Functional Micellar Catalysis

Part 3. ¹—Quantitative Analysis of the Catalytic Effects due to Functional Micelles and Comicelles

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The kinetic treatment of reactions catalysed by functional micelles and comicelles made up of chemically inert and functional surfactants, based on the pseudophase separation approach, allows the evaluation of the parameters defining the catalytic phenomena. The rate enhancements of activated ester hydrolysis due to cationic micelles of previously described functional surfactants, when compared to those due to analogous non-micellar model compounds, can be mainly accounted for by concentration and electrostatic effects. Desolvation and other medium effects on anionic micellar functions are not a relevant source of rate enhancement. The merits of comicellar solutions for the analysis under standard conditions of the catalytic effectiveness of a variety of functional surfactants are also presented.

Interest in refining analogies between micelles and enzymes has led to substantial progress in the field of functional micellar catalysis.² A large variety of functional surfactants ^{1, 3-8} have been tested as micellar catalysts of activated ester (R'-COY) hydrolysis and in most cases a nucleophilic mode of action (see below; $\underline{m}-\underline{R}-FH$: micellar functional surfactant), involving acylation and deacylation of the --FH function, has been shown to be involved.



In spite of the large amount of published data, it is quite difficult to compare the catalytic effectiveness of the various types of functional micelles because of the different conditions used (micelles or solvent composition, pH, buffer, temperature, *etc.*) in the kinetic studies. Moreover, most of the investigations were conducted at low substrate concentration under pseudo-first-order conditions so that only the acylation process was followed.

We have recently undertaken a systematic kinetic analysis ^{2c} of several of the most significant functional micellar reagents as catalysts of activated ester and amide hydrolysis, aimed at defining their relative catalytic effectiveness under identical conditions and also to obtain a better understanding of the factors responsible for the observed rate effects. Analysis in aqueous solutions could not, however, be conducted for homogeneous micellar systems because of the sparing solubility of several surfactants, so we used the following conditions for reasons detailed below: mixed

micelles with CTABr as the inert solubilizing component, Tris buffers of constant ionic strength. We were then faced with the problem of the treatment of kinetic data. Gitler and Ochoa-Solano^{8a} suggested for the case of functional comicelles a treatment based on the separation of active (functional) and inactive regions of the micelle. Such a static model was later criticized by Maugh and Bruice.⁹ More recently, the kinetic treatment of bimolecular micellar reactions based on the pseudophase model has been discussed and reassessed.^{10, 11}

The purpose of this paper is to present a general kinetic treatment for reactions catalysed by functional micelles, both homogeneous and mixed, and to estimate the kinetic parameters of the reactions occurring in the micellar medium and the factors responsible for the catalytic effects observed.

EXPERIMENTAL

The syntheses of surfactants (Ia)-(IVa), of model compounds (Ib)-(IIIb) and of p-nitrophenyl acetate (PNPA) and hexanoate (PNPH) have been described.^{1, 8c, 4} Thiocholine (IVb) was obtained by cleavage of commercially available acetylthiocholine iodide. This was deacylated (disappearance of the ¹H n.m.r. signal at 2.35 δ , in D₂O) in a deoxygenated solution of HCl (2 mol dm⁻³) in methanol, 24 h at room temperature, and, after removal of the solvent, the product was immediately used for the kinetic measurements carried out for de-aerated nitrogen flushed solutions. The thiocholine SH title was determined by Ellman's method.¹²

The procedure used for the kinetic determinations, using a Gilford 2400 or a Varian-Cary 219 spectrophotometer, has been described.^{1, 8c}



THEORETICAL

HOMOGENEOUS FUNCTIONAL MICELLES

Following the phase separation approach,^{13, 14} the overall rate of a reaction catalysed by micelles equals the sum of the rates of two processes: the reaction occurring in the micellar pseudophase of fractional volume v and that in the aqueous pseudophase of fractional volume 1-v.

