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Effects of anionic micelles on intramolecular general base-catalysed aminolysis of ionized phenyl salicylate (PS^-)

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ABSTRACT: The effects of micelles of sodium dodecyl sulphate (SDS) on the rates of reactions of ionized phenyl salicylate (PS^-) with *n*-butylamine, piperidine and pyrrolidine were studied at 35 °C. Pseudo-first-order rate constants (k_{obs}) show a linear increase with increase in the total concentration of amine ($[Am]_T$) at a constant [SDS]. An increase in the total concentration of SDS from 0.0 to 0.2 mol dm^{-3} results in a decrease in the observed nucleophilic second-order rate constants by the factors of *ca* 2.6, 5.2 and 3.9 for the reactions of PS^- with *n*-butylamine, piperidine and pyrrolidine, respectively. The rate constants, k_{obs}, show a non-linear increase with increase in [NaOH] from 0.0 to 0.04 mol dm^{-3} at a constant [SDS] and $[Am]_T$. The observed results of aminolysis of PS^- in the presence of SDS micelles are rationalized in the light of the pseudophase model of micelles. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: phenyl salicylate; *n*-butylamine; piperidine; pyrrolidine; anionic micelles aminolysis; hydrolysis; intramolecular general base catalysis; kinetics

INTRODUCTION

Micelles are perhaps the simplest colloidal assemblage in terms of their structural complexities and effects on chemical reactivities. A huge amount of work has been carried out on the effects of micelles on the rates of hydrolysis of esters, activated aromatic compounds and a few amides.[1–9] Although the aminolysis of esters and related compounds has been extensively studied and the mechanistic details of these reactions have been understood to a great extent, attempts to study micellar effects upon the rates of these reactions appear to be limited. Bunton and co-workers studied the effects of micelles on rates of reactions of tri-(*p*-methoxyphenyl)methyl cation with aliphatic amines[10] and aromatic nucleophilic substitution by both aliphatic and aromatic amines.[11] The kinetics of aminolysis of carboxylic esters, in the presence of micelles, were studied by Behme *et al.*[12] Al-Lohedan *et al.*[13] studied the effects of cationic and anionic micelles upon the reactions of methylamine, dimethylamine and trimethylamine with 2-chloropyridinium salt. Recently, the effects of ionic micelles on the rates of reactions of several secondary amines with alkyl nitrites (2-bromoethyl and 1-phenylethyl nitrites) have been reported.[14,15]

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The most obvious reason for the limited attempts at studies of the rates of aminolysis of esters and related compounds is that these reactions generally require the use of amine buffers and the ionic micelles significantly affect the apparent pK_a values of buffer components owing to differential micellar incorporation of the buffer components. This in turn complicates the kinetic analysis of the aminolysis of organic compounds. In earlier work, we studied the effects of anionic micelles on the rates of reactions of propylamine, 1-aminopropan-2-ol and hydrazine with ionized phenyl salicylate (PS^-), where the use of amine buffers was shown to be unnecessary.[16,17] Recently, the effects of cationic micelles on rates of reactions of *n*-butylamine, piperidine and pyrrolidine with PS^- have been studied in the absence of amine buffers.[18] The present work is an extension of the previous work on the effects of anionic micelles on rates of aminolysis of PS^-. The results and the probable explanations are described in this paper.

EXPERIMENTAL

Materials. Reagent-grade chemicals such as phenyl salicylate, *n*-butylamine, piperidine, pyrrolidine and sodium dodecyl sulphate (SDS) were obtained from BDH, Aldrich and Fluka. All other chemicals were also of reagent grade. Glass-distilled water was used throughout. Stock solutions of phenyl salicylate were prepared in acetonitrile.

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Table 1. Effect of $[SDS]_T$ on the apparent nucleophilic second-order rate constants (k_n) for aminolysis of phenyl salicylate[a]

Amine	$[SDS]_T$ (mol dm^{-3})	$10^4\ k_0$ (s^{-1})	$10^3\ k_n$ (dm^3 mol^{-1} s^{-1})	K_1[b] (dm^3 mol^{-1})	$[Am]_T$[c] (mol dm^{-3})	No. of runs
n-Butylamine[d]	0.0	8.11 ± 0.34[e]	72.8 ± 0.7[e]		0.01–0.07	5
	0.002	7.84 ± 0.72	74.7 ± 1.5		0.01–0.07	5
	0.005	9.48 ± 0.72	69.5 ± 1.1		0.01–0.07	5
	0.007	7.44 ± 0.40	69.8 ± 0.8		0.01–0.07	5
	0.020	5.79 ± 0.86	62.8 ± 1.8	11.7 ± 2.2[e]	0.01–0.7	5
	0.050	3.84 ± 0.81	52.0 ± 1.6	8.6 ± 2.2	0.01–0.07	5
	0.070	3.47 ± 0.67	45.6 ± 1.4	9.0 ± 1.6	0.01–0.07	5
	0.100	2.34 ± 0.87	40.4 ± 0.5	8.4 ± 0.2	0.03–0.10	6
	0.140	1.49 ± 0.30	34.5 ± 0.4	8.2 ± 0.2	0.03–0.10	6
	0.200	1.13 ± 0.85	27.2 ± 1.2	8.5 ± 0.6	0.03–0.10	6
	0.200[f]	4.21 ± 0.34	28.3 ± 0.5	8.1 ± 0.2	0.01–0.10	7
	0.200[g]	-0.6 ± 1.1	29.2 ± 2.7		0.03–0.05	3
Piperidine[h]	0.0	7.68 ± 3.20	323 ± 8		0.01–0.06	5
		(8.22)	323 ± 8			
	0.004	9.96 ± 2.86	311 ± 7		0.01–0.06	5
		(8.22)	317 ± 7			
	0.007	8.43 ± 0.94	303 ± 2		0.01–0.06	5
		(8.22)	304 ± 2			
	0.010	3.49 ± 2.58	305 ± 6		0.01–0.06	5
		(6.80)	293 ± 9			
	0.015	6.61 ± 1.7	273 ± 4		0.01–0.06	5
		(6.60)	273 ± 4			
	0.020	4.68 ± 3.01	267 ± 7		0.01–0.06	5
		(6.29)	260 ± 8			
	0.050	2.19 ± 0.84	198 ± 2		0.01–0.06	5
		(5.62)	185 ± 10			
	0.070	0.53 ± 1.96	171 ± 5		0.01–0.06	5
		(5.04)	155 ± 10			
	0.100	0.51 ± 1.64	136 ± 4		0.01–0.06	5
		(4.36)	122 ± 9			
	0.140	2.66 ± 0.80	94.1 ± 2.5		0.01–0.05	4
		(4.21)	87.8 ± 4.0			
	0.200	1.72 ± 1.15	66.5 ± 2.8		0.01–0.06	5
		(3.37)	61.0 ± 3.1			
Pyrrolidine[h]	0.0	15.6 ± 5.1	797 ± 12		0.01–0.06	5
		(8.22)	823 ± 17			
	0.004	17.9 ± 5.0	767 ± 15		0.01–0.05	5
		(8.22)	810 ± 31			
	0.007	15.5 ± 4.2	744 ± 12		0.01–0.05	5
		(8.22)	776 ± 23			
	0.010	6.44 ± 4.41	775 ± 13		0.01–0.05	5
		(6.80)	774 ± 13			
	0.015	5.00 ± 2.92	754 ± 9		0.01–0.05	5
		(6.60)	748 ± 8			
	0.020	3.42 ± 2.21	726 ± 7		0.01–0.05	5
		(6.29)	713 ± 13			
	0.040	-1.4 ± 2.2	607 ± 7		0.01–0.05	5
		(5.84)	574 ± 24			
	0.080	-7.3 ± 3.8	465 ± 11		0.01–0.05	5
		(5.00)	412 ± 29			
	0.130	-5.6 ± 3.6	343 ± 11		0.01–0.05	5
		(4.05)	302 ± 21			
	0.200	-3.2 ± 2.3	235 ± 7		0.01–0.05	5
		(3.37)	207 ± 16			

