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Micellar inhibited hydrolysis of esters—evaluation of binding constant and cooperativity index

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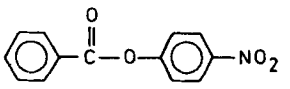
Abstract. The inhibition in the rate of hydrolysis of four esters, by the anionic micelles of sodium laurylsulphate has been explained by a binding model. It provides the critical micelle concentration under reaction conditions. Kinetic data suggest that more than 90% of the substrate is micelle-bound at 0·010 M concentration of the anionic micelle and the binding constants obtained agree with those of other systems studied elsewhere. The marked inhibition in the comicellar phase and the cationic micellar phase of sodium laurylsulphate, cetyldimethylbenzylammonium chloride or cetyltrimethylammonium bromide, has been explained by using the same pseudo model and the binding constant, K_s and the fraction of substrate held at the comicellar surface, F_s^m, indicates greater binding at the comicellar surface. The cooperativity treatment has been extended to micelle-inhibited reactions and the proposed model has been tested with literature data as well as in the present work. The cooperativity index value ranges from 0·59 to 1·51, and a value less than unity indicates negative cooperativity.

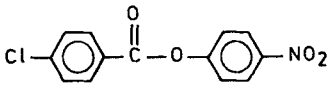
Keywords. Binding model; critical micelle concentration; negative cooperativity; comicelle.

1. Introduction

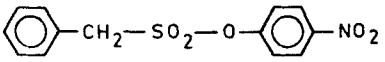
The hydrolyses of various esters, *viz* 4-nitrophenylbenzoate (PNPB), 4-chlorophenyl-4-nitrophenylbenzoate (PCB), 4-nitrophenyl-phenylmethanesulphonate (PMS) and 4-nitrophenyl-N-phenylcarbamate (PCM) in the presence of the anionic micelles of sodium laurylsulphate (SLS) have been studied in the present work. The rate data have been subjected to an equation derived for evaluating the micelle-substrate binding constant, and on the basis of cooperativity treatment, introduced for the first time for micellar-inhibited chemical reactions.



PNPB



PCB



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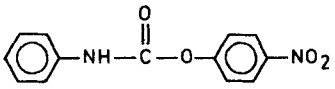
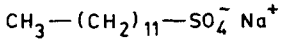


PCM



SLS

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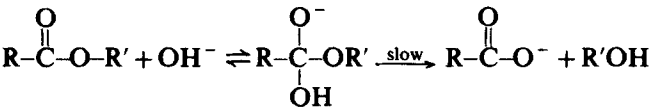
2. Results and discussion

The hydrolysis of esters generally involves an attack of the OH^- on the carbonyl carbon resulting in a negatively charged tetrahedral intermediate.



Therefore, the acceleration or deceleration of the deacylation reactions in the presence of micelles can be rationalised by considering the forces that would stabilise or destabilise the tetrahedral intermediate.

2.1 *Hydrolysis of esters in presence of SLS micelles*

In the hydrolysis of all four esters—PNPB, PCB, PMS and PCM—the increase in SLS concentration progressively decreases the observed rate constants of the reactions (table 1). These esters have also been hydrolysed in hydroxide media, the results are given in table 1. It is evident that at a concentration of 0·010 M of SLS, the hydrolysis rate of all the esters has been reduced tenfold. This can be explained on the basis of electrostatic and hydrophobic interactions. In the anionic micelles of SLS, the esters get incorporated hydrophobically and the anionic hydrolysing agent repelled electrostatically, thus separating the reactants from one another and resulting in the observed inhibition.

2.2 *Evaluation of binding constant*

Micellar reactions can be explained as proceeding *via* the formation of a micelle-substrate complex, as in the scheme below:

$$nD \overset{K}{\rightleftharpoons} D_n$$

$$D_n + S \overset{K_s}{\rightleftharpoons} D_nS$$

$$S + Nu \overset{k_0}{\rightleftharpoons} \text{products},$$

This considers the formation of micelles (D_n) by the aggregation of independent detergent molecules (D), which form a complex (D_nS) with the substrate (S). The nucleophile (Nu) reacts with the substrate in the bulk solvent (K_o) leading to product formation. Also, the qualitative explanation offered above for the observed inhibition would mean that the reaction occurs mostly in the aqueous phase or that the reaction in the micellar phase is negligible, *i.e.* $k_m \approx 0$. The continuous decrease in the rate constants with increase in detergent concentration, usually observed in micellar-inhibited reactions, also supports that $k_m \approx 0$.