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If S and D^f designate the substrate and the functional surfactant, subscripts w and m the aqueous and the micellar pseudophases and * indicates that the concentration is referred to the volume of the corresponding pseudophases indicated by the subscripts, the stoichiometric concentration of S and D^f (when $[D^f]_t > c.m.c.$) are defined by the material balance of eqn (1) and (2):

$$[S]_{t} = [S]_{w} + [S]_{m} = [S]_{w}^{*}(1-v) + [S]_{m}^{*}v$$
(1)

$$[D^{f}]_{t} = c.m.c. + [D^{f}]_{m} = [D^{f}]_{w}^{*}(1-v) + [D^{f}]_{m}^{*}v.$$
(2)

In dilute micellar solutions, when v < 1, the relations $[S]_t = [S]_w + [S]_m^* v$ and $[D^f]_t = c.m.c. + [D^f]_m^* v$ are good approximations. On the other hand, v is defined by the product $\overline{V}[D^f]_m$, \overline{V} being the molar volume of the micelles of D^f , so that $[D^f]_m^* = 1/\overline{V}$. Under such conditions, the overall first-order rate constant, $k'_{\psi} = -d[S]/(dt[S]_t)$, may be given ^{14b} by eqn (3)

$$k'_{\Psi} = \frac{(k'_0 + k''_{\mathsf{w}} \mathsf{c.m.c.})[S]_{\mathsf{w}} + k''_{\mathsf{m}}[S]_{\mathsf{m}}^* [D^f]_{\mathsf{m}}^* v}{[S]_t} = \frac{k_0[S]_{\mathsf{w}} + (k''_{\mathsf{m}}/\overline{\nu})[S]_{\mathsf{m}}^* v}{[S]_t}$$
(3)

where k'' are the second-order rate constants in the corresponding phases for the reaction between S and D^f, k'_0 the pseudo-first-order rate constant for the "spontaneous" hydrolysis of S and k_0 equals $k'_0 + k''_w$ c.m.c. In deriving eqn (3), it has been assumed that the micellar reaction occurs in the whole volume of the micelles; the implications of this assumption will be discussed below.

The k'_{ψ} constant may be conveniently expressed either : (a) in terms of the partition coefficient ¹⁴ of the substrate between the two pseudophases, $P_{\rm s} = [{\rm S}]^*_{\rm m}/[{\rm S}]^*_{\rm w}$, as in eqn (4),

$$k'_{\psi} = \frac{k_0 + (k_m''/\overline{\nu}) P_s v}{1 + (P_s - 1)v},$$
(4)

or (b) in terms of the binding constant of S to the micellized surfactant, $K_{\rm S} = [S]_{\rm m}^{*}v/([S]_{\rm w}[D^{\rm f}]_{\rm m})$. Since $K_{\rm S} = P_{\rm S}v/[D^{\rm f}]_{\rm m}$ and provided $P_{\rm S} \ge 1$, from eqn (4) one obtains eqn (5) or (5') where $k_{\rm c} = K_{\rm S}k_{\rm m}'/\overline{V}$ is the apparent catalytic rate constant which is often used to define the catalytic properties of functional surfactants.

$$k'_{\psi} = \frac{k_0 + (k''_m / \overline{V}) K_{\rm S} [{\rm D}^{\rm f}]_{\rm m}}{1 + K_{\rm S} [{\rm D}^{\rm f}]_{\rm m}}$$
(5)

$$=\frac{k_0+k_c[D^f]_m}{1+K_s[D^f]_m}.$$
(5')

The above rate equations are based on a number of assumption and approximation which are, however, reasonable for very dilute micellar solutions and provided $[S] \leq [D^{f}]_{m}$.

Complementary data for the definition of the catalytic effectiveness of micellar reagents may be obtained using excess substrate, *i.e.*, $[S] \ge [D^{f}]_{m}$. Under these conditions, the treatment in the case of ester (or amide) hydrolysis may be based on the Reaction Scheme following the approach described by Bender and Marshall.¹⁵ Kinetically the reaction may consist of a fast initial release of the alcoholic fragment HY (pre-steady-state) followed by a slow linear formation of HY (steady-state) provided the acylation stage is much faster than that of deacylation. In the pre-steady-state ("burst") portion, the first-order rate constant for the attainment of a steady-state concentration of the acylated intermediate, $\underline{m}-\underline{R}-F-COR'$, is given by eqn (6) where

 k''_{a} is the second-order rate constant for the acylation process, k'_{d} is the pseudo-first-order rate constant for the deacylation reaction and subscript ₀ refers to time zero

$$k' = k''_{a}[S]_{0}^{3} + k'_{d}.$$
 (6)

In the steady-state portion, the rate of formation of HY is given by eqn (7), analogous to the Michaelis-Menten equation, which becomes $d[HY]/dt = k'_d[D^f]_m$ provided $k''_a[S]_0 \ge k'_d$

$$\frac{\mathrm{d}[\mathrm{HY}]}{\mathrm{d}t} = \frac{k_a'' k_d' [\mathrm{S}]_0 [\mathrm{D}^{\mathrm{f}}]_{\mathrm{m}}}{[\mathrm{S}]_0 + k_d' / k_a''}.$$
(7)

The constant $k_a^{"}$ obtained from "burst" experiments is equivalent to the constant k_c obtained under conditions $[S] \leq [D^f]_m$; the values, however, cannot be expected to be the same since all micellar properties are likely to be perturbed when micelles are saturated with respect to the substrate.