[a] $[\text{Phenyl salicylate}]_0 = 2 \times 10^{-4}$ mol dm^{-3}; 35 °C; $\lambda = 350$ nm; reaction mixture for each kinetic run contained 2% (v/v) CH_3CN.
[b] Calculated from Eqn (8) as described in the text.
[c] Total amine concentration range.
[d] Externally added [NaOH] = 0.005 mol dm^{-3} and cmc = 0.008 mol dm^{-3}.
[e] Error limits are standard deviations.
[f] Externally added [NaOH] = 0.04 mol dm^{-3}.
[g] Externally added [NaOH] = 0 mol dm^{-3}.
[h] Externally added [NaOH] = 0.02 mol dm^{-3} and cmc = 0.009 mol dm^{-3}.

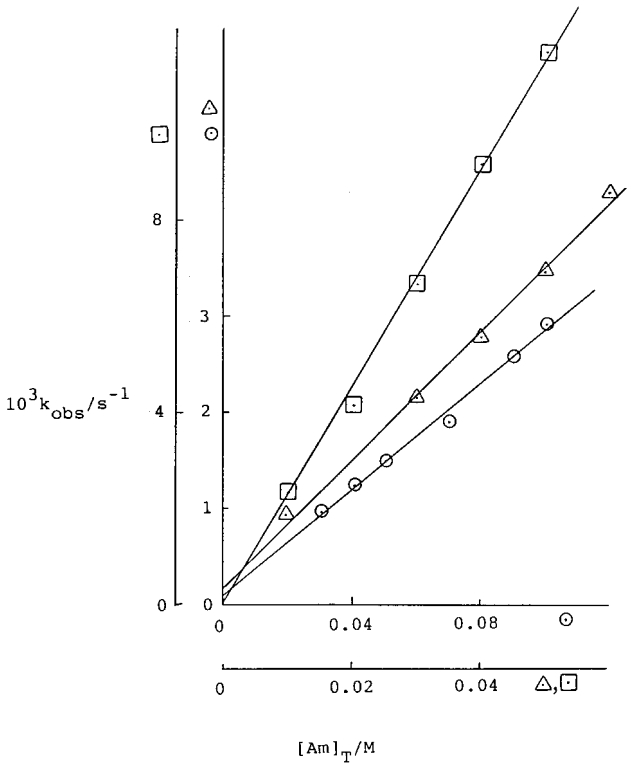


Figure 1. Dependence of the observed pseudo-first-order rate constants (k_{obs}) for aminolysis of ionized phenyl salicylate (PS^-) on total amine concentration ($[Am]_T$) at 0.2 mol dm^{-3} SDS for (○) *n*-butylamine, (△) piperidine and (□) pyrrolidine

Kinetic measurements. Non-ionized phenyl salicylate (PSH), *N*-substituted salicylamide, salicylic acid, phenol, salicylate and phenolate ions do not show detectable absorption at 350 nm. However, PS^- and ionized N-substituted salicylamide show strong and weak absorption, respectively, at 350 nm. The rate of cleavage of phenyl salicylate in an aqueous alkaline solvent containing an amine and SDS was studied spectrophotometrically by monitoring the decrease in absorbance (A_{obs}) at 350 nm. The details of the kinetic procedure and data analysis were same as described elsewhere.[17,19] The absorbance values obtained at a reaction time $t = \infty$ were in agreement with the products formed as *N*-substituted salicylamide, salicylate and phenolate ions.

RESULTS

Effect of [amine] on the cleavage of phenyl salicylate at a constant $[SDS]_T$ and 35 °C

The cleavage of phenyl salicylate was studied at various total amine concentrations ($[Am]_T$) at constant total concentrations of SDS ($[SDS]_T$) and [NaOH]. Pseudo-first-order rate constants (k_{obs}) obeyed the equation

$$k_{obs} = k_0 + k_n[Am]_T \quad (1)$$

where k_0 and k_n represent first- and second-order rate constants for amine-independent and amine-dependent rate of cleavage of PS^-, respectively. The linear least-squares technique was used to calculate k_0 and k_n from Eqn (1) and these values at different $[SDS]_T$ for *n*-butylamine, piperidine and pyrrolodine are summarized in Table 1. The fitting of the observed data to Eqn (1) is evident from some representative plots in Fig. 1 and from the standard deviations associated with the calculated parameters k_0 and k_n (Table 1). The values of k_n for *n*-butylaminolysis of PS^- at 0.2 mol dm^{-3} SDS are almost independent of added [NaOH] within the range 0.0–0.04 mol dm^{-3} (Table 1). This shows that the presence of *n*-butylammonium ions due to the reaction of *n*-butylamine with water is kinetically insignificant.

