The Nature of Mixed Micelles from Anionic Dyes and Cationic Surfactants. A Kinetic Study

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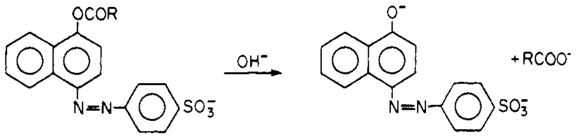
Abstract: The kinetics of the base-catalyzed hydrolysis of acetate and hexanoate esters of an azonaphthol sulfonate dye were studied in aqueous dispersions with dodecyl- and hexadecyltrimethylammonium bromide over a range of surfactant concentrations from equivalent amounts to above the critical micelle concentration (cmc) for surfactant homomicelles. Fresh dispersions consisted of reactive micellar aggregates and a small proportion of nonreactive crystallites. Low stoichiometric surfactant-dye ratios (S/D) inhibit hydrolysis; catalysis occurs at higher S/D but at surfactant concentrations below the cmc for homomicelles. A model involving a continuum of mixed micellar species of changing composition, structure, and surface potential is consistent with the results. Inhibition results from an unfavorable orientation of the reaction site within surfactant-poor mixed micelles of low surface potential that is not compensated by concentration of OH^- in the micellar domains. Catalysis is observed in surfactant-rich micelles with sufficient surface potential to concentrate OH^- and thus overcome unfavorable orientation. Spectral shifts occur at *S/D* ratios giving catalysis. Aging of the dispersions results in particle reorganization that is revealed kinetically. On long standing, the micellar equilibria are shifted by precipitation of the insoluble dye-surfactant salts.

The need to understand the nature of organized aggregates of amphiphilic molecules and the reactions occurring in the aggregates is great in fields such as biology and photography. The purpose of this work was to study colloidal aggregates formed on interaction of two oppositely charged colloidal electrolytes, a dye and a surfactant, by means of a kinetic probe. The spectral changes accompanying solubilization of dyes in surfactant micelles have been studied widely as a result of the use of the dye method for measuring the surfactant critical micelle concentration (cmc). It is generally assumed that the dye affects the micellar structure and the cmc to only a small extent. The use of this method and its shortcomings have been critically reviewed.[1] The principal fault of the method is that some dyes give cmc values that are lower than those obtained independently in the absence of dye, owing to the fact that the dye induces micellization. In most cases, however, the errors are not large.

It is now recognized that the interaction of oppositely charged dyes and surfactants can give rise to aggregates at concentrations below the cmc. These have been designated as suspensions of dye-surfactant salts,[2-5] dye aggregates,[2,6] dyes absorbed to surfactant dimers,[7] or complexes of unspecified composition.[8] The existence of micellar aggregates of oppositely charged dyes and surfactants at concentrations below the cmc for surfactant homomicelles has also been recognized.[2,4,9]

In many instances, however, the belief that surfactant micellization occurs normally in the presence of dye or other amphiphiles has been so strong that qualitative distinctions have been made between "micelles" formed above the cmc for surfactant homomicelles and "premicelles" or "submicelles" formed below the cmc. We hope to show in this paper that in some cases this is an artificial distinction.

We recently showed that soluble micellar aggregates can form by a kinetically controlled process when near-equivalent concentrations of an anionic dye and a cationic surfactant are mixed at concentrations well below the cmc for the surfactant homomicelles.[10] The insoluble dye-surfactant salt was only formed after aging of the solutions for several days. In an effort to shed more light on the nature of the colloids formed from dyes and surfactants of opposite charge, we have used a kinetic method in conjunction with spectral, ultrafiltration, and light-scattering studies. Kinetic methods have an advantage over spectral methods in that they are sensitive to subtle changes in the organization of such aggregates and to changes in concentrations of bound counterions. The dye components of our colloids are esters of anionic azonaphthols (**1** and **2**) which undergo a rapid, base-catalyzed hydrolysis according to eq 1. The cationic



(1)

1 $R = CH_3$

2 $R = C_5H_{11}$

3

surfactants studied were dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (CTAB).