COMICELLES OF INERT AND FUNCTIONAL SURFACTANTS

The quantitative treatment of reactions catalysed by functional comicelles in dilute solutions, under conditions $[S] \leq [D^{f}]_{m}$, may also be based on the phase separation approach followed in the preceding section. The stoichiometric concentrations of substrate and functional surfactant may be given by eqn (1) and (2) where v is now defined by the quantity $-([D^{f}]_{m}+[D^{i}]_{m})\overline{V} = [D^{t}]_{m}\overline{V}$, superscripts i and t denoting inert and total (surfactant) and \overline{V} the molar volume of the comicelle. Therefore, the overall first-order rate constant, in terms of the binding constant of S to comicellized surfactants, D_{m}^{t} , may be expressed by eqn (8) or (8'), the analogues of eqn (5) and (5').

These expressions

$$k'_{\psi} = \frac{k_{0} + (k''_{m}/\bar{V})K_{s}[D^{f}]_{m}}{1 + K_{s}[D^{f}]_{m}}$$
(8)

$$=\frac{k_0 + k_c [D^f]_m}{1 + K_s [D^f]_m}$$
(8')

are based on assumption which are reasonable for dilute micellar solutions where $[D^i]_m \ge [D^f]_m \ge [S]$ and K_s and \overline{V} may be taken as those of the micelles of D^i only. However, such conditions are difficult to realize. If the ratio $[D^i]/[D^f]$ is not very large eqn (8) or (8') may still be applied and K_s and the other kinetic constants referred to that comicellar composition. In this case there are problems in evaluating some of the micellar parameters involved in the kinetic equations such as, for instance, the c.m.c. and, hence, the $[D]_m$ of the individual surfactants unless one assumes, as a non-rigorous approximation,¹⁶ that the binary mixture of Dⁱ and D^f behaves ideally.

Conditions $[D^{i}]_{m}$, $[S] \ge [D^{f}]_{m}$ may be used to obtain kinetic data concerning the deacylation stage. The treatment is here analogous to that described for homogeneous micelles when eqn (6) and (7) applied.

RATE DEPENDENCE ON pH

Most of the functional detergents so far investigated undergo acid dissociation in the range of neutral-alkaline solutions. There are difficulties in the interpretation of acid dissociation in microscopic pseudophases, particularly when charged as in the case of functional ionic micelles, since the K_a value of a function at the micellar surface is different from that in water.¹⁷

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Given a function -FH subject to acid dissociation to $-F^-$ and assuming that the corresponding forms of the surfactant, D^{fH} and D^{f-} , are both reactive species toward S with second-order rate constant, $k_m^{"H}$ and $k_m^{"-}$, respectively, the overall first-order rate constant, assuming that the K_S/\overline{V} ratio does not change appreciably with the degree of dissociation of the function, may be given by eqn (9)

$$k'_{\psi} = \frac{k_0 + (k''_m [D^{fH}]_m + k''_m [D^{f-1}]_m) K_S / \overline{V}}{1 + K_S [D^t]_m}.$$
(9)

On the other hand, the overall dissociation constant, K_a app. = [H+][D^f-]/[D^{fH}], at least for moderately concentrated micellar solutions, may be approximately defined by K_a app. = [H+][D^f-]_m/[D^{fH}]_m. Under such conditions, from eqn (9) one obtains eqn (10) where $k_c^{\rm H} = K_{\rm S} k_m^{"\rm H} / \overline{V}$ and $k_c^{-} = K_{\rm S} k_m^{"-} / \overline{V}$

$$k'_{\psi} = \frac{k_0 + [D^{\rm f}]_{\rm m} (k_{\rm c}^{\rm H} [{\rm H}^+] + k_{\rm c}^- K_{\rm a} {\rm app.}) / ([{\rm H}^+] + K_{\rm a} {\rm app.})}{1 + K_{\rm s} [D^{\rm t}]_{\rm m}}.$$
 (10)

The overall catalytic rate constant is then given by eqn (11)

$$k_{\rm c} = \frac{k_{\rm c}^{\rm H} [{\rm H}^+] / K_{\rm a} {\rm app.} + k_{\rm c}^-}{(1 + [{\rm H}^+] / K_{\rm a} {\rm app.})}$$
(11)

or, when the activity of the undissociated form may be neglected, by $k_c = k_c^{-}/(1 + [H^+]/K_a \text{ app.})$.