The values of k_0 at different $[SDS]_T$ are negligible compared with $k_n[Am]_T$ for highly reactive amines such as piperidine and pyrrolidine. The values of k_n for these amines were also calculated from Eqn (1) by considering k_0 as a known parameter. The known values of k_0 at different $[SDS]_T$ were obtained from experiments carried out under similar experimental conditions with $[Am]_T = 0$.[20] These calculated values of k_n are also shown in Table 1.

The linearity of the plot of k_{obs} versus $[Am]_T$ at a constant $[SDS]_T$ shows that the ratio $[AmH^+]/[Am]$ (where AmH^+ and Am represent protonated and unprotonated amine, respectively) remains unchanged with change in $[Am]_T$. Such a characteristic linear plot also indicates that any micellar structural change due to the change in $[Am]_T$ is kinetically insensitive.

Effect of [NaOH] upon aminolysis of phenyl salicylate at a constant $[Am]_T$ and $[SDS]_T$

The effect of [NaOH] upon the rates of reactions of phenyl salicylate with *n*-butylamine was studied within the [NaOH] range 0.002–0.040 mol dm^{-3} at a constant $[Am]_T$ and $[SDS]_T$. Similar observations were obtained with piperdine and pyrrolidine. Pseudo-first-order rate constants (k_{obs}) were found to fit to the following empirical equation:

$$k_{obs} - k_0' = \frac{\alpha[NaOH]}{\beta + [NaOH] + [^-OH]_{re}} \quad (2)$$

where k_0' is the pseudo-first-order rate constant obtained under similar experimental conditions with [NaOH] = 0 and $[^-OH]_{re}$ represents the hydroxide ion concentration produced by the reversible reaction

$$N + H_2O \overset{K_b}{\rightleftharpoons} NH^+ + {}^-OH \quad (3)$$

where N and NH^+ represent free and protonated form of

Table 2. Values of empirical parameters, α and β, calculated from Eqn (2)[a]

Amine	$[SDS]_T$ (mol dm^{-3})	$10^4\ \alpha$ (s^{-1})	$10^3\ \beta\ [\equiv K_{b(ap)}]$ (mol dm^{-3})	$10^3\ \beta_{calc}$[b] (mol dm^{-3})	$10^3\ \beta_{calc}$[c] (mol dm^{-3})	Y[d]
n-Butylamine[e]	0.02	5.73 ± 0.78[f]	23.0 ± 6.7[f]			0.21
	0.05	6.75 ± 0.87	18.8 ± 5.2			0.34
	0.10	7.19 ± 0.75	26.1 ± 5.4			0.47
Piperidine[g]	0.01	15.0 ± 1.3	10.4 ± 2.9	-	-	0.44
	0.02	17.7 ± 1.4	12.3 ± 2.7	11.6	11.6	0.64
	0.05	18.2 ± 1.1	17.1 ± 2.5	18.4	18.3	0.87
	0.10	14.1 ± 1.9	22.0 ± 6.7	21.2	21.3	2.01
Pyrrolidine[g]	0.01	45.5 ± 2.7	7.16 ± 1.72	8.48	6.90	0.80
	0.02	59.3 ± 4.8	17.0 ± 3.5	16.4	17.2	1.06
	0.05	61.5 ± 6.5	25.9 ± 5.6	25.3	25.8	1.41
	0.10	53.5 ± 2.5	29.2 ± 2.6	29.7	29.2	1.88[h]

[a] $[\text{Phenyl salicylate}]_0 = 2 \times 10^{-4}$ mol dm^{-3}; 35 °C; $\lambda = 350$ nm; reaction mixture for each kinetic run contained 2% (v/v) CH_3CN; unless indicated otherwise, the total number of kinetic runs and the added sodium hydroxide concentration range at each $[SDS]_T$ were 6 and 0.002–0.040 mol dm^{-3}, respectively.
[b] Calculated from Eqn (12) with $K_b = 0.00244$ mol dm^{-3}, $K_{NH} = 494$, $K_N = 61$ dm^3 mol^{-1} and cmc = 0.009 mol dm^{-3} for piperidine and $K_b = 0.00301$ mol dm^{-3}, $K_{NH} = 970 \pm 195$, $K_N = 91 \pm 22$ dm^3 mol^{-1} and cmc = 0.009 mol dm^{-3} for pyrrolidine.
[c] Calculated from Eqn (12) with $K_b = 0.00244$ mol dm^{-3}, $K_{NH} = 447 \pm 147$, $K_N = 54 \pm 23$ dm^3 mol^{-1} and cmc = 0.008 mol dm^{-3} for piperidine and $K_b = 0.00301$ mol dm^{-3}, $K_{NH} = 817 \pm 28$, $K_N = 74 \pm 3$ dm^3 mol^{-1} and cmc = 0.008 mol dm^{-3} for pyrrolidine.
[d] $Y = (k_{obs,\,m} - k_{obs,\,i})/k_{obs\,i}$, where $k_{obs,\,m}$ and $k_{obs,\,i}$ are the observed pseudo-first-order rate constants obtained at the maximum added [NaOH] (= 0.04 mol dm^{-3}) and at [NaOH] = 0.
[e] $[Am]_T = 0.02$ mol dm^{-3}.
[f] Error limits are standard deviations.
[g] $[Am]_T = 0.01$ mol dm^{-3}.
[h] The added [NaOH] range was 0.001–0.040 mol dm^{-3}.

