Effects of Anionic Micelles on Intramolecular General Base-catalysed Aminolysis of Phenyl and Methyl Salicylates

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The effects of micelles of sodium dodecyl sulphate (SDS) on aminolysis of ionized phenyl salicylate (PS^-) and methyl salicylate (MS^-) have been studied at 35 °C. An increase in the total concentration of SDS ($[SDS]_T$) from 0.0 to 0.2 mol dm^{-3} results in a decrease in the observed nucleophilic second-order rate constants (k_n) by a factor of *ca.* 3 for the reactions of PS^- with propylamine and 1-aminopropan-2-ol. At high $[SDS]_T$, plots of observed pseudo-first-order rate constants (k_{obs}) *versus* total propylamine concentration ($[Am]_T$) appear to exhibit smaller slopes at $[Am]_T < 0.01$ mol dm^{-3} compared with those at $[Am]_T > 0.01$ mol dm^{-3}, while for 1-aminopropan-2-ol such deviations from linearity at $[Am]_T < 0.01$ mol dm^{-3} could not be detected. These observations are attributed to the higher hydrophilicity of 1-aminopropan-2-ol compared with that of propylamine. The values of k_n for hydrazinolysis of MS^- are decreased *ca.* 1.7-fold and those for hydroxylaminolysis MS^- are increased *ca.* 2-fold with an increase in $[SDS]_T$ from 0.0 to 0.2 mol dm^{-3}. The values of k_n for methylaminolysis of MS^- are independent of $[SDS]_T$ within the limits 0.0–0.2 mol dm^{-3}. Dimethylamine did not show any detectable nucleophilic reactivity toward MS^- in the presence of 0.03 mol dm^{-3} SDS. This shows that the presence of SDS perhaps does not change the nucleophilic reaction mechanism of aminolysis of salicylate esters. The observed results of aminolysis of PS^- and MS^- are rationalized in the light of the proposal of a porous cluster micellar structure.

Micellar-mediated reactions are generally rationalized in terms of a pseudophase model for micelles.[1-5] Bunton[6] has outlined both the shortcomings and the usefulness of this model. Although a huge amount of kinetic data on micellar catalysis has increased our understanding about micellar structure and catalysis, mechanistic aspects of such catalysis appear to be not yet fully explored. The mechanistic details of aminolysis of carbonyl compounds in aqueous medium have been extensively studied,[7] but it seems that studies on the effects of micelles on these reactions have not been attempted. The most obvious reason for the lack of such studies lies in the fact that aminolysis of carbonyl compounds generally involves the use of amine buffers. Micelles generally affect significantly the apparent pK_a values of buffer components by differential micellar incorporation of these components. This in turn complicates the kinetic analysis of aminolysis of carbonyl compounds.

We have recently studied the mechanism of the aminolysis of phenyl and methyl salicylates.[8-10] These reactions involve intramolecular general base catalysis. The ionized phenyl salicylate (PS^-) is reactive towards both primary and secondary amines while ionized methyl salicylate (MS^-) is reactive towards only primary amines. The rate studies on aminolysis of ionized salicylate esters do not require buffer solutions of amines because the rates of hydrolysis of salicylate esters are independent of [OH] within its range of *ca.* 0.002–0.06 mol dm^{-3}. It has been recently shown that micelles can cause a complete change in aqueous reaction mechanism.[11] We decided to study the effects of anionic micelles on aminolysis of PS^- and MS^- and to see if micelles could cause any change in the aqueous reaction mechanism. Recently, we studied the effects of anionic micelles on the hydrolytic cleavages of PS^- and MS^- and the observed results were explained by the use of a porous cluster micellar model.[12] Although the idea of the rough-surfaced character of the micellar surface (*i.e.* porous cluster micelles) was conceived nearly two decades before,[13,14] its apparent feasibility has emerged only recently through a series of papers

by Menger *et al.*[15-21] Another aim of the present study was to get some insight into micellar structure. The results and the probable explanations are described in this paper.

Experimental

Materials.—The reagent-grade chemicals hydrazine hydrate, phenyl salicylate (PSH), methylammonium chloride, dimethylammonium chloride, and hydroxyammonium chloride were obtained from BDH, and propylamine ($\pm$)-1-aminopropan-2-ol, and sodium dodecyl sulphate (SDS) were obtained from Aldrich. All other chemicals used were also of reagent grade. Methyl salicylate (MSH) was synthesized as described elsewhere.[22] SDS was recrystallized according to the published procedure.[23] Glass-distilled water was used throughout. Stock solutions of PSH and MSH were freshly prepared in acetonitrile for each run.