APPLICATION TO EXPERIMENTAL DATA

EVALUATION OF THE KINETIC PARAMETERS

A typical rate-concentration profile for ester (PNPH) hydrolysis catalysed by homogeneous functional micelles of detergent (Ia) is shown in fig. 1. The approximate k_c value may be simply obtained ^{1, 8c} from the slope of the quasi-linear postmicellar portion of the diagram when, provided $K_{\rm S}[D^{\rm f}]_{\rm m} \ll 1$, eqn (6) becomes $k_c = k'_{\psi}/[D^{\rm f}]_{\rm m}$. Application of eqn (5) in the rearranged form of eqn (12) or, when $k_0 \ll k'_{\psi}$, of eqn (13) allows one to estimate the $k'_{\rm m}/\vec{V}$ and $K_{\rm S}$ values

$$\frac{1}{k'_{\psi} - k_0} = \frac{1}{(k''_{\rm m}/\overline{\nu}) - k_0} + \frac{1}{(k''_{\rm m}/\overline{\nu}) - k_0} \frac{1}{K_{\rm s}[{\rm D}^{\rm f}]_{\rm m}}$$
(12)

$$\frac{[\mathbf{D}^{\mathrm{r}}]_{\mathrm{m}}}{k_{\psi}} = \frac{1}{k_{\mathrm{c}}} + \frac{K_{\mathrm{s}}}{k_{\mathrm{c}}} [\mathbf{D}^{\mathrm{f}}]_{\mathrm{m}} = \frac{1}{K_{\mathrm{s}}k_{\mathrm{m}}''/\overline{\nu}} + \frac{1}{k_{\mathrm{m}}''/\overline{\nu}} [\mathbf{D}^{\mathrm{f}}]_{\mathrm{m}}$$
(13)

from the slope and intercept of the appropriate plots [see fig. 1 for the application of eqn (13)].

In the case of comicelles of inert and functional surfactants, the rate concentration profile obtained at any given $[D^i]/[D^f]$ ratio is shown in fig. 2 [see also ref. (1), (8a) and (8c)] and application of eqn (8) or (8') in the rearranged forms analogous to (12) or (13) may allow determination of the k_m^r/\overline{V} and K_s values. The non-functional surfactant is often not so inert as has been assumed and may catalyse ^{8d} or inhibit the reaction under study. In this case, there are problems in evaluating the k_0 term of eqn (8) or (8'). However, it is possible, by rewriting eqn (8') as eqn (14), to estimate $k'_{corr.}$ by approximating

$$k'_{\rm corr.} = k'_{\psi} - \frac{k_0}{1 + K_{\rm S}[{\rm D}^t]_{\rm m}} = \frac{k_c [{\rm D}^t]_{\rm m}}{1 + K_{\rm S}[{\rm D}^t]_{\rm m}}$$
(14)



[Df]/10⁻⁴ mol dm⁻³

FIG. 1.—Rate-concentration profile: the hydrolysis of PNPH catalysed by surfactant (Ia). Conditions: [PNPH] = $(3-8) \times 10^{-6}$ mol dm⁻³, Tris buffer $\mu = 0.1$ (KCl), pH 7.95, 1 % v/v CH₃CN, 25°C. Inner_plot: [D^f]_m/k'_{\u03c0} against [D^f]_m [see text, eqn (13)]. Kinetic parameters: $k_c = 275$ dm⁻³ mol⁻¹ s⁻¹, $K_S = 1860$ dm³ mol⁻¹, $k''_m/\overline{V} = 0.15$ s⁻¹.



[Df]/10-4 mol dm-3

FIG. 2.—Rate-concentration profile: the hydrolysis of PNPH catalysed by comicelles [CTABr]: [Ia] = 6.7. Conditions: [PNPH] = $(3-5) \times 10^{-6}$ mol dm⁻³, Tris buffer, $\mu = 0.1$ (KCl), pH 7.95, 1 % v/v CH₃CN, 25°C. Inner plot: [D^f]_m/k_y against [D^t]_m [see text, eqn (15)]. Kinetic parameters: $k_c = 290$ dm³ mol⁻¹ s⁻¹, $K_S = 2100$ dm³ mol⁻¹, $k_m^m/\overline{V} = 0.14$ s⁻¹.