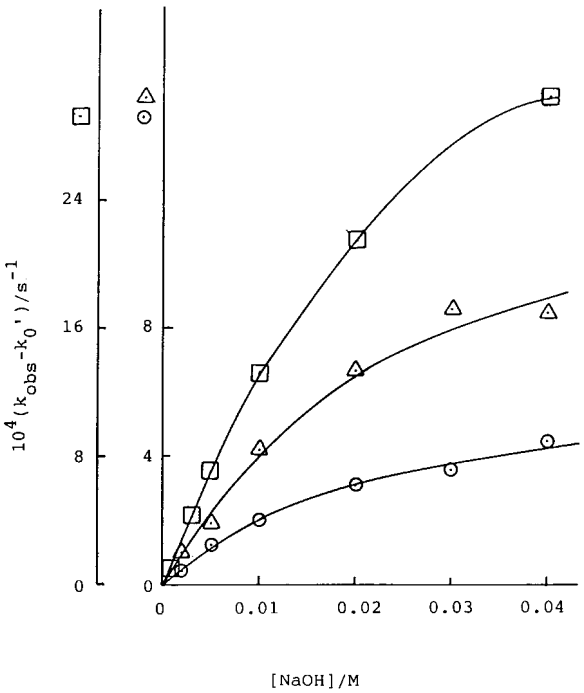


Figure 2. Plots showing the dependence of (k_{obs} - k_0') on [NaOH] for the reaction of PS^- with (○) *n*-butylamine ($[Am]_T = 0.02$ mol dm^{-3}), (△) piperidine ($[Am]_T = 0.01$ mol dm^{-3}) and (□) pyrrolidine ($[Am]_T = 0.01$ mol dm^{-3}) at 0.1 mol dm^{-3} SDS

amine base and $K_b = K_w/K_a$ with $K_w = [H^+]\ [^-OH]$ and $K_a = [N]\ [H^+]/[NH^+]$. The values of $[^-OH]_{re}$ at different [NaOH] were calculated from the equation

$$[^-OH]_{re} = \{-([NaOH] + K_w/K_a) + (([NaOH] + K_w/K_a)^2 + 4(K_w/K_a)[Am]_T)^{1/2}\}/2 \quad (4)$$

where $[Am]_T = [N] + [NH^+]$ and [NaOH] is the externally added hydroxide ion concentration.

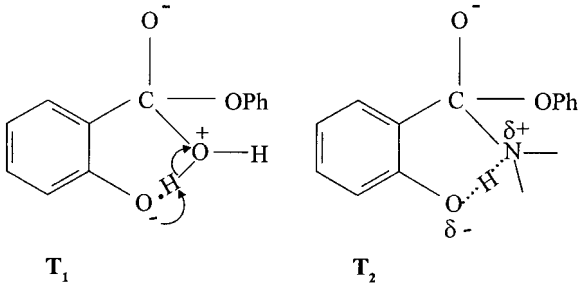
The empirical parameters α and β were calculated from Eqn (2) using the non-linear least-squares technique. The calculated values of these parameters (α and β) at different $[SDS]_T$ for *n*-butylamine, piperidine and pyrrolidine are summarized in Table 2. The fitting of the observed data to Eqn (2) is evident from some representative plots is Fig. 2 where solid lines are drawn through the calculated points using Eqn (2) and from the standard deviations associated with α and β (Table 2). It should be noted that although the fitting of the observed data to Eqn (2) appears to be satisfactory, the values of α and β at low $[SDS]_T$ are not very reliable because, under such conditions, the contribution of α [NaOH]/(β + [NaOH] + $[^-OH]_{re}$) compared with k_0' in Eqn (2) is <50% (Table 2).

DISCUSSION

The values of the molar extinction coefficients (δ_{350}) are 5700–6000 dm^3 mol^{-1} cm^{-1} for PS^- and zero for PSH at 350 nm. The values of initial absorbance (A^0_{obs} at

reaction time $t = 0$) of the reaction mixtures containing 2×10^{-4} mol dm^{-3} phenyl salicylate, ≥ 0.01 mol dm^{-3} amine (*n*-butylamine, piperidine and pyrrolidine) and ≥ 0.005 mol dm^{-3} NaOH were found to be unchanged with change in $[SDS]_T$ from 0 to ≤ 0.2 mol dm^{-3}. If the change in the reaction conditions such as an increase in $[SDS]_T$ increased [PSH], then the values of A^0_{obs} should have decreased with increase in $[SDS]_T$. Hence unchanged values of A^0_{obs} with change in $[SDS]_T$ and in $[Am]_T$ show the presence of 100% ionized form (PS^-) of phenyl salicylate in the reaction mixtures of almost all the kinetic runs carried out in this study.

Pseudo-first-order rate constants (k_{obs}) for hydrolysis of phenyl salicylate were found to be independent of [$^-$OH] within the [$^-$OH] range 0.005–0.060 mol dm^{-3} in the absence of SDS.[16,17] Similarly, k_{obs} turned out to be independent of [$^-$OH] within the [NaOH] range 0.01–0.04 mol dm^{-3} in the presence of 0.03 mol dm^{-3} cetyltrimethylammonium bromide.[20] It has been ascertained unequivocally that the hydrolysis of phenyl salicylate under such conditions involves PS^- and H_2O as the reactants.[19,21] The rate of pH-independent hydrolysis of phenyl salicylate has been shown to be increased by nearly 10^6-fold owing to the occurrence of intramolecular general base (IGB) catalysis (**T_1**). The detailed mechanism of IGB-catalysed hydrolysis of phenyl salicylate has been described elsewhere.[22] It has been concluded elsewhere that the reactions of PS^- with primary and secondary amines including piperidine and pyrrolidine involve IGB catalysis (**T_2**).[23] The mechanism of these reactions in the absence of micelles is discussed elsewhere.[23]



T_1 **T_2**

Effect of $[SDS]_T$ on aminolysis of phenyl salicylate in the presence of constant [NaOH] at 35 °C

An increase in $[SDS]_T$ decreased the nucleophilic second-order rate constants (k_n) for the reactions of phenyl salicylate with *n*-butylamine, piperidine and pyrrolidine (Table 1). These observations may be explained in terms of the pseudophase model of the micelle,[24] which consists of various assumptions[1b,25] including one which considers the aqueous pseudophase and micellar pseudophase as two distinct static phases. Despite the fact that micelles are highly dynamic molecular aggregates,[26] almost all the kinetic data that have so far appeared in the literature were found to fit satisfactorily the presumed static micellar pseudophase. The reaction scheme for the cleavage of phenyl salicylate, in the presence of amine and SDS micelles, may be given as shown in Scheme 1 where the subscripts W and M represent the aqueous pseudophase and micellar pseudophase, respectively, N and NH^+ represent respective free and protonated form of amine base and D_n is the micellized SDS.

