8,13]. We



Scheme 1.

Table 2

The values of the calculated parameters,  $C$  ( $C = f_M^{PS^-} k_M^h$ ) and  $K_S^{app}$  from Eqs. 1 and 2 for the hydrolysis of phenyl salicylate in the presence of SDS<sup>a</sup>

[NaOH] M	$10^5 C^b$ $s^{-1}$	$K_S^{app b}$ $M^{-1}$	$K_S^{app c}$ $M^{-1}$	$K_{S,calc}^{app d}$ $M^{-1}$	Max. dev. <sup>e</sup> %	$\gamma^f$	[SDS] <sub>T</sub> range M
0.0030	$4.49 \pm 2.22^g$	$22.9 \pm 2.4^g$	$19.1 \pm 3.4^g$	18.5	-32	0.940	0.02–0.40
	$9.03 \pm 2.71$	$26.7 \pm 1$	$16.6 \pm 5$	16.7	-7		0.02–0.20
0.0050	$-0.4 \pm 1.5$	$11.6 \pm 0.6$	$11.6 \pm 0.7$	12.4	-6	0.925	0.02–0.40
	$-6.3 \pm 2.0$	$10.2 \pm 0.5$	$11.7 \pm 0.7$	11.4	-2		0.02–0.20
0.0075	$-4.54 \pm 1.38$	$8.2 \pm 0.3$	$9.3 \pm 0.7$	9.3	3	0.911	0.02–0.40
	$-0.51 \pm 2.54$	$8.9 \pm 0.5$	$8.9 \pm 0.3$	8.7	2		0.02–0.20
0.0095	$-9.5 \pm 2.2$	$6.1 \pm 0.3$	$7.3 \pm 1.2$	8.0	3	0.901	0.02–0.40
	$-18.9 \pm 5.5$	$5.2 \pm 0.5$	$6.9 \pm 1.0$	7.6	1		0.02–0.20
0.0200	$-8.5 \pm 6.6$	$4.7 \pm 0.6$	$5.8 \pm 0.8$	5.4	6	0.866	0.02–0.40
	$11.3 \pm 10.5$	$6.8 \pm 1.7$	$5.6 \pm 0.8$	5.3	5		0.02–0.20
0.04000	$-3.5 \pm 0.4$	$2.6 \pm 0.2$	$4.4 \pm 0.9$	4.2	3	0.827	0.02–0.40
	$-25.8 \pm 18.9$	$2.9 \pm 0.7$	$3.9 \pm 0.5$	4.3	2		0.02–0.20
0.0600	$-23.5 \pm 12.1$	$2.9 \pm 0.5$	$4.3 \pm 1.1$	3.8	-5	0.801	0.02–0.40
	$-6.4 \pm 7.6$	$1.95 \pm 1.24$	$4.2 \pm 1.3$	3.9	-4		0.02–0.20
0.003 <sup>h</sup>	$3.50 \pm 0.57$	$27.4 \pm 1.3$	$21.5 \pm 3.1$		-2	0.941	0.02–0.20

<sup>a</sup> Conditions: [Phenyl salicylate]<sub>0</sub> =  $2 \times 10^{-4}$  M, 37°C,  $\lambda = 350$  nm, aqueous reaction mixture contained 1%, v/v, MeCN.

<sup>b</sup> Calculated from Eq. 1.

<sup>c</sup> Calculated from Eq. 2.

<sup>d</sup> Calculated from Eq. 5 as described in the text.

<sup>e</sup> Max. dev. =  $100(k_{obs} - k_{calc})/k_{obs}$ .

<sup>f</sup> Calculated from Eq. 6.

<sup>g</sup> Error limits are standard deviations.

<sup>h</sup> Values of parameters at 30°C.

assume that the same mechanism is operating in the hydrolysis of both  $PS_W^-$  and  $PS_M^-$ . In terms of these conclusions, the reaction steps for the hydrolysis of  $PSH_W$  and  $PSH_M$  have been omitted from Scheme 1.