Kinetic Measurements.—The rates of aminolysis of PSH and MSH were studied spectrophotometrically by monitoring the decrease in absorbance (A_{obs}) at 350 nm on an Hitachi 100-50 double-beam u.v.–visible spectrophotometer. All the kinetic runs which involved the stock solutions of free amines (such as hydrazine hydrate, propylamine, and 1-aminopropan-2-ol) were studied in the presence of 0.005 mol dm^{-3} NaOH. Stock solutions of protonated amines (such as methylammonium chloride, dimethylammonium chloride, and hydroxyammonium chloride) were prepared in water solvent which contained sodium hydroxide at a concentration larger (by 0.05 mol dm^{-3}) than the protonated amine concentration. In a typical kinetic run, reaction mixtures containing required amounts of amine, hydroxide ion, and SDS were equilibrated at 35 °C for a few minutes. The reaction was then initiated by adding the appropriate amount of salicylate ester in acetonitrile solution. The total volume of the reaction mixture in each kinetic run was 50 cm^3 which contained 1% MeCN. Details of the kinetic procedure and analysis were the same as described elsewhere.[24]

Table. The apparent nucleophilic second-order rate constants for aminolysis of salicylate esters in the absence and presence of SDS.[a]

Ester	Amine	$[SDS]_T$[b]	$10^3 k_o/min^{-1}$	$10 k_n/l\ mol^{-1}\ min^{-1}$	$[Am]_T$[c] range/ mol dm^{-3}	No. of runs
PSH	Propylamine	0.0	63.0 ± 5.2[d]	42.4 ± 0.8[d]	0.02–0.10	5
			46.3 ± 4.5 (41.5)[e]	44.6 ± 0.9	0.001–0.10	8
		0.03	25.0 ± 4.6	34.1 ± 0.7	0.02–0.10	5
			29.4 ± 2.1 (31.5)	33.6 ± 0.4	0.001–0.10	8
		0.07	11.4 ± 2.6 (24.2)	26.2 ± 0.4	0.02–0.10	5
		0.10	-8.6 ± 5.7 (22.7)	27.4 ± 0.9	0.02–0.10	5
		0.15	3.8 ± 2.9 (18.3)	19.6 ± 0.5	0.02–0.08	4
		0.20	3.7 ± 5.0 (17.9)	15.9 ± 0.8	0.02–0.10	5
	1-Aminopropan-2-ol	0.0	43.2 ± 3.3	19.6 ± 0.5	0.02–0.10	5
		0.03	29.6 ± 3.4	21.9 ± 0.5	0.02–0.10	5
		0.07	27.7 ± 1.6	16.2 ± 0.2	0.02–0.10	5
		0.10	17.3 ± 2.2	13.7 ± 0.4	0.02–0.08	4
		0.15	13.0 ± 4.4	10.8 ± 0.7	0.02–0.10	5
		0.20	19.8 ± 2.3	7.28 ± 0.34	0.02–0.10	5
MSH	Hydrazine	0.0	11.4 ± 0.4	3.30 ± 0.05	0.02–0.10	5
		0.02	12.6 ± 1.4	2.95 ± 0.11	0.02–0.10	5
		0.06	8.49 ± 1.22	2.82 ± 0.10	0.02–0.10	5
		0.10	10.4 ± 1.1	2.43 ± 0.17	0.02–0.10	5
		0.15	13.3 ± 1.4	2.10 ± 0.12	0.02–0.10	5
		0.20	10.7 ± 1.4	1.94 ± 0.11	0.02–0.10	5
	Hydroxylamine	0.0	13.7 ± 5.5	1.34 ± 0.06	0.1–0.5	5
		0.02	5.89 ± 1.87	1.59 ± 0.06	0.1–0.5	5
		0.04	11.5 ± 0.9	2.16 ± 0.08	0.02–0.20	5
		0.06	7.65 ± 4.3	2.64 ± 0.35	0.02–0.20	5
		0.10	9.41 ± 0.99	2.23 ± 0.08	0.02–0.20	5
		0.15	8.10 ± 2.28	2.80 ± 0.19	0.02–0.20	5
		0.20	6.52 ± 1.46	2.42 ± 0.12	0.02–0.20	5
	Methylamine	0.0	10.9 ± 0.7	0.579 ± 0.020	0.1–0.5	5
		0.03	8.33 ± 1.55	0.583 ± 0.047	0.1–0.5	5
		0.10	10.4 ± 1.3	0.524 ± 0.040	0.1–0.5	5
		0.20	7.62 ± 0.43	0.582 ± 0.013	0.1–0.5	5
	Dimethylamine	0.03	10.5 ± 0.6	0.016 ± 0.020	0.1–0.5	5

[a] Conditions: $[PSH]_o$ 2×10^{-4} mol dm^{-3}, $[MSH]_o$ 1.97×10^{-4} mol dm^{-3}, 35 °C, aqueous reaction mixture contained 1% MeCN. [b] Total concentration of sodium dodecyl sulphate. [c] Total amine concentration. [d] Error limits are standard deviations. [e] Parenthesized values were obtained in the absence of amine (ref. 12).