The kinetics of hydrolysis of esters solubilized in micelles have been studied widely and reviewed extensively.[11] In most previous studies, the esters have been uncharged and it was assumed that they had negligible effects on the cmc's and micellar structures. In many studies involving anionic esters and cationic surfactants, little attention has been given to surfactant concentrations much below the cmc for surfactant homomicelles.[12-14] In most cases no kinetic effects were found at surfactant concentrations below the cmc,[15] whereas in other cases, rate depressions were noted.[5,9] Our interest in studying ester hydrolysis in colloidal aggregates has been to use kinetics as a probe for changes in aggregate structure rather than to study micellar catalysis. We find evidence for a wide range of mixed micellar species arising at concentrations of surfactant far below the cmc's for surfactant homomicelles. We also find that a given surfactant can either inhibit or catalyze hydrolysis, depending on the composition and organization of the micelle. The present paper deals with the nature of the aggregates and the accompanying paper with salt effects on the kinetics and micellar structure.

Experimental Section

Materials. Gel chromatography[16] of commercially available Orange I sodium salt (**3**) yielded six colored bands in addition to the desired dye. The crude material was purified by chromatography in 200-mg batches on a 5.5 × 13-cm column of Sephadex G-25 gel, using 0.01 *N* potassium or sodium hydroxide for elution. Acidification and concentration of the eluates followed by recrystallization

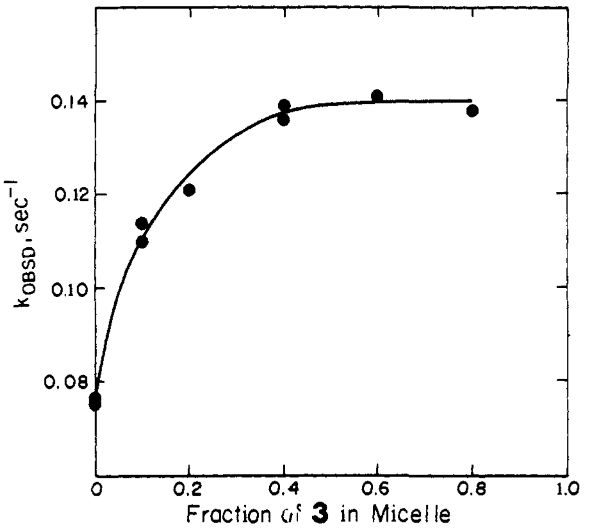


Figure 1. Effect of added product on the initial hydrolysis rate of **1** in mixed micelles with CTAB: [1] + [3] = 1.25×10^{-5} *M*. [CTAB] = 5.0×10^{-5} *M*.

of the product from water gave the pure dye as the monosodium or potassium salt monohydrate.

Anal. Calcd for $C_{16}H_{11}KN_2O_4S \cdot H_2O$: C, 50.0; H, 3.4; N, 7.3. Found: C, 50.1; H, 3.3; N, 7.4.

The esters were prepared by treating the dye salts with a threefold excess of acetic or hexanoic anhydride and triethylamine in DMF at room temperature. The esters crystallized spontaneously or on concentration of the mixtures and were recrystallized from DMF-acetone.

Anal. Calcd for $C_{18}H_{13}N_2NaO_5S$: C, 55.1; H, 3.3; N, 7.1. Found: C, 55.3; H, 3.3; N, 7.2; λ_{max} (H_2O) 376.5 nm (ϵ 1.15×10^4).

Anal Calcd for $C_{22}H_{21}KN_2O_5S$: C, 56.9; H, 4.6; N, 6.0. Found: C, 56.4; H, 4.6; N, 5.9; λ_{max} (H_2O) 377.5 nm (ϵ 1.12×10^4).

A commercially available sample of DTAB failed to give the correct cmc after repeated recrystallizations. Eastman reagent grade dodecyltrimethylammonium chloride was dialyzed against 3 *M* sodium bromide and then against distilled water. The DTAB recovered was recrystallized four times from a mixture of absolute alcohol and dried ethyl acetate and was dried under vacuum at 80°.

Anal. Calcd for $C_{15}H_{34}BrN$: C, 58.4; H, 11.1; N, 4.6; Br, 25.8. Found: C, 58.6; H, 10.7; N, 4.7; Br, 26.2; cmc (by conductivity) 1.7×10^{-2} *M* (lit.[1] 1.4-1.5×10^{-2} *M*).

Eastman practical grade CTAB was recrystallized four times from ethanol-ethyl acetate and was dried at 60° under vacuum: cmc 9.0×10^{-4} *M* (lit.[1] 9.20×10^{-4} *M*).