The observed rate law:  $rate = k_{obs}[Sub]_T$  ( $[Sub]_T = [PS^-]_T + [PSH]_T$ ), and Scheme 1 give Eq. 1

$$k_{obs} = \frac{k_W^h + k_M^h f_M^{PS^-} K_S^{app} [D_n]}{1 + K_S^{app} [D_n]} \quad (1)$$

where  $f_M^{PS^-} = K_{a,M}/(a_{H,M} + K_{a,M})$ ,  $K_{a,M}$  and  $a_{H,M}$  are the respective ionization constants of  $PSH_M$  and activity of proton in the micellar pseudophase,  $K_S^{app} = ([PS_M^-] + [PSH_M])/([PS_W^-] + [PSH_W])[D_n]$  and  $[D_n] = [SDS]_T - cmc$  (where  $cmc$  is the critical micelle concentration). In an earlier report [8], it has been shown quali-

tatively that the fraction of micellized  $PS^-$  molecules,  $f_M^{PS^-}$ , remains essentially unchanged with change in  $[SDS]_T$  at a constant  $[NaOH]$ .

The observed data (Fig. 1) were used to calculate the unknown parameters,  $k_M^h f_M^{PS^-}$  and  $K_S^{app}$ , from Eq. 1 (with  $cmc = 0.008$  M) using the non-linear least squares method. These results are summarized in Table 2. The values of  $k_M^h f_M^{PS^-}$  and  $K_S^{app}$  were also calculated using observed data obtained within the  $[SDS]_T$  range 0.02–0.20 M for the mere reason that at considerably high detergent concentration, a phase transition of a micellar structure such as from spherical to rod-shaped and then to liquid crystalline phase takes place. Under such structural transitions of a micelle, the validity of Eq. 1 may be suspected. It is interesting to note that the values of  $K_S^{app}$  calculated from the observed data obtained within the  $[SDS]_T$  range

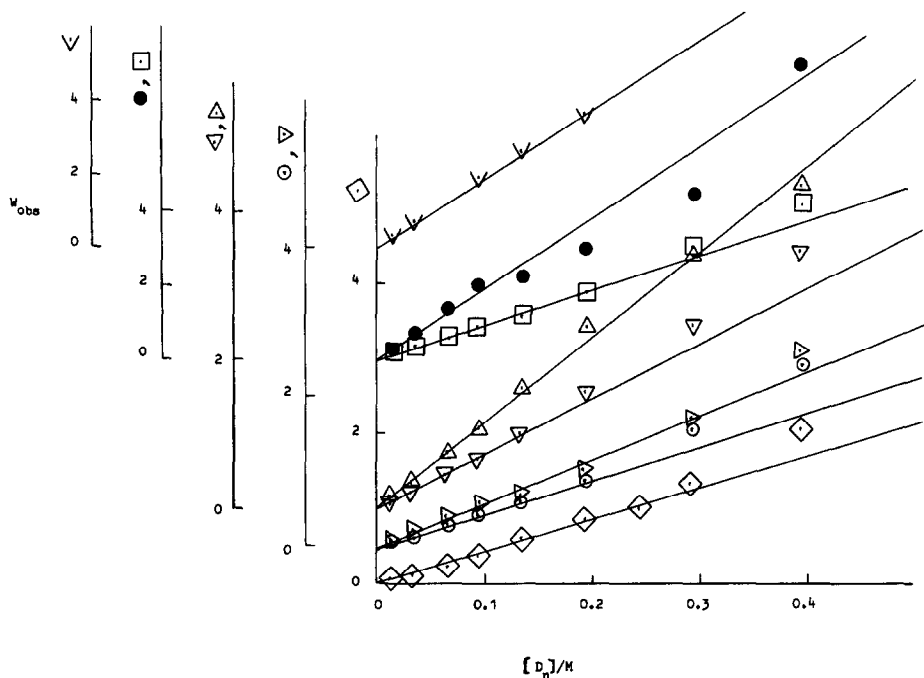


Fig. 3. Dependence of  $W_{\text{obs}} = (k_{\text{W}}^{\text{h}} - k_{\text{obs}}) / k_{\text{obs}}$  upon  $[D_n]$  for hydrolysis of phenyl salicylate at 30°C and 0.003 M NaOH ( $\nabla$ ), 37°C and 0.003 M NaOH ( $\circ$ ), 0.005 M NaOH ( $\triangle$ ), 0.0075 M NaOH ( $\square$ ), 0.0095 M NaOH ( $\nabla$ ), 0.020 M NaOH ( $\triangleleft$ ), 0.040 M NaOH ( $\bullet$ ), and 0.060 M NaOH ( $\diamond$ ). The solid lines are drawn through the calculated points as described in the text.