$$PS^-_W + D_n \overset{K_1}{\rightleftharpoons} PS^-_M$$

$$N_W + D_n \overset{K_N}{\rightleftharpoons} N_M$$

$$NH^+_W + D_n \overset{K_{NH}}{\rightleftharpoons} NH^+_M$$

$$PS^-_W \xrightarrow{k^h_W} \text{product(s)}$$

$$PS^-_M \xrightarrow{k^h_M} \text{product(s)}$$

$$PS^-_W + N_W \xrightarrow{k^n_W} \text{product(s)}$$

$$PS^-_M + N_M \xrightarrow{k^n_M} \text{product(s)}$$

Scheme 1

The equilibrium for micellar binding of PSH and the reaction steps for hydrolysis and aminolysis of PSH are not included in Scheme 1 for the reason described at the beginning of the Discussion that $[PSH]_T \approx 0$ (where $[PSH]_T = [PSH_W] + [PSH_M]$) under the experimental conditions imposed.

The observed rate law ($\text{rate} = k_{obs}[PS^-]_T$, where $[PS^-]_T = [PS^-_W] + [PS^-_M]$) and Scheme 1 lead to the equation

$$k_{obs} = \frac{k^h_W + k^h_M K_1[D_n]}{1 + K_1[D_n]} + \frac{(k^n_W f^N_W + k^{ns}_M K_1 K_{Am}{}^{app} f^N_M[D_n])[Am]_T}{(1 + K_1[D_n])(1 + K_{Am}{}^{app}[D_n])} \quad (5)$$

where $K_{Am}{}^{app} = ([N_M] + [NH^+_M])/([N_W] + [NH^+_W])[D_n]$ with $[D_n] = [SDS]_T - \text{cmc}$ (critical micelle concentration), $f^N_W = K_a{}^N{}_W/(a_{H,W} + K_a{}^N{}_W)$, $f^N_M = K_a{}^N{}_M/(a_{H,M} + K_a{}^N{}_M)$ with $K_a{}^N$ and a_H representing the ionization constant of NH^+ and activity of proton, respectively, $[Am]_T = [N_W]_T + [N_M]_T$ with $[N_W]_T = [N_W] + [NH^+_W]$ and $[N_M]_T = [N_M] + [NH^+_M]$ and $k^{ns}_M = k^n_M/V$, where V is the micellar molar volume in which micellar-mediated reaction occurs. It may be noted that the derivation of Eqn (5) involves many assumptions which are critically discussed by Bunton[1b] and Romsted.[25]

Equation (5) is similar to Eqn (1) with

$$k_0 = \frac{k^h_W + k^h_M K_1[D_n]}{1 + K_1[D_n]} \quad (6)$$

and

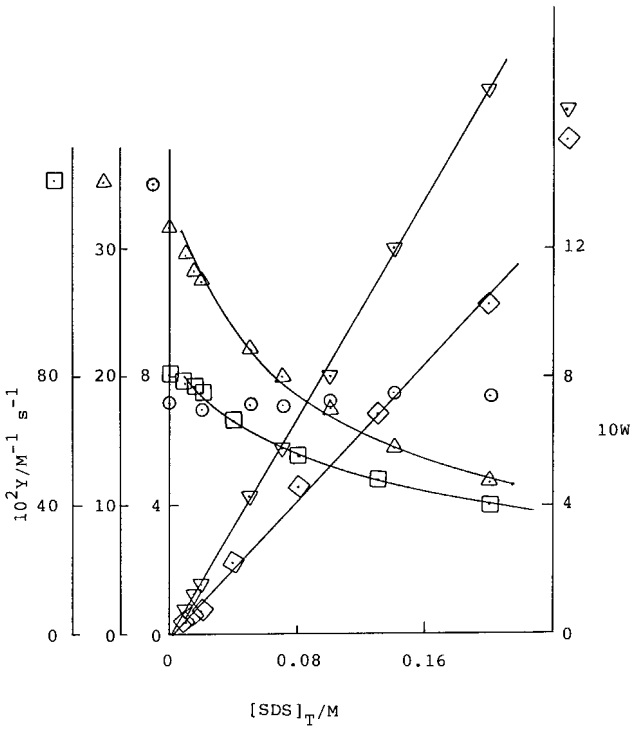


Figure 3. Plots of Y versus $[SDS]_T$ for the reaction of PS^- with (○) *n*-butylamine, (△) piperidine and (□) pyrrolidine, where $Y = k_n(1 + K_1[D_n])$, and plots showing the dependence of W on $[SDS]_T$ for the reaction of PS^- with (▽) piperidine and (◊) pyrrolidine, where $W = (k^n_W f^N_W - Y)/Y$

$$k_n = \frac{k^n_W f^N_W + k^{ns}_M f^N_M K_1 K_{Am}^{app}[D_n]}{(1 + K_1[D_n])(1 + K_{Am}^{app}[D_n])} \qquad (7)$$

In order to fit the observed data (Table 1) to Eqns (6) and (7), one needs the cmc values under the present experimental conditions. The values of cmc were determined using the graphical technique of Broxton *et al*.[27] and the values obtained are shown in Table 1. The values of k_0 (Table 1) obtained for *n*-butylaminolysis of PS^- were treated with Eqn (6) using the non-linear least-squares technique. The values of k^h_M and K_1 turned out to be $(-0.2 \pm 0.5) \times 10^{-4}$ s^{-1} and 26 ± 5 dm^3 mol^{-1}, respectively. The value of k^h_W used was obtained from the kinetic runs carried out at $[SDS]_T = 0$ and also $[SDS]_T <$ cmc. The negative value of k^h_M with a standard deviation of >200% merely indicates that the contribution of $k^h_M K_1 [D_n]$ is insignificant compared with k^h_W in Eqn (6). Similar observations were obtained at different [NaOH] in the absence and presence of hydrazine.[17] The calculated value of K_1 (= 26 dm^3 mol^{-1}) is larger than the more reliable value (= 8.9 dm^3 mol^{-1}).[28] The values of k^h_M and K_1 obtained in the present study are less reliable because they are derived from k_0 values whose contributions towards k_{obs} vary from 48 to 12% within the $[Am]_T$ range 0.01–0.07 mol dm^{-3} at 0.02 mol dm^{-3} SDS and from 12 to 4% within the $[Am]_T$ range 0.03–0.10 mol dm^{-3} at 0.20 mol dm^{-3} SDS.