Kinetic Measurements. Hydrolysis rates were measured at 25° under pseudo-first-order conditions by mixing the ester-surfactant dispersions in water with excess sodium hydroxide solution in a Durrum stopped-flow spectrophotometer equipped with a 2-cm cuvette, and monitoring the decrease in transmittance at 518 nm resulting from formation of product **3**. In most runs the ester and base concentrations, after mixing, were 1.25×10^{-5} and 0.1 *M*, respectively. Separate experiments showed that the rates of aggregate reequilibration accompanying the increase in ionic strength were faster by at least two orders of magnitude than the hydrolysis rates. The slower runs with the hexanoate ester were measured with a Beckman DK-2A recording spectrophotometer equipped with a temperature-controlled cell holder and were timed with a stopwatch. Photographs of the oscilloscope tracings of the stopped-flow runs were read with a curve reader interfaced with a Digital Equipment Corp. PDP-8/i computer. The computer performed a least-squares analysis of ln ($A_\infty - A$) as a function of time and calculated a pseudo-first-order rate constant and the correlation coefficient, where A_∞ and A are the absorbances after 10 or more half-lives and at some time, *t*. Plots of the printed-out values of ln ($A_\infty - A$) vs. time were made whenever the correlation coefficient was less than 0.9996 and the rate constant was obtained graphically from the initial slope. The dispersions used for the rate measurements were prepared by adding an aliquot of the ester stock solution in water with stirring to a diluted solution of the surfactant in a volumetric flask. The same order of mixing and stirring rate was used throughout. All the stopped-flow measurements could be completed within 5 min of mixing the ester and surfactant. The sodium hydroxide solutions were standardized each day they were used. Second-order rate constants were obtained by dividing the pseudo-first-order rate constants by the hydroxide concentration.

Optical Measurements. Spectrophotometric curves were measured on a Beckman DK-2A spectrophotometer. The scattering from the suspensions made a negligible contribution to the absorbance measurements. Suspensions for spectrophotometric measurements were prepared in water in the same way as those prepared for the kinetic measurements. Aliquots (5 ml) of the suspensions and of a 0.2 *M* electrolyte solution were emptied against a stirrer in impinging streams from pipettes having the same flow rates. Yields of Orange I (**3**) from the rate runs were determined from the final transmittance values of the kinetic runs. Molar absorptivities were calculated from absorption curves of **3** measured in 0.1 *M* sodium hydroxide at the corresponding surfactant concentration. Solutions used for light-scattering observations were filtered under pressure through fine sintered glass prior to mixing. The usual precautions for maintaining dust-free conditions were taken. Qualitative observations of scattering were made by illuminating the solutions in vials with the focused beam of a high-intensity microscope lamp in a darkroom. Ultrafiltration experiments were performed with 13-mm disks of Nuclepore membranes having pore sizes of 0.2 and 1.0 μm. held in a Millipore Swinny adapter attached to a 20-ml syringe. Absorbance measurements were made on the suspensions before and after filtration.

Results

Kinetics. The pseudo-first-order rate constants for hydrolysis of the acetate, measured by stopped-flow, showed a first-order dependence on hydroxide concentration in the range of 0.01-1.0 *M* and were independent of ionic strength. Replicate measurements of the second-order rate constant for hydrolysis of the acetate, taken over a period of more than a year, gave $k \pm$ standard error = 3.47 ± 0.09 M^{-1} sec^{-1}. The precision of runs made in the presence of surfactant was nearly as good. Second-order rate constants were independent of the concentration of both esters over the range 1×10^{-6} to 1.3×10^{-5} *M*. Solutions of the acetate obeyed Beer's law in water and in 0.1 *M* sodium chloride at concentrations up to 5×10^{-5} *M*. Thus, the dye esters do not appear to aggregate in the concentration range used for these studies.

First-order rate plots for hydrolysis in micelles were linear initially, but often showed curvature as reaction progressed. Negative curvature was usually observed at low stoichiometric surfactant-dye ratios (S/D). Figure 1 shows that the acceleration results from accumulation of the doubly charged dye product in the micellar aggregates. Nonlinearity of first-order plots can also result from a distribution of particle sizes of a given aggregate. If the various particle sizes have characteristic rate constants, then $d \ln [\text{Dye}]_T/dt = \sum_i k_i'[P_i]/[\text{Dye}]_T$, where $[P_i]$ is the concentration of the *i*th particle size. Polydispersity of a given aggregate should give first-order plots that are concave upward. In all cases of curvature, initial rate constants were computed from the linear portions of the first-order plots.