0.02–0.40 M and 0.02–0.20 M are different from each other only by <20% at several  $[\text{NaOH}]$  (Table 2). The negative values of  $k_{\text{M}}^{\text{h}} f_{\text{M}}^{\text{PS}^-}$  obtained at all  $[\text{NaOH}]$  (except at 0.003 M NaOH where the maximum contributions of  $k_{\text{M}}^{\text{h}} f_{\text{M}}^{\text{PS}^-} [D_n]$  are 29% and 32% at 30 and 37°C, respectively) and considerably low maximum deviations between observed and calculated values of the rate constants (Table 2), indicate that  $k_{\text{M}}^{\text{PS}^-} f_{\text{M}}^{\text{PS}^-} K_{\text{S}}^{\text{app}} [D_n]$  is negligible compared with  $k_{\text{W}}^{\text{h}}$  under the experimental conditions imposed. Thus, the conclusion that  $k_{\text{W}}^{\text{h}} \gg k_{\text{M}}^{\text{h}} f_{\text{M}}^{\text{PS}^-} K_{\text{S}}^{\text{app}} [D_n]$  reduces Eq. 1 to Eq. 2.

$$\frac{k_{\text{W}}^{\text{h}} - k_{\text{obs}}}{k_{\text{obs}}} = K_{\text{S}}^{\text{app}} [D_n] \quad (2)$$

The apparent binding constant,  $K_{\text{S}}^{\text{app}}$ , was calculated from Eq. 2 and the values at different  $[\text{NaOH}]$  are summarized in Table 2. The fitting of the observed data to Eq. 2 is evident from the plots of Fig. 3 where solid lines are drawn through the calculated points. Almost insignificant difference between the magnitudes of  $K_{\text{S}}^{\text{app}}$  obtained

from using Eqs. 1 and 2 under identical conditions shows the validity of inequality  $k_{\text{W}}^{\text{h}} \gg k_{\text{M}}^{\text{h}} f_{\text{M}}^{\text{PS}^-} K_{\text{S}}^{\text{app}} [D_n]$ . It is noteworthy that at 0.003 M NaOH, the values of  $K_{\text{S}}^{\text{app}}$  are almost identical at 30 and 37°C (Table 2).

By definition

$$K_{\text{S}}^{\text{app}} = \frac{[\text{PS}_{\text{M}}^-] + [\text{PSH}_{\text{M}}]}{([\text{PS}_{\text{W}}^-] + [\text{PSH}_{\text{W}}]) [D_n]} \quad (3)$$

Scheme 1 and Eq. 3 can lead to Eq. 4.

$$K_{\text{S}}^{\text{app}} = \frac{K_1 K_{\text{a,w}} + K_2 a_{\text{H,w}}}{a_{\text{H,w}} + K_{\text{a,w}}} \quad (4)$$

The pH of the reaction mixtures containing  $2 \times 10^{-4}$  M phenyl salicylate, and 0.003 M NaOH turned out to be 11.10–11.20 within the  $[\text{SDS}]_{\text{T}}$  range 0.02–0.40 M at 30°C. In terms of these observations,  $K_{\text{a,w}} \gg a_{\text{H,w}}$  ( $K_{\text{a,w}} = 5.67 \times 10^{-10}$  at 30°C) under the experimental conditions of the present study. The application of inequality,  $K_{\text{a,w}} \gg a_{\text{H,w}}$ , reduces Eq. 4 to Eq. 5

$$K_{\text{S}}^{\text{app}} = K_1 + \frac{K_2 K_{\text{w,w}}}{K_{\text{a,w}} a_{\text{OH,w}}} \quad (5)$$

Table 3

The values of the calculated parameters  $Y_1$  ( $=K_1[D_n]$ ) and  $Y_2$  ( $=K_2K_{w,w}[D_n]/K_{a,w}$ ) from Eq. 7 for the hydrolysis of phenyl salicylate in the presence of SDS<sup>a</sup>