The rate constant for the above scheme can be given in terms of the fraction of substrate (F_S^w) and of nucleophile (F_{Nu}^w) present in aqueous phase as,

$$k_{obs} = k_0 F_S^w F_{Nu}^w.$$

Table 1. Effect of SLS concentration on the observed rate constant.

$10^3 \times$ [SLS] M	PNPB[a]	PMS[b]	PCB[a]	PCM[c]
0·00	5·5 (220)	3·4 (99)	5·2 (112)	6·2[d]
0·50	5·0 (59)	2·5 (67)	2·7 (46)	1·45
1·00	2·8 (26)	2·2 (31)	1·79 (18·5)	0·83
1·50	—	—(18·4)	—(12·9)	0·74
2·0	1·90 (9·5)	1·53 (13·7)	1·64 (9·7)	0·71
2·5	—	—(10·6)	—	0·64
4·0	1·03 (5·0)	0·84 (6·9)	1·06 (3·4)	—
6·0	0·89	0·66	0·75	—
8·0	0·71	0·50	0·60	—
10·0	0·61	0·47	0·57	—

[ester] = $1{\cdot}50 \times 10^{-5}$ M; pH = 9·2; [NaCl] = 0·10 M; temperature = 30°C a) $10^4\ k_{obs}\,s^{-1}$; b) $10^3\ k_{obs}\,s^{-1}$; c) $10^2\ k_{obs}\,s^{-1}$ at pH = 7·4 in 10/aqueous acetonitrile with [PCM] = $4{\cdot}0 \times 10^{-5}$ M for $10 \times$ [SLS] M d) This value is calculated by extrapolation of rate constants obtained at different solvent compositions. The rate constants for the hydrolysis of the esters in $5{\cdot}0 \times 10^{-3}$ M [OH^-] at 30°C in presence of $10 \times$ [SLS] M are given in parentheses.

As the nucleophile is electrostatically repelled by anionic micelles, most of it will stay in the aqueous phase and hence it is assumed that $F^w_{Nu} = 1$ (very nearly) or $F^m_{Nu} = 0$. Therefore,

$$k_{obs} = k_0\, F^w_S. \tag{1}$$

The fraction of substrate present in the bulk phase can be arrived at in terms of the micelle-substrate binding constant, K_s and the micelle concentration, $[D_n]$ as,

$$F^w_S = 1/(1 + K_s[D_n]). \tag{2}$$

From (1) and (2), it can be easily shown that,

$$(k_0 - k_{obs})/k_{obs} = K_s[D_n].$$

Expressing $[D_n]$ in terms of the total detergent concentration, $[C_D]$, as

$$[D_n] = [C_D] - \text{CMC}/N,$$

where N is the aggregation number, one can arrive at the following equation:

$$(k_0 - k_{obs})/k_{obs} = K_s([C_D] - \text{CMC})/N. \tag{3}$$

Equation (3) predicts a linear relationship between $[C_D]$ and the ratio, $(k_0 - k_{obs})/k_{obs}$. Menger and Portnoy (1967) provided a similar model (4) to evaluate the binding constant in micellar-inhibited reactions.

$$1/(k_0 - k_{obs}) = 1/(k_0 - k_m) + N/(k_0 - k_m)\, K_s\, ([C_D] - \text{CMC}) \tag{4}$$

Though (4) reduces to (3) when $k_m \approx 0$, the utility of the latter cannot be over-emphasised. The advantage of (3) rests in its capacity to provide the CMC value of the detergent under the conditions employed in each reaction, while the other treatment requires the CMC value, which depends on the medium and the electrolyte concentration

used. Knowing the CMC value under the reaction conditions and N, one can easily calculate the fraction of micelle-bound substrate at any detergent concentration, using (2). Table 2 contains the constants derived from (2) and (3) for various micellar-inhibited reactions, taking the value of N for SLS in 0·10 M NaCl as 95 from literature (Bennion *et al* 1969). Table 2 shows that at 0·010 M of SLS, most of the substrate molecules (> 90%) is micellar bound, which is again in keeping with the inhibition observed with an increase in detergent concentration.