The effect of surfactant concentration on the hydrolysis rates is shown in Figure 2. Rate constants relative to that obtained in the absence of surfactant are plotted logarithmically. The plots show that a given surfactant can cause both inhibition and catalysis of hydrolysis, depending on the S/D ratio. The concentrations corresponding to the cmc values for the surfactant homomicelles in the absence of added electrolyte are indicated by arrows. The equivalence point is shown as the broken vertical line. The location of rate maxima near the cmc values corresponds to the results

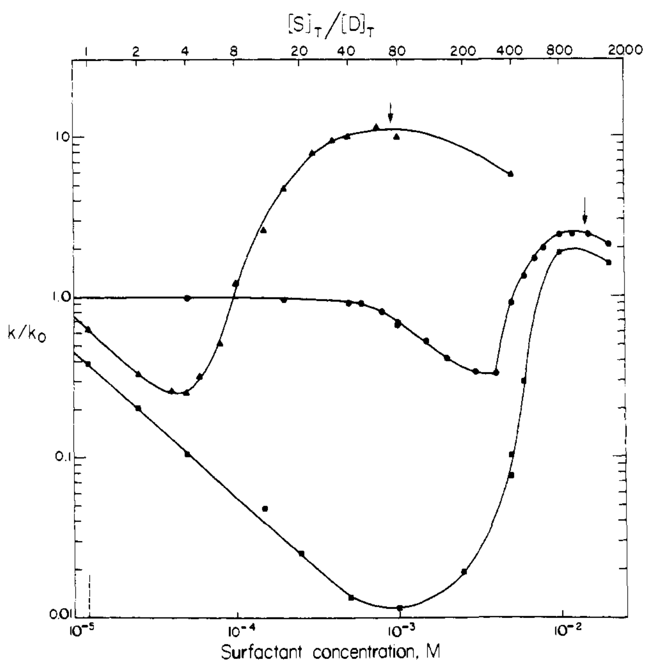


Figure 2. Effect of surfactant concentration on the relative hydrolysis rates of dye esters at 25°: $[\text{ester}]_T = 1.25 \times 10^{-5}$ *M*; $[\text{OH}^-] = 0.1$ *N*. Acetate + DTAB (●); acetate + CTAB (▲); hexanoate + DTAB (■). Arrows indicate the cmc's for homomicelles.

Table I. Ultrafiltration and Product Yields from Fresh Dispersions

$10^4[S]_T$, *M*	S/D	Product yield, %	$(A_0 - \Delta A)/A_0$, %	
			1 µm	0.2 µm
		A. S = DTAB		
12	48	95	95.1, 92.3	78.8
20	80	96	96.1	87.0
30	120	93	95.9	90.0
40	160		97.3	89.2
60	240	96	98.1	91.8
100	400	92		92.4
200	800	98		100.9
		B. S = CTAB		
0.25	1	93	97.5	92.9
0.50	2	92	98.1	92.6
1.0	4	94	97.7	88.4, 96.1
2.0	8	96	99.2	91.5
4.0	16	94		96.4
15	60	98		100.5

found by others in studies of solubilized ester substrates. The important results shown in Figure 2 are that kinetically significant dye–surfactant species are formed at surfactant concentrations far below the cmc for formation of homomicelles. The acetate and CTAB and hexanoate and DTAB give rate depressions even at equimolar concentrations of 1.25×10^{-5} *M*. The more hydrophobic hexanoate gives a 100-fold decrease in rate at the minimum on interaction with DTAB below the cmc, compared to a threefold decrease with the acetate. There is not a corresponding increase in the acceleration with the more hydrophobic ester, in contrast to what is often observed.[17-19]

To verify that the shapes of the profiles in Figure 2 result from interactions peculiar to oppositely charged dyes and surfactants, hydrolysis rates of the acetate were measured in the presence of a nonionic surfactant, Triton X-100. The results showed that no kinetically significant interaction with the nonionic surfactant occurs at concentrations below the cmc. A sharp rate decrease occurred at the cmc. This is typical of the effect of anionic and nonionic surfactants on base-catalyzed hydrolysis of other anionic dyes.[5]