Product Analysis.—The apparent molar extinction coefficient of products of the reactions of primary amines with PS$^-$ and MS$^-$ were found to be within the range 1 250–1 400 dm^3 mol^{-1} cm^{-1} at 350 nm. Aqueous solutions of salicylate ion, phenolate ion, and methanol (products of hydrolysis of PS$^-$ and MS$^-$) did not show any detectable absorption at 350 nm. These observations show that the primary amines did not act as intermolecular general base catalysts for hydrolysis.

It appeared that at a constant concentration of SDS, $[SDS]_T$, the nucleophilic second-order rate constants, k_n, for the reactions of propylamine with PS$^-$ were significantly smaller at total propylamine concentrations, $[PrNH_2]_T < 0.02$ mol dm^{-3} compared with those at $[PrNH_2]_T \geqslant 0.02$ mol dm^{-3}. The observed pseudo-first-order rate constants, k_{obs}, obtained at a constant $[SDS]_T$ and in the absence of propylamine as well as within $[PrNH_2]_T$ range 0.001–0.100 mol dm^{-3}, were used to estimate the values of absorbance at $t = \infty$. A_∞^{350}, assuming phenolate ion, salicylate ion, and ionized propylsalicylamide as the only products. These estimated values of A_∞^{350} were similar (within the limits of experimental uncertainty) to the corresponding values of A_∞^{350} obtained from the kinetic analysis as described elsewhere.[24] These calculations indicate that the products of propylaminolysis of PS$^-$ at varying $[SDS]_T$ and $[PrNH_2]_T$ remained the same although at $[SDS]_T \geqslant 0.07$ mol dm^{-3} the values of k_n were significantly smaller at

$[PrNH_2]_T < 0.02$ mol dm^{-3} than those at $[PrNH_2]_T \geqslant 0.02$ mol dm^{-3}.

Results

Reaction of Primary Amines with PS$^-$.—Several kinetic runs were carried out at 35 °C to study the effects of total concentration of SDS, $[SDS]_T$, on the rates of the reactions of propylamine and 1-aminopropan-2-ol with PS$^-$. The reactions were carried out under the experimental conditions in which both PSH and amines existed in completely ionized and unprotonated forms, respectively. At a constant $[SDS]_T$, the observed pseudo-first-order rate constants, k_{obs}, obtained over the total amine concentrations, $[Am]_T$, range 0.02–0.10 mol dm^{-3}, obeyed equation (1) where k_o and k_n represent first- and

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

second-order constants for hydrolysis and aminolysis of PS$^-$, respectively. Since non-buffered amine solutions were used, the pH of the reaction medium was bound to increase slightly with an increase in $[Am]_T$, but such a change in pH would not affect the magnitude of k_o because the rate of hydrolysis of PS$^-$ appeared to be independent of $[OH]$ over the range 0.002–
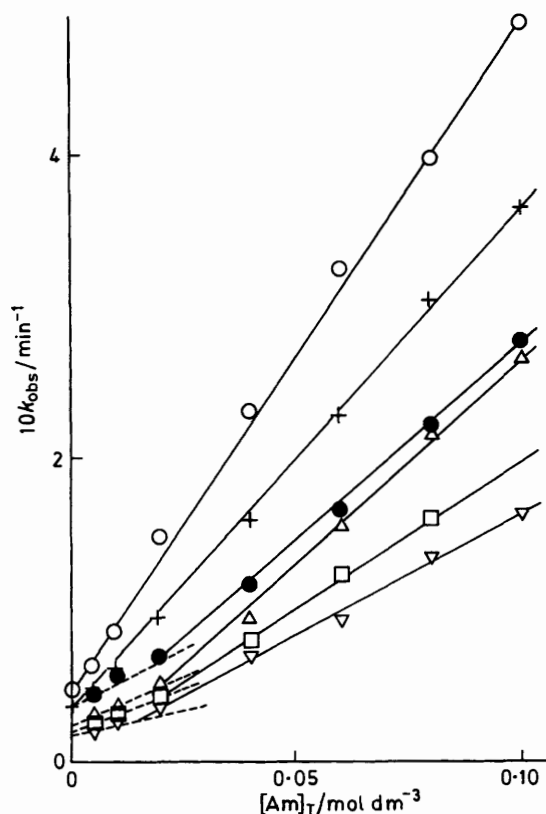
Figure 1. Plots showing the dependence of observed rate constants, k_{obs}, *versus* total amine concentrations $[Am]_T$, for the reactions of PS^- with propylamine at 0.0 mol dm^{-3} SDS (○), 0.03 mol dm^{-3} SDS (+), 0.07 mol dm^{-3} SDS (●), 0.1 mol dm^{-3} SDS (△), 0.15 mol dm^{-3} SDS (□), and 0.2 mol dm^{-3} SDS (▽).