2.3 *Comicellar effect on the hydrolysis of PNPB, PCB, PMS and PDI*

The formation of comicelles of SLS and cetyldimethylbenzylammonium chloride (CDBAC) or cetyltrimethylammonium bromide (CTAB) requires an optimum ratio of the concentrations of the constituting surfactants and when the ratio of [SLS]/[CDBAC] < 10, precipitation occurs. Table 1 summarises the influence of SLS on the deacylation of PNPB. For a 100-fold increase in concentration of CDBAC, the observed increase in rate is only marginal.

The data on the effect of [SLS] on the rate of hydrolysis of esters employed in the absence and the presence of cationic surfactant are presented in tables 3 and 4 respectively. Though added SLS ($4{\cdot}0 \times 10^{-2}$ M) by itself reduces the hydrolysis rate of PNPB about 40 times, the reduction in rate caused by the comicellar surface of SLS and CDBAC is about 100-fold. The micellar surface formed at each SLS concentration in the absence of the cationic detergent will be anionically charged, as the presence of cationic phase may partly neutralise the charge on the anionic phase. Therefore, if the electrostatic forces alone are operative, retardation in rate should be more in the comicelles of SLS and CDBAC. But the reactivity pattern observed is just the reverse, suggesting that some forces (other than electrostatic) are taking part.

2.4 *Cooperativity treatment in micellar inhibited reactions*

The term cooperativity with reference to enzymes is defined as the stimulation (or inhibition) of the interaction of additional molecule(s) of the substrates to an enzyme as a result of the interaction of the first molecule of the substrate with the enzyme. This has been, by analogy, extended to micellar catalysis by Piskiewicz (1977).

Although the experimentally measured CMC value for SLS under reaction conditions is $4{\cdot}0 \times 10^{-3}$ M, table 1 reveals that the surfactant can exercise its decelerating effect even at lower concentrations. This confirms the interaction of the substrate with detergent monomers favouring micellisation. Also, as the absorption of one of the reactants and the repulsion of the other by micelles have been considered for micellar inhibition, the possibility of induced micellisation cannot be overlooked, and has also been evidenced by the decrease in CMC (table 2) under reaction conditions as against the reported value for SLS ($8{\cdot}0 \times 10^{-3}$ M) in water (Fendler and Fendler 1975). When the micellisation of surfactants is induced by substrates or other foreign substances present in solution, the term cooperativity can be invoked in micellar systems also. Therefore, an expression has been derived for the treatment of micellar-inhibited reactions in terms of cooperativity.

From the scheme proposed above and from (1) and (2), it can be shown that

$$k_{obs} = k_0/(1 + K_S[D_n]). \tag{5}$$

Table 2. Values of derived constants from (2) and (3) for various micellar inhibited reactions.

Reaction	$10^{-3}\ K_s/N\ M^{-1}$	10^3 CMC M	F_S^m	Reference
Hydrolysis of N-(trifluoroacetyl) indole in the presence of SLS	0·435	1·42	0·79[a]	(Cipiciancy *et al* 1981)
4-Chlorobenzylidene-1,1-dimethylethylaniline in CTAB at 25°C	0·527	0·034	c	(Behme *et al* 1965)
Bis-4-nitrophenylphenylphosphonate in igepal[d]	4·5	0·28	c	(Manod *et al* 1965)
4-Nitrophenylbenzoate at pH = 9·2 in SLS	1·17	0·33	0·92[a]	present work
4-Chlorophenyl-4-nitrophenylbenzoate at pH = 9·2 in SLS	1·96	0·0173	0·95[a]	-do-
4-Nitrophenylphenylmethanesulphonate at pH = 9·2 in SLS	0·74	0·121	0·88[a]	-do-
4-Nitrophenylbenzoate in 0·0050 M OH^- in SLS	1·19	2·63	0·90[b]	-do-
4-Chlorophenyl-4-nitrophenylbenzoate in 0·0050 M OH^- in SLS	0·84	3·3	0·85[b]	-do-
4-Nitrophenylmethanesulphonate in 0·0050 M OH^- in SLS	0·366	3·4	0·97[b]	-do-
Hydroxylaminolysis of 4-nitrophenylbenzoate at pH = 6·15 in SLS	0·292	0·021	0·75[b]	-do-

F_S^m values are calculated at 0·010 M of micelles taking $N = 95$ (a) and 62 (b); (c) the aggregation numbers for these detergents are not available under reaction conditions and hence F_S^m is not calculated; (d) Igepal refers to a neutral micelle *eg* igepal DM 570 is dialkylphenoxypoly(ethyleneoxy) ethanol.