The plots of k_n $(1 + K_1$ $[D_n])$ versus $[D_n]$ for *n*-butylamine, piperidine and pyrrolidine are shown in Fig. 3. The values of K_1 used are 8.9 dm^3 mol^{-1} for *n*-butylaminolysis at 0.005 dm^3 mol^{-1} NaOH and 4.8 dm^3 mol^{-1} for piperidinolysis and pyrrolidinolysis of PS^- at 0.02 mol dm^{-3} NaOH. The values of $K_1 = 8.9$ and 4.8 dm^3 mol^{-1} were obtained at 0.0075 and ≥0.02 mol dm^{-3} NaOH, respectively, in the absence of any amine.[28]

The plot for *n*-butylamine in Fig. 3 indicates that the k_n $(1 + K_1$ $[D_n])$ values are almost independent of $[D_n]$ within the $[SDS]_T$ range 0.0–0.2 mol dm^{-3}. Similar observations were obtained for hydrazinolysis of PS^- at 0.0075 and 0.050 mol dm^{-3} NaOH.[17] As concluded elsewhere,[17] these observations indicate that $k^n_W f^N_W \approx k^{ns}_M f^N_M K_1$. Under such conditions, Eqn (5) yields

$$K_1 = \{k^n_W f^N_W [Am]_T - (k_{obs} - k_0)\}/(k_{obs} - k_0)[D_n] \qquad (8)$$

where k_0 is pseudo-first-order rate constant at $[Am]_T = 0$, $[Am]_T$ is the total concentration of *n*-butylamine, $10^3 k^n_W f^N_W = 71.7$ dm^3 mol^{-1} s^{-1} and cmc = 0.008 mol dm^{-3}. Equation (8) was used to calculate K_1 at different $[Am]_T$ with a constant $[SDS]_T$. The average values of K_1 at different $[SDS]_T$ are summarized in in Table 1. The values of K_1 at $[SDS]_T \geq 0.05$ mol dm^{-3} are not significantly different from K_1 (= 8.9 dm^3 mol^{-1}) obtained under similar experimental conditions with $[Am]_T = 0$. The value of K_1 (= 11.7 ± 2.2 dm^3 mol^{-1}) at 0.02 mol dm^{-3} SDS is associated with a high standard deviation and is higher than K_1 obtained at $[SDS]_T \geq 0.05$ mol dm^{-3}. This may be attributed to a slight error in the cmc value. The statistical reliability of $k_0 + k^n_W f^N_W [Am]_T - k_{obs}$ apparently decreases as $[D_n] \rightarrow 0$ and also $[D_n]^{-1} \rightarrow \infty$ as $[D_n] \rightarrow 0$. Thus, the data treatment with Eqn (8) is very sensitive to errors when $[D_n] \rightarrow 0$.

The plots of k_n $(1 + K_1$ $[D_n])$ versus $[D_n]$ for piperidinolysis and pyrrolidinolysis of PS^- reveal negative slopes (Fig. 3). These data were treated with the equation

$$k_n(1 + K_1[D_n]) = \frac{k^n_W f^N_W + k^{ns}_M f^N_M K_1 K_{Am}^{app}[D_n]}{1 + K_{Am}^{app}[D_n]} \qquad (9)$$

which is the rearranged form of Eqn (7). The non-linear least-squares calculated respective values of $k^{ns}_M f^N_M K_1$ and K_{Am}^{app} are $(4.59 \pm 2.80) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and 13.2 ± 3.2 dm^3 mol^{-1}, respectively, for piperidine and 0.2 ± 4.0 dm^3 mol^{-1} s^{-1} and 9.1 ± 1.2 dm^3 mol^{-1}, respectively, for pyrrolidine. The fitting of the observed data to Eqn (9) may be seen from the plots in Fig. 3 where solid lines are drawn through the calculated points.

The calculated values of $k^{ns}_M f^N_M K_1$ are associated

with extremely high standard deviations and therefore these values are not statistically reliable. The maximum contribution of $k^{ns}_M f^N_M K_1 K_{Am}^{app}[D_n]$, obtained at the highest $[SDS]_T$ (= 0.2 mol dm^{-3}), turned out to be 27 and 30% for piperidinolysis and pyrrolidinolysis of PS^-, respectively. Hence $k^{ns}_M f^N_M K_1 K_{Am}^{app}[D_n]$ may be neglected compared with $k^n_W f^N_W$ in Eqn (9). Under such conditions Eqn (9) is reduced to

$$(k^n_W f^N_W - Y)/Y = K_{Am}^{app}[D_n] \qquad (10)$$

where $Y = k_n (1 + K_1[D_n])$. The observed data appeared to fit Eqn (10) (Fig. 3) and the calculated values of K_{Am}^{app} are 10.1 ± 1.8 dm^3 mol^{-1} for piperidine and 6.3 ± 0.7 dm^3 mol^{-1} for pyrrolidine.