Figure 2. Plots showing the dependence of observed rate constants, k_{obs}, *versus* total amine concentrations, $[Am]_T$, for the reactions of PS^- with 1-aminopropan-2-ol at 0.0 mol dm^{-3} SDS (○), 0.03 mol dm^{-3} SDS (+), 0.07 mol dm^{-3} SDS (●), 0.1 mol dm^{-3} SDS (▲), 0.15 mol dm^{-3} SDS (□), and 0.2 mol dm^{-3} SDS (△).

0.060 mol dm^{-3}. The values of k_o and k_n at different $[SDS]_T$ were calculated from equation (1) using linear least-squares techniques and are summarized in the Table. The fit of the observed data to equation (1) is evident from the plots shown in Figures 1 and 2 where solid lines are drawn through the least-squares-calculated points.

Reaction of Amines with MS$^-$.—The nucleophilic cleavage of MS$^-$ was studied under varying total amines concentration, $[Am]_T$, at 35 °C. The experimental conditions imposed were such that both methyl salicylate and amines were in completely ionized and free base forms, respectively. The observed rate constants, k_{obs}, obeyed equation (1) reasonably well for amines such as methylamine, hydrazine, and hydroxylamine. The least-squares-calculated values of k_o and k_n are summarized in the Table. The fit of the observed data to equation (1) is evident from the standard deviations associated with k_o and k_n. A few kinetic runs were carried out to detect any nucleophilic reactivity of dimethylamine towards MS$^-$. However, no detectable nucleophilic reactivity was observed (Table).

Discussion

The nucleophilic reactivity of amines towards PS^- and MS^- in the presence of SDS may be easily explained in terms of the pseudophase model of micelles. One of the various assumptions introduced in this model[1] is that, in a bimolecular reaction, the micellar incorporation of one reactant is independent of the other reactant. Thus, the nucleophilic cleavages of PS^- and MS^- may be shown by the Scheme.
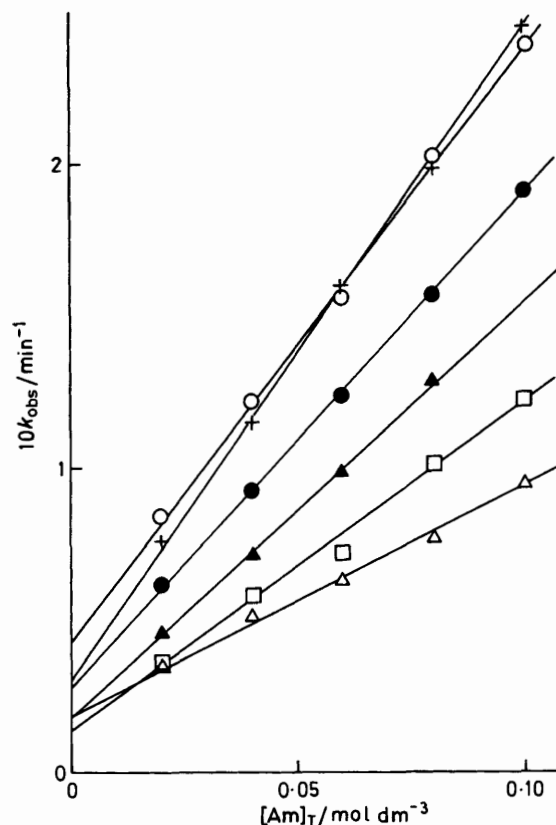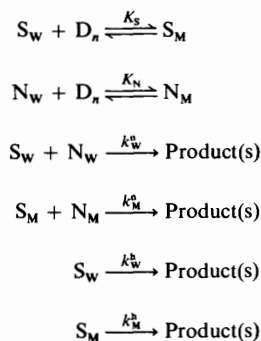
In the Scheme, subscripts w and M denote the aqueous and micellar pseudophases and S, N, and D_n represent substrate (ionized salicylate ester), nucleophile (amine), and micelle (formed from *n* monomers), respectively. The observed rate law, rate = $k_{obs}[S]_T$, and the Scheme easily yield equation (2)

$$S_W + D_n \underset{}{\overset{K_S}{\rightleftharpoons}} S_M$$

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

$$S_W + N_W \xrightarrow{k_W^n} \text{Product(s)}$$

$$S_M + N_M \xrightarrow{k_M^n} \text{Product(s)}$$

$$S_W \xrightarrow{k_W^h} \text{Product(s)}$$

$$S_M \xrightarrow{k_M^h} \text{Product(s)}$$

Scheme.