Light Scattering and Ultrafiltration. The solutions used for the kinetic measurements showed no turbidity toward transmitted light at ester concentrations of 2.5×10^{-5} *M* when prepared from carefully filtered stock solutions and water. When the samples were illuminated by an intense light beam, scattering was seen at all CTAB concentrations and at DTAB concentrations of 2×10^{-4} *M* and higher. The scattering came from a relatively few highly reflecting crystallites mixed with a background of amorphous particles. The crystallinity of the largest particles in a DTAB dispersion of the acetate at S/D = 12 was established by their birefringence in a light microscope under darkfield illumination. The proportions of crystallites were generally higher at low S/D ratios but were evident at all surfactant concentrations up to the cmc for surfactant homomicelles. The results suggest that under the conditions used for preparing the dispersions, amorphous aggregates and crystal nuclei are formed competitively. To estimate the proportion of the dispersions that consisted of filterable particles of a given size, the suspensions were filtered through Nuclepore membranes with maximum pore sizes of 1.0 and 0.2 µm. Absorbances of the filtrates were measured within 8 min of preparing the suspensions. After filtration, only light scattering from the amorphous aggregates was seen. The scattering intensity decreased significantly at surfactant concentrations near the cmc. The results of the filtration experiments are given in columns 4 and 5 of Table I, where the percent of the original absorbance remaining after filtration is tabulated. Assuming that the dye ester has a uniform absorptivity in the particles, the values are estimates of the fraction of material removed. For comparison, column 3 lists the yields of product dye, **3**, determined from final transmittance values of kinetic runs. These final values and those obtained in the aging experiments showed no drift for periods of several tens of half-lives. This shows that there is a sharp distinction between reactive and nonreactive particles and the absence of an effect from polydispersity of particle sizes. We suggest that the distinction between particle types is one of crystallinity.

Spectral Changes. Dispersions of the surfactants and acetate, prepared in water at a series of S/D ratios, were mixed with an equal volume of 0.2 *M* KF solution. Fluoride ion was chosen as a nonreacting analog of hydroxide ion because of its similarity in binding to polyelectrolytes[20] and cationic micelles.[21] Shifts in the wavelengths of maximum absorption occur as shown in Figure 3. The absorbances at low S/D ratios were lower than that of the acetate in molecular dispersion, and then increased at the same S/D ratios at which the most significant shift to longer wavelengths occurs. It is clear that the ester is experiencing a change in microenvironment at S/D ratios where the large spectral changes are seen. This change occurs at surfactant concentrations significantly below the cmc for surfactant homomicelles (arrows). Simple ion pairing between the sulfo group and a quaternary ammonium ion does not perturb the chromophore.[10,22] The red shifts in the spectrum and the rate increases begin at the same surfactant concentrations (Figure 2). It appears that the onset of rate acceleration corresponds to the change in microenvironment of the ester in the aggregates. Absorption curves of the acetate were measured in several polar organic solvents to try to correlate the red shift in the aggregates with bulk solvent properties. Table II lists the absorption maxima of the acetate in the solvents along with the dielectric constants, surface tensions, and solubility parameters. The red shift in the surfactant aggregates is not correlated by bulk solvent properties associated with either polarity or cohesion.

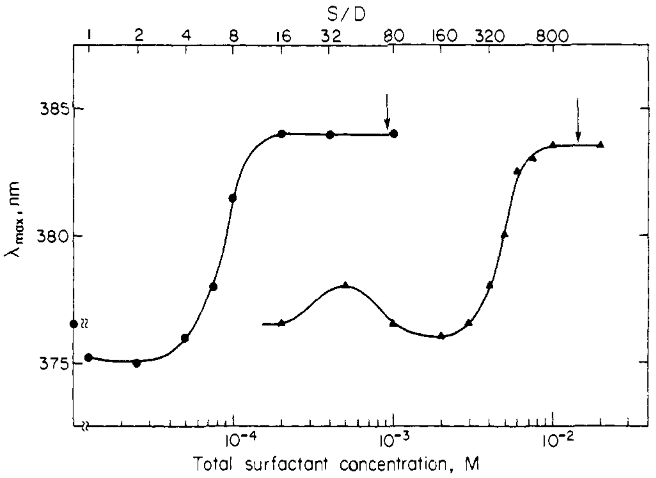


Figure 3. Plots of the absorption maximum of dye acetate as a function of log $[S]_T$ in 0.1 *M* KF. (●) S = CTAB; (▲) S = DTAB. Arrows indicate cmc's for surfactant homomicelles in the absence of dye and added electrolyte.