[SDS] <sub>T</sub> M	10 <sup>2</sup> Y <sub>1</sub>	10 <sup>3</sup> Y <sub>2</sub> M	Max. dev. <sup>b</sup> %	K <sub>1</sub> <sup>c</sup> M <sup>-1</sup>	K <sub>2</sub> <sup>d</sup> M <sup>-1</sup>	[NaOH] range M
0.02	4.97 ± 3.64 <sup>e</sup>	0.656 ± 0.160 <sup>e</sup>	-34	4.1 ± 3.0 <sup>e</sup>	2139 ± 522 <sup>e</sup>	0.003–0.030
0.10	14.6 ± 20.7	4.32 ± 0.91	-29	1.6 ± 2.2	1837 ± 387	0.003–0.030
0.20	61.1 ± 7.3	8.27 ± 0.32	-7	3.2 ± 0.4	1685 ± 65	0.003–0.030

<sup>a</sup> Conditions are same as mentioned in Table 2, except temp. = 30°C.

<sup>b</sup> Max. dev. = 100(W<sub>obs</sub> - W<sub>calc</sub>)/W<sub>obs</sub>, where W<sub>obs</sub> = (k<sup>w</sup> - k<sub>obs</sub>)/k<sub>obs</sub> and W<sub>calc</sub> represents the calculated value of W<sub>obs</sub> using Eq. 7.

<sup>c</sup> Calculated from K<sub>1</sub>[D<sub>n</sub>] with [D<sub>n</sub>] = [SDS]<sub>T</sub> - 0.008.

<sup>d</sup> Calculated from K<sub>2</sub>K<sub>w,w</sub>[D<sub>n</sub>]/K<sub>a,w</sub> with [D<sub>n</sub>] = [SDS]<sub>T</sub> - 0.008, K<sub>w,w</sub> = 1.449 × 10<sup>-14</sup> M<sup>2</sup> [15] and K<sub>a,w</sub> = 5.67 × 10<sup>-10</sup> M.

<sup>e</sup> Error limits are standard deviations.

where  $K_{w,w} = a_{H,w} \cdot a_{OH,w}$ ,  $a_{OH,w} = [\text{OH}_w^-] / \gamma_{OH} [\text{OH}_w^-]$  (because  $[\text{OH}_M^-] \ll [\text{OH}_w^-]$ ) and  $\gamma_{OH}$  is the activity coefficient of hydroxide ion. The magnitudes of  $\gamma_{OH}$  at different [NaOH] were calculated from Davies equation [14], Eq. 6, and the results are summarized in Table 2.

$$\log \gamma = -AZ^2 \left( \frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.2\mu \right) \quad (6)$$

In Eq. 6,  $A = 0.5207$  at 37°C and  $A = 0.5138$  at 30°C. The calculated values of  $K_S^{\text{app}}$  at different [NaOH] (Table 2) were used to calculate  $K_1$  and  $K_2$  from Eq. 5. The least squares calculated respective values of  $K_1$  and  $K_2$  are  $2.9 \pm 0.4 \text{ M}^{-1}$  and  $1130 \pm 54 \text{ M}^{-1}$  when  $K_S^{\text{app}}$  values used were obtained from observed data covering [SDS]<sub>T</sub> range 0.02–0.40 M and  $3.1 \pm 0.3 \text{ M}^{-1}$  and  $986 \pm 36 \text{ M}^{-1}$  when the  $K_S^{\text{app}}$  values were obtained from observed data covering [SDS]<sub>T</sub> range 0.02–0.20 M. The values of  $K_{w,w}$  and  $K_{a,w}$  used in the calculation of  $K_1$  and  $K_2$  were  $2.976 \times 10^{-14} \text{ M}^2$  [15] and  $7.66 \times 10^{-10} \text{ M}$ , respectively. The fitting of the observed data to Eq. 5 is evident from the standard deviations associated with the calculated values of  $K_1$  and  $K_2$  and from the calculated values of  $K_S^{\text{app}}$  as summarized in Table 2.