$$k_{obs} = \frac{k_W^h + k_M^h K_S[D_n]}{1 + K_S[D_n]} + \frac{(k_W^n + k_M^{ns} K_N K_S[D_n])[Am]_T}{(1 + K_S[D_n])(1 + K_N[D_n])} \quad (2)$$

where $[D_n] = [SDS]_T - cmc$ with $[SDS]_T$ and cmc representing the total concentration of SDS and critical micelle concentration, respectively. In equation (2), $[Am]_T = [N_W] + [N_M]$ where $[N_W]$ and $[N_M]$ represent the concentration of nucleophile in aqueous and micellar pseudophases, respectively, k^h and k^n are the first- and second-order rate constants for
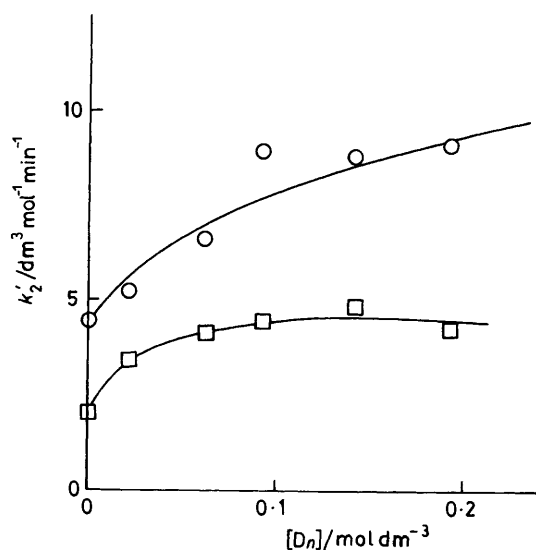
Figure 3. Plots of k_2' versus $[D_n]$ for the reactions PS^- with propylamine ($\bigcirc$) and 1-aminopropan-2-ol ($\square$). The solid lines are drawn through the calculated points as described in the text. $[D_n] = [SDS]_T - cmc$ and $k_2' = k_n (1 + K_S[D_n])$.

hydrolysis and aminolysis, respectively, $K_N = [N_M]/[N_W][D_n]$, and $K_S = [S_M]/[S_W][D_n]$. The magnitude of a second-order rate constant depends upon the choice of the concentration units. A micellar pseudophase is not a homogeneous phase and hence the location of the reaction site cannot be assigned with certainty. Thus, the volume element of the occurrence of the bimolecular reaction in the micelles is difficult to determine with any degree of reliability. As discussed by Bunton and Romsted,[25] one way of avoiding the problem of volume element of the reaction is to define the second-order rate constants in terms of the mole ratio of bound N to micellized surfactant, m_S^N, so that equation (3) holds where r_1 is the rate of reaction of

$$k_M^{ns} = r_1/[S_M]m_S^N \qquad (3)$$

S_M and N_M and $m_S^N = [N_M]/[D_n]$. Thus, the rate constant, k_M^{ns}, used in equation (2) has units of a first-order rate constant. Comparison of equations (1) and (2) yields equations (4) and (5).

$$k_o = \frac{k_W^h + k_M^h K_S[D_n]}{1 + K_S[D_n]} \qquad (4)$$

$$k_n = \frac{k_W^n + k_M^{ns} K_N K_S[D_n]}{(1 + K_S[D_n])(1 + K_N[D_n])} \qquad (5)$$

In our study[12] of the hydrolysis of PS^- and MS^- in the presence of varying $[SDS]_T$, we found that k_o values for hydrolysis of PS^- obeyed equation (4) with $10^3 k_W^h = 41.5$ min^{-1}, $10^3 k_M^h = 12.8$ min^{-1}, and $K_S = 24.6$ l mol^{-1}, but the k_o values for MS^- were found to be independent of $[SDS]_T$. Mathematically, k_o seems to be independent of $[SDS]_T$ under two conditions: (i) either $k_W^h = k_M^h$ or (ii) $K_S[D_n] = 0$.

The values of k_o obtained for the reactions of PS^- with 1-aminopropan-2-ol are essentially similar to those obtained in the absence of amine under similar experimental conditions. However, the calculated values of k_o at $[SDS]_T \geqslant 0.07$ mol dm^{-3} for propylaminolysis of PS^- are not statistically different from zero. This is inconceivable in terms of the experimental facts. A closer look at the plots of Figure 1 reveals that, at $[SDS]_T \geqslant 0.07$ mol dm^{-3}, the slope k_n, [equation (1)] is significantly lower at $[Am]_T < 0.01$ mol dm^{-3} than that at