Table 3. Effect of added CDBAC on SLS-influenced hydrolysis of PNPB.

[CDBAC] M	$10^3 k_{obs}\,s^{-1}$
—	2·6
$5·0 \times 10^{-6}$	3·1
$5·0 \times 10^{-4}$	3·6
$1·0 \times 10^{-3}$	3·7

[PNPB] = $1·50 \times 10^{-5}$ M; [OH^-] = $5·0 \times 10^{-3}$ M; [SLS] = $1·0 \times 10^{-2}$ M; temperature = 30°C

Table 4. Effect of added SLS on the cationic micelle influenced hydrolysis of esters.

	PNPB	PMS	PCB	PDI*
$10^2 \times$ [SLS] M	$10^3 k_{obs}\,s^{-1}$	$10^2 k_{obs}\,s^{-1}$	$10^3 k_{obs}\,s^{-1}$	$10^4 k_{obs}\,s^{-1}$
—	72	21	23	2·9
0·50	7·2	—	1·64	—
1·0	3·6	1·85	1·11	2·4
2·0	1·59	0·89	0·56	1·88
3·0	—	0·56	—	1·68
4·0	0·71	0·38	0·27	—
5·0	—	0·31	—	—

[substrate] = $1·5 \times 10^{-5}$ M; [OH^-] = $5·0 \times 10^{-3}$ M; [CDBAC] = $5·0 \times 10^{-4}$ M; temperature = 30°C.
*values reported for the hydrolysis of [PDI] = $3·0 \times 10^{-4}$ M with $4·0 \times 10^{-2}$ M OH^- in the presence of $5·0 \times 10^{-4}$ M CTAB (instead of CDBAC) in 20% aqueous CH_3CN.

In (5), by replacing the micelle concentration in terms of K, as

$$[D_n] = K[D]^n,$$

and by rearranging, we get

$$(k_0 - k_{obs})/k_{obs} = K_S K [D]^n.$$

Rewriting this in logarithmic form,

$$\log (k_0 - k_{obs}/k_{obs}) = n \log [D] + \log (K \cdot K_S). \tag{6}$$

In (6), the product $K \cdot K_S$ represents the overall binding constant for the step,

$$n D + S \rightleftharpoons D_n S.$$

According to this equation, a plot of $\log [(k_0 - k_{obs})/k_{obs}]$ *vs* $\log [D]$ for a micelle-inhibited reaction is linear with a slope of n, and at $\log [(k_0 - k_{obs})/k_{obs}] = 0$, $n \log [D] = -\log (K \cdot K_S)$. Also, at $\log [(k_0 - k_{obs})/k_{obs}] = 0$, the detergent shows one half of its maximum inhibiting effect. The $\log [D]$ at this point is designated as $\log [D]_{50}$ $(= -\log (K \cdot K_S)/n)$.

Data taken from literature and some of our own work were used to construct plots of $\log [(k_0 - k_{obs})/k_{obs}]$ *vs* $\log [D]$. k_0 values were taken as the rate constants observed in the absence of detergent. Slopes of these plots were calculated by least square analysis: correlation coefficients, r, were calculated to indicate the fitness of the data in graphical analysis.