Eqs. 2 and 5 yield Eq. 7.

$$\frac{k_W^h - k_{\text{obs}}}{k_{\text{obs}}} = K_1 [D_n] + \frac{K_2 K_{w,w} [D_n]}{K_{a,w} a_{OH,w}} \quad (7)$$

The observed pseudo first-order rate constants,  $k_{\text{obs}}$ , obtained at a constant [SDS]<sub>T</sub> and within the [NaOH] range 0.003–0.030 M (Fig. 2) were treated with Eq. 7 with cmc = 0.008 M. The least squares calculated values of  $K_1[D_n]$  and  $K_2K_{w,w}[D_n]/K_{a,w}$  are summarized in Table 3. The fitting of the observed data to Eq. 7 is evident from the plots of Fig. 4 where solid lines are drawn through the least squares calculated points. The average values of  $K_1$  ( $= 3.0 \text{ M}^{-1}$ ) and  $K_2$  ( $= 1887 \text{ M}^{-1}$ ) calculated from the values of  $K_1[D_n]$  and  $K_2K_{w,w}[D_n]/K_{a,w}$  as shown in Table 3 may be compared with  $K_1$  ( $= 3.1 \text{ M}^{-1}$ ) and  $K_2$  ( $= 986 \text{ M}^{-1}$ ) obtained at 37°C as discussed earlier.

The calculated values of  $K_1$  at 30°C are not very reliable because they are associated with considerably high standard deviations (Table 3). Probably the more reliable value of  $K_1$  ( $= 5.9 \text{ M}^{-1}$ ) at 30°C has been the one reported elsewhere [8]. The increase in temperature from 30 to 37°C seems to decrease both  $K_1$  and  $K_2$  by nearly 50%.

The kinetically insignificant contribution of  $k_M^h f_M^{\text{PS}} K_S^{\text{app}} [D_n]$  compared to  $k_W^h$  in Eq. 1 indicates that the rate of hydrolytic cleavage of  $\text{PS}_M^-$  is much slower than that of  $\text{PS}_W^-$ . The insignificant rate of hydrolysis of  $\text{PS}_M^-$  cannot be attributed to medium effect. The dielectric constant of micellar surface has been shown to be 36–47 [16]. According to simple electrostatic theory, the rate of a reaction involving an ionic reactant and a neutral reactant should increase with decrease in the die-

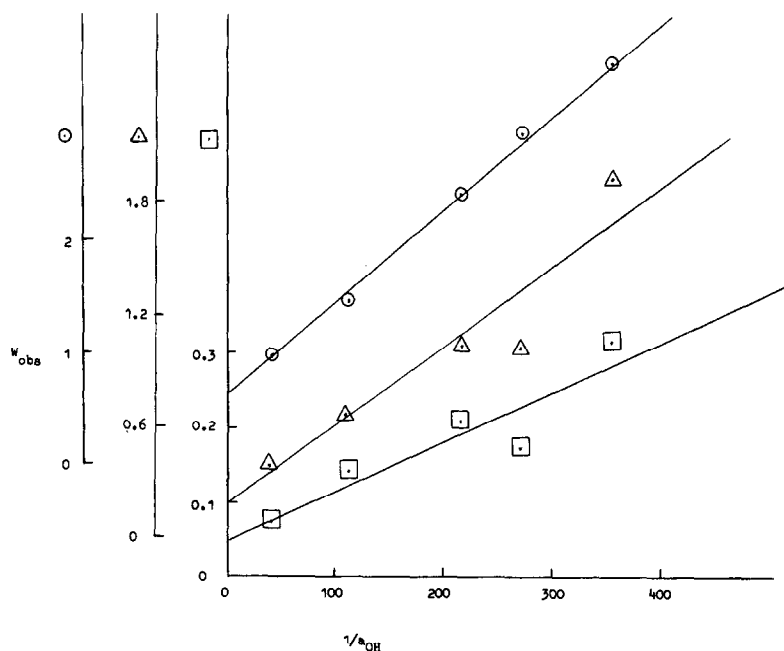


Fig. 4. Plots showing the dependence of  $W_{\text{obs}} \{ = (k_{\text{W}}^{\text{h}} - k_{\text{obs}}) / k_{\text{obs}} \}$  upon  $1/a_{\text{OH}}$  for hydrolysis of phenyl salicylate at 30°C and in the presence of 0.02 M SDS ( $\square$ ), 0.10 M SDS ( $\Delta$ ) and 0.20 M SDS ( $\circ$ ). The solid lines are drawn through the least squares calculated points as described in the text.