Table II. Wavelengths of Maximum Absorption of Orange I Acetate in Solvents

Solvent	ϵ^a	γ,^{a} dyn/cm	δ,^{a} $(\text{cal/cm}^3)^{1/2}$	λ_{max}, nm
Ethanol	24.55	21.85	12.7	378
N,N-Dimethylformamide	36.71	35.2	12.1	380
Acetonitrile	37.5	29.3^b	11.9	376
Water	78.39	71.81	23.4	376
Formamide	109.5	57.91	19.2	383
N-Methylpropionamide	172.2	31.7		383
N-Methylformamide	182.4	38.9	16.1	383

^{a} 25°. ^{b} 20°.

Crystal Growth. Dispersions prepared at S/D ratios giving rate inhibition (Figure 2) gave precipitates of crystalline needles on standing. This tendency was greater with the DTAB suspensions. At an ester concentration of 2.5×10^{-5} *M*, DTAB dispersions prepared at S/D ratios of 20 to 80 showed crystalline precipitates detectable by eye in 1-2 hr. Crystallization still occurred if the crystallites present initially were separated. At the same ester concentration, a CTAB dispersion at S/D = 2 began to crystallize in 2.5 hr, whereas 2 and 3 days were required at S/D ratios of 4 and 12, respectively, before visible precipitates formed. The progress of the aging was followed by three separate measurements. (1) The gross rate of increase in particle size was followed by ultrafiltration of aliquots from undisturbed dispersions through 0.2- and 1.0-μm Nuclepore membranes after standing for various times. (2) The rates of conversion of reactive to nonreactive particles were followed by measuring the change in product yields (final transmittance) in kinetic runs as a function of aging time. (3) Changes in organization of reactive particles were monitored by measuring the rates of hydrolysis of the ester in the reactive particles as a function of aging time. The results are shown in Figure 4 and lead to the following conclusions.

(1) There is little overall correlation between rates of growth of filterable particles, rates of conversion from reactive to nonreactive particles, and rates of hydrolysis in the remaining reactive particles. Thus, with the DTAB dispersion corresponding to Figure 4A, considerable particle growth occurs with little change in hydrolysis rate of ester in the particles. In contrast, the CTAB dispersion of Figure 4D shows significant rate changes in the particles with very little change in particle size or crystallinity. This difference in behavior must result from differences in the original organization and in the ways the particles are reorganized on aging. The DTAB dispersion (Figure 4A, S/D = 48) gives hydrolysis rates that are only slightly less than that of ester in molecular dispersion (Figure 2) so that the particles are probably salt-like and particle growth probably involves little reorganization. The CTAB dispersion of Figure 4D (S/D = 4) corresponds to the rate minimum of Figure 2 and probably involves micellar aggregates initially. The aging effect in this dispersion must involve slow reorganization with little particle growth until an arrangement suitable for nucleation is achieved. (2) Increasing S/D ratios give more stable dispersions with respect to rates of particle reorganization, although crystallization still occurs after several days.