$[Am]_T > 0.01$ mol dm^{-3}. These observations could be explained in terms of the preferential different locations of the PS^- and propylamine reactants in the micelles. It appeared that propylamine molecules were dragged deep into the interior of the micelles where the environment was more like that of liquid paraffin. The PS^- molecules are not expected to be dragged deep into the interior of the micelles because of the presence of the ionized hydroxy group. As suggested in our earlier study,[12] the micellized PS^- molecules were most likely to be located in the region where a sufficient number of methylene groups of the micellar monomers were exposed to water molecules in the porous cluster micelles. The concentration of water in this region of the micelles remains significantly lower than that at the outer surface or the shear surface of the micelles. It seems that at significantly low $[Am]_T$ and at $[SDS]_T \geqslant 0.07$ mol dm^{-3}, most of the micellized propylamine molecules were dragged into the micellar region where the concentration of micellized PS^- was negligible or almost zero. As a result of this differential location of reactant molecules, the k_M^{ns} term becomes negligible compared with the k_W^n term in equation (5). Thus, under such experimental conditions, equation (5) is reduced to equation (6).

$$k_n = \frac{k_W^n}{(1 + K_S[D_n])(1 + K_N[D_n])} \qquad (6)$$

It seems that, at $[Am]_T > 0.01$ mol dm^{-3}, the micellar core (hydrocarbon-like) became saturated with propylamine molecules and hence as the $[Am]_T$ became larger than $ca.$ 0.01 mol dm^{-3} at a constant $[SDS]_T$, the concentration of propylamine became significant in the micellar region where micellized PS^- molecules existed. Under such circumstances, the k_M^{ns} term cannot be neglected compared with the k_W^n term in equation (5) and the observed values of k_n (within the $[Am]_T$ range 0.02–0.10 mol dm^{-3}) obeyed equation (5). The rearranged equation (7)

$$k_n(1 + K_S[D_n]) = \frac{k_W^n + AK_N[D_n]}{1 + K_N[D_n]} \qquad (7)$$

was used to calculate A and K_N where $A = k_M^{ns} K_S$. The values of $K_S[D_n]$ at different $[D_n]$ values were calculated using $K_S = 24.6$ dm^3 mol^{-1}. The assumption that the value of K_S was not appreciably changed due to the presence of varying concentrations of amine ($[Am]_T$) seems to be valid for the following reason. The values of k_o at different $[D_n]$ values (Table) obtained in the presence of varying concentrations of 1-aminopropan-2-ol are similar to those obtained in the absence of amine under essentially similar experimental conditions. The least-squares-calculated values of A and K_N are 12.8 ± 3.7 dm^3 mol^{-1} min^{-1} and 7.7 ± 6.7 dm^3 mol^{-1}, respectively. The value of A was used to calculate k_M^{ns} (0.520 min^{-1}) with known value of K_S (24.6 dm^3 mol^{-1}). The fit of the observed data to equation (7) is evident from the plot shown in Figure 3 where the solid line is drawn through the least-squares-calculated points.

The calculated values of k_n for 1-aminopropan-2-ol also obeyed equation (7) as shown in Figure 3. The calculated values of A and K_N are 4.9 ± 0.4 dm^3 mol^{-1} min^{-1} and 48 ± 30 dm^3 mol^{-1}, respectively. The calculated value of k_M^{ns} from A is 0.20 min^{-1}. The observed data as shown by Figure 2 do not follow equation (6) at sufficiently low concentrations of amine. This shows that 1-aminopropan-2-ol, unlike propylamine, probably could not penetrate deep into the micellar hydrocarbon-like core. This is conceivable since the presence of the 2-hydroxy group makes 1-aminopropan-2-ol more hydrophilic compared with propylamine. This is evident from the reported values of partition coefficients (K) of ethylamine (K 16.8 at 18 °C) and 2-hydroxyethylamine (K 823 at 19 °C) obtained in a water–ether solvent mixture.[26]

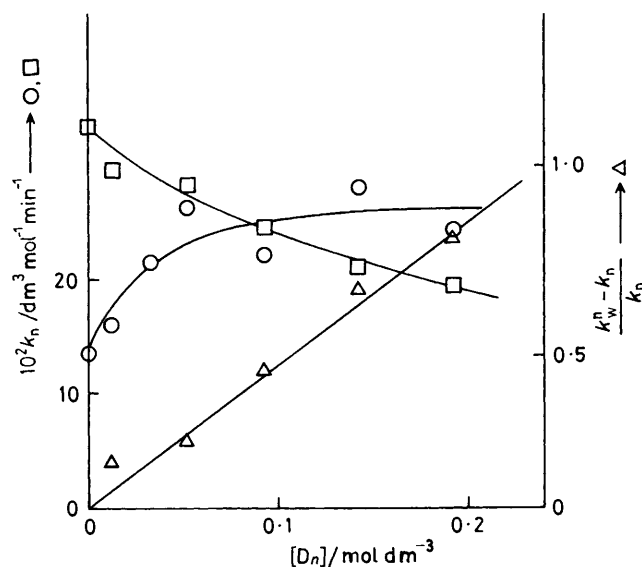The effective molarity of the micellar-mediated nucleophilic