Although the calculated values of $k^{ns}_M f^N_M K_1$ are not very reliable, as concluded earlier, the values of $k^{ns}_M f^N_M$ may be calculated from these values as 9.6×10^{-3} s^{-1} for piperidine and 4.2×10^{-2} s^{-1} for pyrrolidine with $K_1 = 4.8$ dm^3 mol^{-1}. The value of $k^{ns}_M f^N_M$ (= 8.1×10^{-3} s^{-1}) for *n*-butylaminolysis of PS^- may be calculated from the relationship $k^{ns}_M f^N_M K_1 = k^n_W f^N_W$, where $K_1 = 8.9$ dm^3 mol^{-1}. The values of second-order rate constants ($k^n_M f^N_M = V k^{ns}_M f^N_M$ with $V = 0.14$ dm^3 mol^{-1})[1b] turned out to be 1.1×10^{-3} dm^3 mol^{-1} s^{-1} for *n*-butylamine, 1.4×10^{-3} dm^3 mol^{-1} s^{-1} for piperidine and 5.9×10^{-3} dm^3 mol^{-1} s^{-1} for pyrrolidine. These calculated values indicate that $k^n_W f^N_W / k^n_M f^N_M$ are 65 for *n*-butylamine, 225 for piperidine and 135 for pyrrolidine. Although these calculated values of $k^n_W f^N_W / k^n_M f^N_M$ are not reliable because of the large errors in the $k^n_M f^N_M$ values, they do indicate that the rate of aminolysis of PS^- is much slower in the micellar pseudophase than in the aqueous pseudophase. Similar results were obtained in the nitrosation of piperidine[14] and pyrrolidine[15] with 2-bromoethyl nitrite and 1-phenylethyl nitrite in the presence of SDS micelles.

The micellar-mediated reactions are believed to occur in an environment of significantly low dielectric constant.[29] An increase in CH_3CN content from 2 to 50–60% (v/v) in mixed aqueous solvents decreased the rate of *n*-butylaminolysis, piperidinolysis and pyrrolidinolysis of PS^- by nearly 6–8-fold.[30] A further increase in CH_3CN content from 50 or 60% to 80 or 90% (v/v) did not bring any appreciable change in k_n. Hence the significantly low rate of aminolysis of PS^- in the micellar pseudophase compared with that in the aqueous pseudophase cannot be attributed only to a medium effect.

The micelles are dynamic molecular aggregates and as such the micellar pseudophase may not be expected to be similar to the aqueous pseudophase in terms of medium properties. Experimental observations indirectly show that the micellar pseudophase is non-homogeneous in terms of polarity, concentration of water and distribution of different types of micellized molecules. Hence it may not be unreasonable to propose that different average locations of amines and PS^- molecules in the micellar pseudophase are partly responsible for the lower value of k^n_M compared with k^n_W.

The values of K_{am}^{app} of 13 or 10 dm^3 mol^{-1} for piperidine and 9 or 6 dm^3 mol^{-1} for pyrrolidine may be compared with the corresponding values (3.0–5.5 dm^3 mol^{-1} for piperidine[14] and 1.4 dm^3 mol^{-1} for pyrrolidine[15]) obtained by a spectrophotometric technique. A recent compilation of a large number of K_S values shows a considerable spread in the experimental values of K_S determined by different techniques.[31]

Effect of [NaOH] on aminolysis of phenyl salicylate in the presence of constant $[Am]_T$ and $[SDS]_T$ at 35 °C

The apparent base ionization constant $[K_{b(ap)}]$ of the amine in the presence of SDS micelles can be defined by the equation

$$K_{b(ap)} = \frac{[NH^+]_T[^-OH]_T}{[N]_T} = \frac{([NH^+_W] + [NH^+_M])([^-OH_W] + [^-OH_M])}{[N_W] + [N_M]} \qquad (11)$$

or

$$K_{b(ap)} = \frac{K_b(1 + K_{OH}[D_n])(1 + K_{NH}[D_n])}{1 + K_N[D_n]} \qquad (12)$$

where K_{OH} $[D_n] = [^-OH_M]/[^-OH_W]$ and $K_b = [NH^+_W][^-OH_W]/[N_W]$. In Eqn 11, $[^-OH]_T = [^-OH]_{ad} + [^-OH]_{re}$, where $[^-OH]_{ad}$ and $[^-OH]_{re}$ represent hydroxide ion concentrations produced by added NaOH and by the reaction between amine and water, respectively.

Scheme 1 and Eqn (11) lead to

$$k_{obs} - k'_0 = \frac{(k^n_W + k^{ns}_M K_1 K_N[D_n])[^-OH]_{ad}[Am]_T}{(1 + K_1[D_n])(1 + K_N[D_n])\{K_{b(ap)} + [^-OH]_T\}} \qquad (13)$$

where k'_0 is the observed rate constant at $[^-OH]_{ad} = 0$. Equation (13) is similar Eqn (2) with $\alpha = (k^n_W + k^{ns}_M K_1 K_N [D_n])[Am]_T/\{(1 + K_1 [D_n])(1 + K_N [D_n])\}$ and $\beta = K_{b(ap)}$.

It is evident from Eqns (7) and (13) that $\alpha/[Am]_T$ must be equal to k_n provided that $K_{am}^{app} = K_N$ and $f^N_W = f^N_M = 1$ at 0.02 mol dm^{-3} [NaOH] (= $[^-OH]_{ad}$). This prediction appears to be correct only at 0.1 mol dm^{-3} SDS for *n*-butylamine and $\geq$0.05 mol dm^{-3} SDS for piperidine and pyrrolidine (Tables 1 and Table 2). At lower values of $[SDS]_T$, the $\alpha/[Am]_T$ values are considerably lower than the corresponding k_n values. The most obvious reason for such a discrepancy is the considerable uncertainty in the α values at low $[SDS]_T$, as discussed earlier.

The value of $K_{b(ap)}$ (= 0.017 mol dm^{-3}) obtained at

Table 3. Values of K_{Am}^{app} calculated from Eqn (16) at different [NaOH] in the presence of 0.1 mol dm^{-3} SDS and 0.01 mol dm^{-3} amine

Piperidine			Pyrrolidine		
$10^3[^-OH]_T$[a] (mol dm^{-3})	K_{Am}^{app} (dm^3 mol^{-1})	$(K_{am}^{app})_{calc}$[b] (dm^3 mol^{-1})	$10^3[^-OH]_T$[a] (mol dm^{-3})	K_{am}^{app} (dm^3 mol^{-1})	$(K_{am}^{app})_{calc}$[b] (dm^3 mol^{-1})
3.868	39.2	38.1	4.180	40.2	38.4
5.196	30.7	31.7	4.836	36.7	34.8
7.464	25.0	24.6	6.250	26.9	28.7
11.72	15.8	17.2	7.788	21.4	23.8
21.04	10.0	10.4	12.01	13.4	15.4
30.74	7.0	7.3	21.24	7.3	7.2
40.57	7.1	5.6	40.69	3.5	1.1

[a] Total concentration of hydroxide ion (= $[^-OH]_{ad} + [^-OH]_{re}$).
[b] Calculated from Eqn (16) with $[^-OH_W] \approx [^-OH]_T$ and $K_{NH} = 93 \pm 3$ dm^3 mol^{-1} and $K_N = -0.3 \pm 0.9$ dm^3 mol^{-1} for piperidine and $K_{NH} = 95 \pm 5$ dm^3 mol^{-1} and $K_N = -6.5 \pm 2.0$ dm^3 mol^{-1} for pyrrolidine.