2.5 *Parameters in micellar inhibition*

In micellar-inhibited reactions, as most of the reactions take place in the bulk aqueous phase, the rate constant for the reaction on the micellar phase, k_m is nearly zero. The ratio of k_{obs}/k_0 indicates the rate deceleration effected by micelles. Log $[D]_{50}$ or the quantity $-\log (K \cdot K_S)/n$, is equal to the logarithm of detergent concentration at which half the initial rate is observed. Generally, this can be directly read from a graph drawn using (6), and it corresponds to that value of the abscissa at which the ordinate vanishes. The slope of this plot n functionally denotes the index of cooperativity in micelle formation by analogy to cooperativity in enzymatic reactions (Boyer 1970). A value of n greater than unity would indicate positive cooperativity *i.e.* the binding of the first molecule of a substance, substrate or another detergent molecule to the detergent molecule, makes it easier for subsequent molecules to bind: a value less than unity would indicate a negative cooperativity, *i.e.* the first molecule bound makes it more difficult for the next to bind: and when n is equal to 1, it would indicate a non-interacting site. Values of n, however, should be accepted with caution because their evaluation involves the whole range of detergent concentration and $\log [(k_0 - k_{obs})/k_{obs}]$ values drop rapidly at extreme concentrations. The Hill plots for enzymatic reactions also suffer from a similar drawback (Bowden and Koshland 1975). Also, since the term, $-\log (K \cdot K_S) = n \log [D]_{50}$, the unit for $K \cdot K_S$ varies with n and this limits the utility of the product of the formation constants, $K \cdot K_S$, for comparing different micelle-inhibited reactions.

2.6 *Verification of the treatment*

Plots of $\log [(k_0 - k_{obs})/k_{obs}]$ *vs* $\log [D]$ were attempted for data taken from literature and also of our own work: some representative plots are shown in figure 1. Though a large number of the data have been analysed to check the validity of (6), we include only some of the model reaction plots. However, the reactions and data derived from (6) have been presented in tables 5 and 6. The linearity observed in these plots (figure 1) and the generally high correlation coefficients of the data for the linear treatment (table 6) suggest that this treatment can be applied at least empirically to quantify micellar-inhibited reactions. The n value now obtained ranges from 0·59 to 1·51. Theoretically, $n < 1$ indicates negative cooperativity and means that the incorporation of the first substrate molecule renders the association of more detergent molecules difficult. In other words, it can be visualised that in the equilibrium, $n\,D \rightleftharpoons D_n$, if n is fractional, more detergent molecules interact and form more than one micelle, in which case n gives the ratio of detergent molecules involved in the formation of all the micelles, rather than the absolute number of detergent molecules in each micelle. It is significant that a similar positive and negative cooperativity have also been observed in enzymatic reactions and that these are both accommodated by the model proposed by Koshland *et al* (1966). However, the availability of different conformations of micelles and their

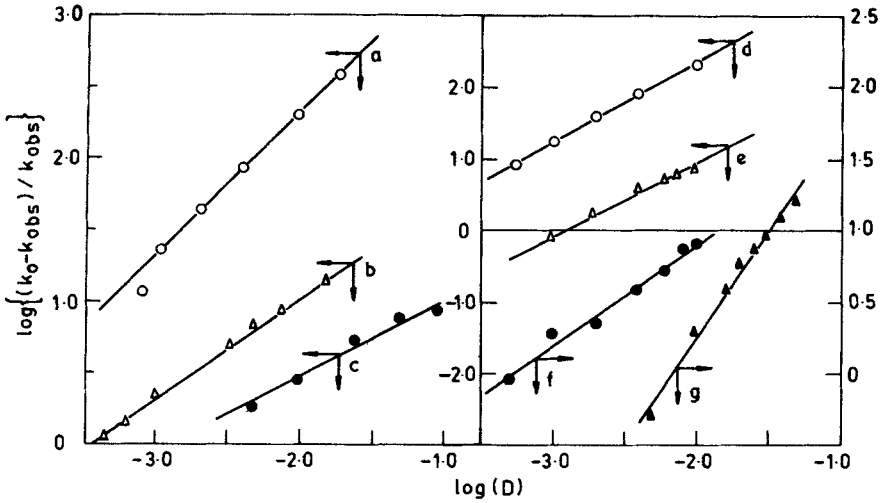


Figure 1. Plots of $\log\{(k_0 - k_{obs})/k_{obs}\}$ *vs* $\log[D]$ according to (6) for reactions inhibited by detergents: a) electron transfer from *n*-butyl ferrocene to Fe^{3+} in the presence of CTAB: b) acid hydrolysis of N-(trifluoroacetyl) indole in CTAB: c) the hydroxyaminolysis of PNPB at pH = 6·15 in SLS: d) electron transfer from *n*-butyl ferrocene to Fe^{3+} in CTAB: e) hydrolysis of PNPB at pH = 9·2 in SLS: f) hydrolysis of PCB at pH = 9·2 in SLS: g) hydrolysis of PMS in 0·0050 M OH^- in SLS.