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the $k_0/(1 + K_s[D^i]_m)$ term at any $[D^i]_m$ to the overall first-order rate constant observed for solutions of Dⁱ only, at $[D^i]_m = [D^i]_m$. This may easily be obtained from the rate-concentration profile determined for solutions of Dⁱ and the reaction considered. Eqn (15) may then be applied

$$\frac{[\mathbf{D}^{t}]_{m}}{k_{\text{corr.}}^{\prime}} = \frac{1}{k_{\text{c}}} + \frac{K_{\text{s}}}{k_{\text{c}}} [\mathbf{D}^{t}]_{m} = \frac{1}{K_{\text{s}}k_{\text{m}}^{\prime\prime}/\overline{\nu}} + \frac{1}{k_{\text{m}}^{\prime\prime}/\overline{\nu}} [\mathbf{D}^{t}]_{\text{m}}.$$
(15)

The above problem is virtually absent under the conditions we used for the kinetic analysis of various functional surfactants (see above and fig. 2 for details) since CTABr in Tris buffers is virtually inert (a slight inhibition is actually observed ^{8a}) in the hydrolysis of *p*-nitrophenyl esters. Another advantage in the use of CTABr comicelles in these solutions is their very low c.m.c. $\{(3-5) \times 10^{-5} \text{ mol dm}^{-3};$ [CTABr]/[D^f] $\approx 7:1$ } which, on one hand, minimizes the approximations in evaluating the c.m.c.^f value and, hence, [D^f]_m and, on the other hand, allows a complete kinetic analysis to be conducted for very low [D^f]_m (compare fig. 1 and 2).



FIG. 3.—" Burst " experiment. Conditions: $[PNPH]_0 = 1.59 \times 10^{-4} \text{ mol } dm^{-3} [Ia]_m = 1.15 \times 10^{-5}$, $[CTABr] = 7.8 \times 10^{-5} \text{ mol } dm^{-3}$, Tris buffer, $\mu = 0.1$ (KCl), pH 7.95, 1.5 % v/v CH₃CN, 25°C. Kinetic parameters: $k_a^{"} = 190 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} k_d^{'} = 6 \times 10^{-3} \text{ s}^{-1}$.

For analogous reasons, the kinetic analysis using excess substrate over the functional surfactant is generally more accessible for mixed than for homogeneous micelles. A "burst" experiment carried out for a solution of comicellized (Ia) is shown in fig. 3 together with the kinetic parameters calculated using eqn (6) and (7) and the described procedures.¹⁵

In cases where comparison was possible, as in those illustrated by fig. 1 and 2 for surfactant (Ia), the k_m''/\overline{V} values determined for homogeneous and mixed micelles were substantially the same. The k_a'' value obtained from "burst" kinetics were, instead, generally lower than the k_c values evaluated from measurements using excess functional surfactant over the substrate [compare data of fig. 3 with those of fig. 1 and 2; see also ref. (18)].

RELATIVE REACTIVITY OF NUCLEOPHILIC SURFACTANTS IN MICELLAR AND AQUEOUS MEDIA

One of the most interesting questions in the field of functional as well as of bimolecular micellar catalysis concerns the relative reactivity, k_m''/k_w'' , of a give nucleophilic reagent, *i.e.*, its activity as an aggregate in micelles relative to that as a monomer in aqueous bulk phase. This problem is related to that of desolvation, particularly of anionic functions, which may occur in the relatively hydrophobic micellar pseudophase and could be a factor responsible for the rate enhancements observed.^{6a, 7, 19}

Direct measurements of the activity of monomeric surfactants in very dilute solutions ($[D^{f}] < c.m.c.$) are not easily accessible and may be complicated by premicellar associations of reagents. The second-order rate constant $k_{w}^{"}$ is more conveniently, although indirectly, obtained by measuring the activity of structurally analogous non surfactant models.^{1, 8a,c e}.