Figure 4. Plots showing the dependence of observed second-order rate constants, k_n, versus $[D_n]$ for the reactions of MS^- with hydroxylamine (○) and hydrazine (□), and the dependence of $(k_W^n - k_n)/k_n$ upon $[D_n]$ for hydrazinolysis of MS^- (△). The solid lines are drawn through the calculated points as described in the text. $[D_n] = [SDS]_T - cmc$.

cleavage of PS^- is ca. 0.1 mol dm^{-3} ($= k_M^{ns}/k_W^n$) for both propylamine and 1-aminopropan-2-ol. Such a low value of the effective molarity indicates that neither reactant is effectively localized in a specific region of the micelle. The neutral amines used are sufficiently hydrophilic and their hydrophobic surface areas are small. Hence these amines presumably prefer to lie in the region of micelles where $[H_2O]$ is not significantly different from $[H_2O]$ in the aqueous pseudophase. The micellized PS^- molecules are thus assumed to lie in the micellar region where $[H_2O]$ is considerably decreased compared with $[H_2O]$ in the aqueous pseudophase.

It is not possible to compare quantitatively the k_W^n values with the nucleophilic second-order rate constant, k_M^n, for the reaction occurring inside the micelles because of the uncertainty of the volume element of the reaction site. However, if we assume that the micellar reactions take place in the Stern layer and that the molar volume[1] of the Stern layer is 0.14 dm^3 mol^{-1} then the values of k_M^n ($= 0.14$ k_M^n) turn out to be 0.073 dm^3 mol^{-1} min^{-1} and 0.028 dm^3 mol^{-1} min^{-1} for propylamine and 1-aminopropan-2-ol, respectively. The estimated values of k_W^n/k_M^n of ca. 61 and 71 for propylamine and 1-aminopropan-2-ol, respectively, may be attributed to both a medium effect and probable uncertainty in the assumed molar volume (0.14 dm^3 mol^{-1}) of the reaction site. These values may not be attributable to different mechanisms taking place in aqueous and micellar pseudophases because we observed no change in the reaction mechanism of aminolysis of PS^- with change of propan-1-ol content from 0 to 70% (v/v) in mixed aqueous solvent.[27] An increase of propan-1-ol content from 0 to 70% (v/v) did reveal a decrease of 3.6- and 6.5-fold in k_n values for the reactions of PS^- with hydrazine and N-methylpiperazine, respectively.

The present and previous studies[12] on the effects of $[SDS]_T$ on hydrolysis of MS^- reveal that the observed rate constants are independent of $[SDS]_T$. To explain these observations, we proposed that the micellar-mediated hydrolysis takes place at the interface of the micellar and aqueous pseudophases where the micellar-bound MS^- molecules lie at or near the outer surface of the micelles. The micellar-mediated reactions which occur across the interfacial boundary, i.e. the reactions between

micellar-bound reactant and the reactant in the aqueous pseudophase, have been reported in a few cases in recent years.[28] The concentration of water in the region of micelle-bound MS^- is essentially not different from that in the aqueous pseudophase.[2] It seems that MS^- molecules are loosely bound by the micelles and hence we presume that $K_S[D_n] < 1$ within the $[SDS]_T$ range 0.0–0.2 mol dm^{-3}. Under such conditions, equation (5) is reduced to equation (8) where $A = k_M^{ns} K_S$.

$$k_n = \frac{k_W^n + A K_N[D_n]}{1 + K_N[D_n]} \tag{8}$$

Equation (8) seems to be obeyed by the observed data for hydroxylaminolysis of MS^- (Figure 4). The unknown parameters A and K_N were calculated from equation (8) using the non-linear least-squares technique and the values thus obtained are 0.28 ± 0.03 dm^3 mol^{-1} min^{-1} and $39 \pm$ dm^3 mol^{-1}, respectively. Since the value of K_S is not known, the value of k_M^{ns} cannot be determined easily. However, the value of K_S seems to be less than unity and hence $k_M^{ns} > 0.28$ min^{-1}. The effective molarity ($= k_M^{ns}/k_W^n$) is therefore >2 mol dm^{-3}. It is interesting to note that the effective molarity for hydroxylaminolysis of micellized MS^- is significantly larger than that for the reaction of 1-aminopropan-2-ol with micellized PS^-. These observations support the proposal that the micellized MS^- molecules lie in a significantly higher hydrophilic region than that occupied by micellized PS^-.[12]