Table 5. Kinetic parameters from the pseudo phase model and positive cooperativity.

Substrate	$10^2 K_s/N$ M^{-1}	$10^4 K_s$ M^{-1}	10^3 CMC	F_s^{m*}	*n*	$\log[D]_{50}$
PNPB	11·9	7·4	2·6	0·98	1·35	−2·64
	(26)	(16·4)	(2·4)	(0·99)	(1·17)	(−3·1)
PCB	8·3	5·2	3·3	0·97	1·45	−2·4
	(21)	(17·3)	(0·75)	(0·99)	(1·04)	(−3·2)
PMS	3·7	2·3	3·4	0·93	1·51	−2·2
	(14)	(9·2)	(9·2)	(0·98)	(1·20)	(−2·8)
PDI	$10^3 \times 2{\cdot}6$	0·16	9·9	0·72	2·7	−1·47
	$10^3 \times 2{\cdot}6$	0·159	(0·17)	—	(1·13)	(−1·42)

values in parentheses correspond to comicellar systems SLS/CDBAC or CTAB. *the F_s^m values have been evaluated at [SLS] = $4{\cdot}0 \times 10^{-2}$ M except for PDI, for which values refer to [SLS] = $2{\cdot}5 \times 10^{-2}$ M.

subunits as in the models proposed by Monod *et al* (1965) for enzymes also cannot be ruled out.

It is evident from table 6 that the comicellar surface of SLS/CDBAC or CTAB, binds the substrate more strongly than the normal anionic micelle of SLS.

2.7 *Correlation of log* $[D]_{50}$ *with* CMC

Since the incorporation of substrate into the micelle and the repulsion of the nucleophile by the micelle are responsible for the micellar inhibition, the reaction

Table 6. Values of the parameters derived from (6) for various micellar inhibited reactions.

Reaction	r	n	$\log[D]_{50}$	Reference
Hydrolysis of N-(trifluoroacetyl) indole in SLS	0·994	1·41	−2·41	(Cipiciancy *et al* 1981)
4-Chlorobenzilydene-1,1-dimethylaniline in CTAB at 25°C	0·989	1·16	−2·61	(Behme *et al* 1965)
4-Nitrophenylbenzoate at pH = 9·2 in SLS	0·953	1·33	−2·77	present work
4-Nitrophenylphenylmethane sulphonate at pH = 9·2 in SLS	0·995	1·01	−2·82	-do-
4-Chlorophenyl-4-nitrophenyl benzoate at pH = 9·2 in SLS	0·989	0·71	−3·31	-do-
4-Nitrophenyl-N-phenylcarbamate at pH = 7·4 in SLS	0·957	0·59	−2·25	-do-
Hydroxyaminolysis of 4-nitro-phenylbenzoate at pH = 6·15 in SLS	0·978	1·24	−2·41	-do-
Electron transfer from *n*-butylferrocene to Fe^{3+} in cetyltrimethylammonium nitrate	0·999	1·10	−4·16	(Bunton and Cerichelli 1980)

would naturally depend on the concentration of micelle present, which in turn depends on CMC. Since, log $[D]_{50}$ gives the concentration of detergent required to reduce the velocity to half its value, the CMC would also influence log $[D]_{50}$. An attempt was made to study the nature of this relationship between these parameters, *viz* log $[D]_{50}$ and CMC (figure 2). Though, the variation in CMC parallels that in log $[D]_{50}$ values, the relationship does not seem to be a simple one. This may probably be because log $[D]_{50}$ is related to D_nS, and CMC depends on detergent concentration.