TABLE 1.—SECOND-ORDER RATE CONSTANTS $(dm^3 mol^{-1} s^{-1})$ for the reaction of (I)-(IV) with *p*-nitrophenyl acetate (A) and hexanoate (H) at $25^{\circ}C^{a}$

catalyst	ester	k_{c}	$k''_{\mathbf{m}}$	$k_{m}^{''-}$	k''_{w}	$k_{\text{rel.}}^{b}$
(I)	A	6.8	0.087	31	16	1.9
	\mathbf{H}	295.	0.048	19	24	0.8
(II)	Α	1.6¢	0.017¢	58	144	0.4
	н	1.3	2.3×10^{-4}	6.5	48	0.15
(III)	Α	6.1	0.065	23.5	12.5	1.9
	н	210.	0.045	15.9	11.5	1.4
(IV)	Α	580.	4.1	5.1	2.8	1.8
	н	1750.	0.4	0.5	1.3	0.4

^a The k_c and $k_m^{''}$ constants have been determined at pH 7.95, unless otherwise indicated. The $k_m^{''}$ were calculated using the following pK_a app. values: (Ia), 10.5 [ref. (8c)]; (IIa), 12.4 [ref. (3c)]; (IIIa), 10.5 [the dissociation of the imidazole group, ref. (1)]; (IVa), 7.3 [ref. (4)]. ^b The ratio $k_m^{''}/k_w^{''}$. ^c At pH 8.9.

We here report some of the available data for functional surfactants (I-IV)*a* and their models (I-IV)*b* for the hydrolysis of PNPA and PNPH. Table 1 shows for each surfactant the rate constants evaluated from kinetic measurements carried out for solutions of comicelles, [CTABr]/[D^f] \approx 7, Tris buffers of constant ionic strength ($\mu = 0.1$, KCl), containing CH₃CN (1 % v/v) added to ensure solubility of the esters. The rate constants k_c and $k_m^{"}$ were obtained by applying mainly eqn (15) to experimental data and using for the comicelles the molar volume of CTABr micelles, $\overline{V} = 0.36 \text{ dm}^3 \text{ mol}^{-1}$,²⁰ and the $k_m^{"-}$ constants were obtained after correction for incomplete acid dissociation by means of eqn (11), assuming negligible, at least at pH \geq 8, the contribution of the undissociated form. The $k_w^{"-}$ constants were obtained by measuring the rate of hydrolysis of the esters for solutions of Tris or borate buffers, $\mu = 0.1$ (KCl), 1 % v/v CH₃CN, and varying concentrations of model compounds, and corrected for incomplete acid dissociation of the functions using known p K_a values.^{1, 3, 4}

The $k_m^{"}$ and hence the k_{rel} values of table 1 are probably overestimated by a factor ≈ 2 related to the use of the molar volume \overline{V} . As discussed by Bunton,¹¹ micellar reactions are known to occur mainly in the Stern layer and not in the core of micelles and the Stern-layer volume is estimated to be approximately half that of micelles.

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For these reasons and because of the uncertainties of so many parameters used to evaluate the k'' constants, these values are to be taken as very approximate. Yet the k_{rel} values are remarkably close to unity [but in the case of surfactant (IIa) due possibly to a large uncertainty $^{3a, c}$ in pK_a and pK_a app.] and apparently larger in the case of PNPA than in that of PNPH. On the whole there is no evidence of any substantial difference in reactivity of a given nucleophilic function bound to a surfactant when at the head of a micelle or in the aqueous bulk phase.

CONCLUSIONS

Although based on a number of assumptions and approximations which are less rigorous than desirable, the kinetic treatment discussed here is adequate to evaluate the various parameters which define the rates of reactions catalysed by nucleophilic surfactants.

The analysis of comicellar solutions may provide a useful method for the determination of the catalytic properties of a functional surfactant when it is insoluble or only slightly soluble in water, or it is very reactive.

The results reported in table 1, although restricted to a limited number of cases and the hydrolysis of activated esters, thus confirming data reported by Bunton¹¹ and by Berezin and coworkers¹⁴ for bimolecular micellar reactions and also for some reactions of surfactant (II*a*), indicate that the essential factors responsible for the functional micellar catalysis are hydrophobic (proximity or concentration effects) and electrostatic (changes in the acid dissociation of the functions) in character.

The effect of changing the reaction medium from an aqueous to a micellar phase does not significantly affect the activity of an anionic function: enhancement of its nucleophilic properties due to desolvation is apparently not relevant. This is surprising since the properties 2 of the Stern layer, in terms of dielectric constant (medium polarity) and solvation capability, would have suggested higher rates in the micellar than in the aqueous medium. This could perhaps indicate that micellar reactions occur mostly on the surface of the Stern layer without benefit of the lower polarity and of the lower water content of the interior part of the layer.

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