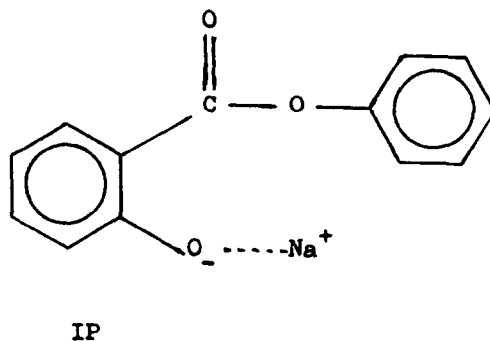
lectric constant of the reaction medium [17] and hence the rate of hydrolysis of  $\text{PS}_{\text{M}}^-$  should be higher than that of  $\text{PS}_{\text{W}}^-$ .

The ionic strength of the ionic micellar surface has been estimated to be nearly 3–5 M, and the activity of water at the ionic micellar surface is not different from water activity in the aqueous pseudophase [17]. But the rates of hydrolysis of salicylate esters have been found to be unchanged with increase in the ionic strength from 0.1 to  $\leq 4.0$  M (maintained by KCl or  $\text{Me}_4\text{NCl}$ ) at 0.05 M NaOH [9,18]. Thus, the insignificant rate of hydrolysis of  $\text{PS}_{\text{M}}^-$  cannot be attributed to the ionic strength effect.

The most probable cause for the extremely slow rate of hydrolysis of  $\text{PS}_{\text{M}}^-$  compared to that of  $\text{PS}_{\text{W}}^-$  is that the  $\text{PS}_{\text{M}}^-$  molecules occupy the specific micellar region where water concentration,  $[\text{H}_2\text{O}_{\text{M}}]$ , is significantly smaller than the water concentration,  $[\text{H}_2\text{O}_{\text{W}}]$ , of aqueous pseudophase. The increase in the acetonitrile content from 3 to 84%, v/v, in mixed  $\text{H}_2\text{O}$ –MeCN solvents decreased the rate of hydrolysis of  $\text{PS}^-$  by nearly 2.5-fold [19]. It appears that the water concentra-

tion of the micellar region where  $\text{PS}_{\text{M}}^-$  molecules are located is even  $< 15\%$ , v/v, if the entire rate reduction is attributed to merely water concentration effect. It is apparent that if we assume that  $\text{PS}_{\text{M}}^-$  molecules exist at the micellar surface i.e. Stern layer, then the micellar surface cannot be considered a homogeneous region in terms of water concentration.

If  $\text{PS}_{\text{M}}^-$  molecules occupy the micellar region where dielectric constant is nearly 36–47 and  $[\text{H}_2\text{O}_{\text{M}}] \ll [\text{H}_2\text{O}_{\text{W}}]$ , then under such conditions, the existence of ion-pair (IP) cannot be completely ruled out.





The formation of **IP** is expected to reduce the efficiency of **IGB** catalysis which is responsible for exceptionally high rate enhancement for the hydrolytic cleavage of  $\text{PS}^-$ . Such ion-pair formation may therefore be also attributed to the reduced rate of hydrolysis of  $\text{PS}_M^-$ .

The observed pseudo first-order rate constants,  $k_{\text{obs}}$ , obtained for hydrolysis of methyl salicylate at 0.03 M NaOH, were found to be almost independent of  $[\text{SDS}]_T$  within its range 0.02–0.40 M (Table 1). Under such experimental conditions, methyl salicylate exists into nearly 100% ionized form,  $\text{MS}^-$ , i.e.  $f_M^{\text{MS}^-} \approx 1$ . The rate of hydrolysis of  $\text{MS}^-$  may be assumed to follow the reaction paths shown by Scheme 1. The observed data may be ascribed to either one of the following possibilities: (i)  $K_S^{\text{app}} \approx K_1 = 0$ , (ii)  $k_W^h \gg k_M^h f_M^{\text{MS}^-} K_S^{\text{app}} [D_n]$  and  $1 \gg K_S^{\text{app}} [D_n]$ , and (iii)  $k_W^h = k_M^h f_M^{\text{MS}^-}$  (and  $f_M^{\text{MS}^-} = 1$  under the experimental conditions imposed).