3. Experimental

p-Nitrophenyl benzoate (PNPB) or *p*-chloro-*p*-nitrophenyl benzoate (PCB) was prepared by refluxing equimolar quantities of benzoyl chloride with *p*-nitrophenol in the presence of a catalytic amount of pyridine for 4 hr in 30 ml of alcohol-free dry chloroform. The solution was washed with dilute HCl, dilute bicarbonate solution and water. The organic layer was then dried over anhydrous sodium sulphate and the solvent evaporated. The crude sample was then recrystallised from a chloroform–hexane mixture. *p*-Nitrophenylphenyl methane sulphonate (PMS) and *p*-nitrophenyl-N-phenyl carbamate (PCM) were prepared by the procedure evolved by Williams (1972) and Davy *et al* (1977). *m*-Nitrophenyl-N-N-diphenylphosphodiamidate (PDI) was prepared by refluxing a mixture of aniline, $POCl_3$ and *m*-nitrophenol in the ratio 2:1:1 in the presence of a catalytic amount of pyridine. The refluxing was continued for 4 hr, the mixture then cooled, and the solid compound which separated, recrystallised from a

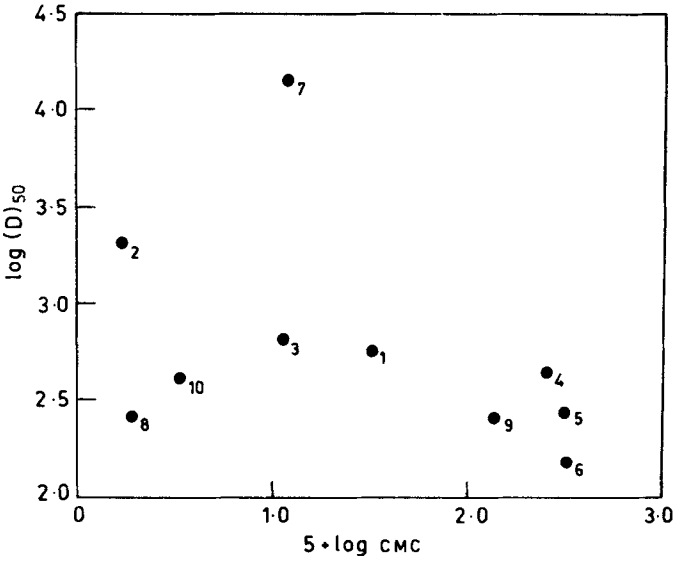


Figure 2. Attempted correlation of log $[D]_{50}$ with log CMC in micellar inhibited reactions in the presence of SLS: 1) PNPB at pH = 9·2; 2) PCB at pH = 9·2; 3) PMS at pH = 9·2; 4) PNPB in 0·0050 M OH^-; 5) PCB in 0·0050 M OH^-; 6) PMS in 0·0050 M OH^-; 7) electron transfer from *n*-butyl ferrocene to Fe^{3+}; 8) hydroxyaminolysis of PNPB at pH = 6·15; 9) hydrolysis of N-(trifluoroacetyl)- indole; 10) hydrolysis of 4-chlorobenzilidene-1,1-dimethylethylanilene in CTAB.

chloroform–hexane mixture (m.p. 172°C). The purity of the esters was checked by determination of their melting points and also from the amount of phenol released after complete hydrolysis. The detergent SLS (BDH) was purified following the procedure of Duynstee and Grunwald (1959) till the CMC agreed with the reported value (Fendler and Fendler 1975).

All the reactions except those of PCM, were carried out at pH = 9·2 in a 0·050 M borax buffer in 0·10 M NaCl at 30°C, the solvent used was almost pure water but for the very small amount of acetonitrile added in making up the substrate solution. For comicellar work, $[OH^-] = 5{\cdot}0 \times 10^{-3}$ M was used at 30°C in an aqueous medium. The reactions of PCM, being too fast, were carried out at pH = 7·4 [0·050 M Tris in 10% acetonitrile-90% water]. Whenever the detergent was used, the pH of the buffer solution was adjusted in the presence of the required amount of detergent using a digital pH meter. The CMC of the surfactant was measured spectrophotometrically using the dye, pararosaniline ($\lambda_{max} = 630$ nm) as probe: (CMC for SLS at pH = 9·2, maintained by 0·050 M borax on 0·10 M NaCl, is $4{\cdot}0 \times 10^{-3}$ M). Reactions were monitored by following the release of *p*-nitrophenoxide ion at 400 nm using a Carl Zeiss VSU2-P spectrophotometer provided with a chart recorder. Infinite values of absorbances were experimentally determined after eight or nine half-lives. The rate constants for the reactions were evaluated from the slopes of the regression lines for correlations of $\log [A_\infty - A_t]$ *vs* time. The linear regression analysis was performed on a MICRO programmable calculator (Hindustan Computers).

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