0.05 mol dm^{-3} SDS for piperidine may be compared with the values of $K_{b(ap)}$ of 0.032 in the nitrosation of piperidine by 2-bromoethyl nitrite and of 0.029 mol dm^{-3} in the nitrosation of piperidine by 1-phenylethyl nitrite at 0.055 mol dm^{-3} SDS and 25 °C.[14] Although the values of $K_{b(ap)}$ are not very reliable at lower values of $[SDS]_T$, an attempt was made to fit the $K_{b(ap)}$ values to Eqn (12) by considering $1 \gg K_{OH}[D_n]$. The non-linear least-squares technique gave the respective K_{NH} and K_N values as 494 ± 178 and 61 ± 28 dm^3 mol^{-1} with cmc = 0.009 mol dm^{-3} and 447 ± 147 and 54 ± 23 dm^3 mol^{-1} with cmc = 0.008 mol dm^{-3} for piperidine and 970 ± 195 and 91 ± 22 dm^3 mol^{-1} with cmc = 0.009 mol dm^{-3} and 817 ± 28 and 74 ± 3 dm^3 mol^{-1} with cmc = 0.008 mol dm^{-3} for pyrrolidine. The reasonably good fit of the $K_{b(ap)}$ values to Eqn (12) (Table 2) appears to be fortuitous as the calculated K_N values are significantly larger than the experimentally observed values.

Pseudo-first-order rate constants (k_{obs}) obtained for aminolysis of PS^- at a constant $[Am]_T$ and $[SDS]_T$ with various concentrations of NaOH were also treated with the equation

$$K_{Am}^{app} = \frac{k^n_W f^N_W [Am]_T - (k_{obs} - k_0)X}{(k_{obs} - k_0)X[D_n]} \qquad (14)$$

which is the rearranged form of Eqn (5) where $k_0 = k_{obs}$ at $[Am]_T = 0$ and $X = (1 + K_1[D_n])$. The assumption involved in the use of Eqn (14) is that the rate of aminolysis is negligible in the micellar pseudophase compared with that in aqueous pseudophase under the experimental conditions of this study.

The values of k_{obs} at different [NaOH] were used to calculate K_{Am}^{app} from Eqn (14) with $K_1 = 4.8$ dm^3 mol^{-1}, cmc = 0.009 mol dm^{-3}, $[SDS]_T = 0.1$ mol dm^{-3}, $[Am]_T = 0.01$ mol dm^{-3} and $k^n_W f^N_W = 0.315$ dm^3 mol^{-1} s^{-1} for piperidine and 0.803 dm^3 mol^{-1} s^{-1} for pyrrolidine ($k^n_W f^N_W$ values were obtained at 0.02 mol dm^{-3} NaOH and $[D_n] = 0$). These results, summarized in Table 3, reveal a decrease in K_{Am}^{app} with increase in [NaOH]. The K_{Am}^{app} values were not calculated at $[SDS]_T < 0.1$ mol dm^{-3} because as $[D_n] \to 0$, $[D_n]^{-1} \to \infty$ and $k^n_W f^N_W [Am]_T - (k_{obs} - k_0) X \to 0$, and hence under such limits slight errors in the cmc and $k^n_W f^N_W$ would add a large amount of uncertainty to the calculated values of K_{Am}^{app}.

The decrease in K_{Am}^{app} with increase in [NaOH] may be explained as follows. By definition,

$$K_{Am}^{app} = \{[NH^+_M] + [N_M]\}/\{([NH^+{}_W] + [N_W])[D_n]\} \qquad (15)$$

The following equation can be easily derived from Scheme 1 and Eqn (15):

$$K_{Am}^{app} = (K_{NH}K_{w,W} + K_N K_{a,}{}^N{}_W[^-OH_W])/(K_{w,W} + K_{a,}{}^N{}_W[^-OH_W]) \qquad (16)$$

where $K_{w,W} = [H^+{}_W]\,[^-OH_W]$.

The non-linear least-squares technique was used to calculate K_{NH} and K_N from Eqn (16) using the known values of $k_{w,W}$ (= 2.43×10^{-14} mol^2 dm^{-6}) and $K_{a,}{}^N{}_W$ (= 8.96×10^{-12} mol dm^{-3} for piperidine and 7.31×10^{-12} mol dm^{-3} for pyrrolidine). The calculated respective values of K_{NH} and K_N are 93 ± 3 and -0.3 ± 0.9 dm^3 mol^{-1} for piperidine and 95 ± 5 and -6.5 ± 2.0 dm^3 mol^{-1} for pyrrolidine. The negative values of K_N with significantly high standard deviations merely indicate that the values of K_N are not different from zero. The experimentally determined values of K_N (= 3.8 dm^3 mol^{-1} for piperidine[14] and 1.4 dm^3 mol^{-1} for pyrrolidine[15] at 25 °C) were also used to calculate K_{NH} from Eqn (16) and these calculated values turned out to be 70 ± 16 dm^3 mol^{-1} for piperidine and 65 ± 22 dm^3 mol^{-1} for pyrrolidine. Although the calculated values of K_{NH} are associated with high standard deviations, these K_{NH} values appear to be realistic because the cetyltrimethylammonium bromide micellar binding constants of

relatively more hydrophobic substrates such as ionized acetylsalicylic acid[32] and *N*-hydroxyphthalimide[33] are 120 and 102 $dm^3\ mol^{-1}$, respectively.

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