The apparent nucleophilic second-order rate constants, k_n, for the reaction of hydrazine with MS^- with varying $[SDS]_T$ were also used with equation (8) and the calculated values of A and K_N are 0.05 ± 0.12 dm^{-3} mol^{-1} min^{-1} and 4.9 ± 3.3 dm^{-3} mol^{-1}, respectively. The fit of the observed data to equation (8) is evident from the plot of Figure 4 where the solid line is drawn through the calculated points. It is interesting to note that the maximum contribution of the $A K_N[D_n]$ term is ca. 13% and the minimum contribution of the k_W^n term is ca. 87% within the experimental conditions of the present study. Thus, it may not be unreasonable to assume that $A K_N[D_n]$ is negligible compared with k_W^n within the limits of the experimental conditions. Application of this assumption reduced equation (8) to equation (9).

$$k_n = \frac{k_W^n}{1 + K_N[D_n]} \tag{9}$$

It is evident from equation (9) that a plot of $(k_W^n - k_n)/k_n$ versus $[D_n]$ should be linear with zero intercept. Such a plot as shown in Figure 4 is essentially linear and the linear least-squares-calculated value of K_N is 3.8 ± 0.2 dm^3 mol^{-1}.

Although the value of A of 0.05 dm^3 mol^{-1} min^{-1} for hydrazinolysis of MS^- is not very reliable, it is undoubtedly smaller than that for hydroxylaminolysis of MS^-. These observations could be explained in terms of different locations of micellized hydroxylamine and hydrazine within the micelles. As discussed earlier, the presence of a hydroxy group in an amine increases its hydrophilicity many times compared with that of an amine without a hydroxy group. Thus, it may be assumed that hydrazine could penetrate deep into the micellar core where the medium is more hydrophobic while hydroxylamine could not penetrate so deeply. Micellized hydroxylamine molecules lie in the highly hydrophilic region (i.e. the outer surface of the Stern layer of shear surface) of the micelles. Micellized hydrazine molecules, however, lie in both the Stern layer as well as the hydrocarbon-like micellar core. Thus, the concentration of micellized hydrazine is considerably lower. The fact that micellized MS^- molecules lie in the highly hydrophilic region of the micelles and that the apparent

concentration of hydrazine is considerably lower in this region compared with that in the aqueous pseudophase make $AK_N[D_n]$ negligible compared with k^a_W.

The second-order rate constants, k_n, (Table) for methylaminolysis of MS^- are independent of $[SDS]_T$. It seems that micellar incorporation of methylamine does not occur. This is surprising since although hydrazine binds very weakly with micelles of SDS, it has a significant rate-retarding effect on hydrazinolysis of MS^- (the increase in $[SDS]_T$ from 0.0–0.2 mol dm^{-3} has caused ca. 40% reduction in k_n values). The reactivity of methylamine is nearly 6-fold smaller than that of hydrazine and if binding of methylamine with micelles is quite weak, the concentration of micellized methylamine may not be enough to cause any detectable effect on k_n values.

Dimethylamine did not show a detectable nucleophilic reactivity towards MS^- in the presence of 0.03 mol dm^{-3} SDS. Several secondary amines including dimethylamine did not reveal any nucleophilic reactivity towards MS^- in aqueous medium.[10] These results show that the presence of micelles could not change the reaction mechanism of these reactions. The mechanistic details of the aminolysis of salicylate esters have been described elsewhere.[8–10]

Although the binding constants (K_N) of propylamine, 1-aminopropan-2-ol, hydroxylamine, and hydrazine to the micelles are not very reliable because of the considerably higher standard deviations associated with these values, it is interesting to note that the values of K_N for propylamine (7.7 dm^3 mol^{-1}) and hydrazine (4.9 or 3.8 dm^3 mol^{-1}) are considerably smaller than those for hydroxylamine (39 dm^3 mol^{-1}) and 1-aminopropan-2-ol (48 dm^3 mol^{-1}). These results indicate that the amines containing a hydroxy group have a larger affinity towards anionic micelles compared with those containing no hydroxy group but of essentially similar structure.

Conclusions.—The observed bimolecular rate constants for the reactions of PS^- with propylamine and 1-aminopropan-2-ol and MS^- with hydroxylamine, hydrazine, and methylamine in the presence of SDS can be explained by the proposal that (i) micellized PS^- molecules lie in the region which is exposed significantly to the methylene groups of SDS and consequently the water concentration in this region is reduced compared with that in the aqueous pseudophase, (ii) micellized MS^- molecules lie in the outer surface of the micelles, *i.e.* at the interfacial region of the micellar and aqueous pseudophases. This region of the micelle does not presumably differ from an aqueous pseudophase in terms of water concentration, but the apparent charge density or ionic strength of this region is possibly larger than that of an aqueous pseudophase. These observations favour the porous cluster micellar structure.

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