The first possibility that  $K_S^{\text{app}} = 0$  does not seem to be correct because it means that  $\text{MS}^-$  molecules do not bind with SDS micelles. It is clear from the observed data on the effects of  $[\text{SDS}]_T$  upon rate of hydrolysis of  $\text{PS}^-$  that there is a significant amount of hydroxide ions deep in the micellar region where  $\text{PS}_M^-$  molecules exist. These data may be used to estimate the binding constant,  $K_{\text{OH}}$ , of hydroxide ion with SDS micelles and such an estimated value of  $K_{\text{OH}}$  is nearly  $0.01 \text{ M}^{-1}$ . An ionized methyl salicylate molecule,  $\text{MS}^-$ , is much more hydrophobic than  $\text{OH}^-$ . Recently, we found the evidence for the presence of significant amount of acetyl salicylate ion (a molecule almost similar to  $\text{MS}^-$  in hydrophobicity) at the junctural region of Gouy–Chapman and Stern layers where the effective ionic strength is quite high compared to the ionic strength of the aqueous pseudophase [20]. It may be noted that the binding constant to cetyltrimethylammonium bromide of  $\text{PS}^-$  is only about 3 times greater than that of  $\text{MS}^-$  [20].

It is not possible from the present data to differentiate between possibilities (ii) and (iii). But we prefer possibility (iii) (i.e.  $k_W^h = k_M^h$ ) as the

most probable one. The  $\text{MS}_M^-$  molecules are located in the specific micellar region where water concentration is similar to the water concentration in the aqueous pseudophase [13]. Since the rate of hydrolysis of  $\text{MS}^-$  is insensitive to the ionic strength [18], it is obvious that  $k_W^h = k_M^h$ .

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## References

- [1] A.R. Fersht, *Enzyme Structure and Mechanism*, W.H. Freeman, San Francisco, 1977; W.P. Jencks, *Catalysis in Chemistry and Enzymology*, McGraw-Hill, New York, 1969.
- [2] M.L. Bender, F.J. Kezdy and B. Zerner, *J. Am. Chem. Soc.*, 85 (1963) 3017.
- [3] B. Capon and B.C. Ghosh, *J. Chem. Soc. (B)*, (1966) 472.
- [4] M.N. Khan, *J. Mol. Catal.*, 40 (1987) 195.
- [5] M.N. Khan, *J. Phys. Chem.*, 92 (1988) 6273; M.N. Khan, *Int. J. Chem. Kinet.*, 20 (1988) 443.
- [6] M.N. Khan, *J. Chem. Soc., Perkin Trans 2*, (1989) 199.
- [7] E.H. Cordes and C. Gitler, *Progr. Bioorg. Chem.*, 2 (1973) 1; F.M. Menger, *Acc. Chem. Res.*, 12 (1979) 111.
- [8] M.N. Khan, *J. Chem. Soc., Perkin Trans. 2*, (1990) 445.
- [9] M.N. Khan and S.K. Gambo, *Int. J. Chem. Kinet.*, 17 (1985) 419.
- [10] F.M. Menger and C.E. Portnoy, *J. Am. Chem. Soc.*, 89 (1967) 4698.
- [11] C.A. Bunton, *Catal. Rev.-Sci. Eng.*, 20 (1979) 1.
- [12] N.H. Lajis and M.N. Khan, *Pertanika*, 14 (1991) 193.
- [13] M.N. Khan, M. Dahiru and J. Naaliya, *J. Chem. Soc. Perkin Trans. 2*, (1989) 623.
- [14] C.W. Davies, *J. Chem. Soc.*, (1938) 2093.
- [15] C.D. Ritchie, D.J. Wright, D.-S., Huang and A.A. Kamego, *J. Am. Chem. Soc.*, 97 (1975) 1163.
- [16] P. Mukerjee, in K.L. Mittal (Ed.), *Solution Chemistry of Surfactants*, Vol. 1, Plenum Press, New York, 1979, p. 153.
- [17] E.H. Cordes, *Pure Appl. Chem.*, 50 (1978) 617.
- [18] M.N. Khan, T.O. Olagbemi and U.Z. Umar, *Tetrahedron*, 39 (1983) 811; M.N. Khan and T.O. Olagbemi, *J. Org. Chem.*, 47 (1982) 3695; M.N. Khan and M. Yakubu, *J. Chem. Res. (S)*, (1986) 346.
- [19] M.N. Khan, *Int. J. Chem. Kinet.*, 19 (1987) 757.
- [20] M.N. Khan, unpublished observations.