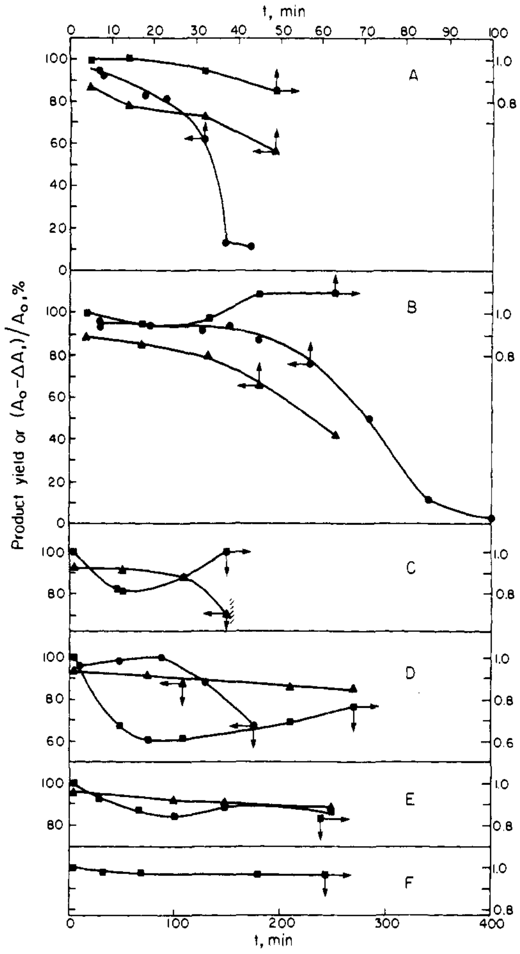


Figure 4. Effect of aging of dispersions in water. A: S = DTAB; S/D = 48. B: S = DTAB; S/D = 80. C: S = CTAB; S/D = 2. D: S = CTAB; S/D = 4. E: S = CTAB; S/D = 8. F: S = CTAB; S/D = 12. (●) $(A_0 - \Delta A)/A_0$ after ultrafiltration through 1.0-μm (A and B) and 0.2-μm (D) membranes, left-hand ordinate. $[\text{Ester}]_T = 2.5 \times 10^{-5}$ *M*. (▲) Product yields from kinetic runs, left-hand ordinate. $[\text{Ester}]_T = 1.25 \times 10^{-5}$ *M*, *t* = 25°. (■) Hydrolysis rate relative to freshly prepared suspensions, right-hand ordinate. $[\text{Ester}]_T = 1.25 \times 10^{-5}$ *M*, *t* = 25°. Shaded area is point of precipitation.

Effect of Concentration at Constant S/D Ratios. Hydrolysis rates of the acetate were measured as a function of concentration in dispersions with CTAB at constant S/D ratios of 2, 4, and 8. The ester concentration varied between 1.25×10^{-6} and 2.0×10^{-5} *M*. The results are shown in Figure 5. The open data points are those from Figure 2. The rate changes obtained by varying total concentrations at constant S/D are the same as those obtained by varying surfactant concentration at constant ester concentration. The fact

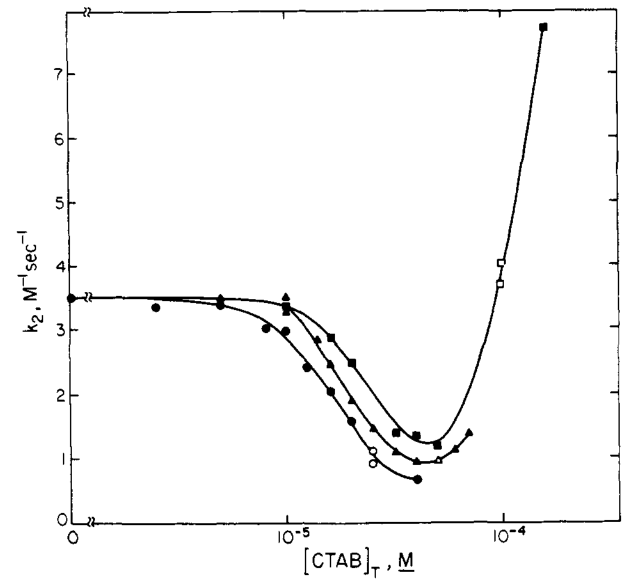


Figure 5. Second-order rate constants for hydrolysis of dye acetate in fresh dispersions as a function of concentration at constant S/D ratios of 2 (●), 4 (▲), and 8 (■) (t = 25°).

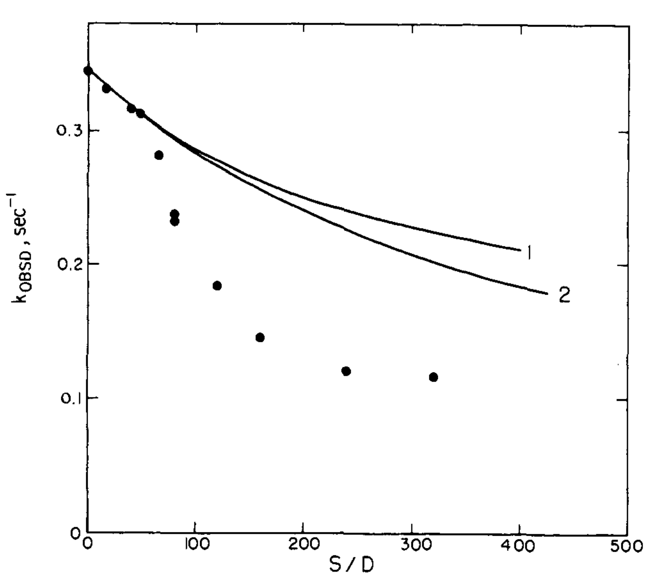


Figure 6. Comparison of calculated plots of $k_{obsd} = f([S]_T/[D]_T)$ from eq 3 and 4 with experimental values (data points). Curve 1, K_c = 280 l-mol^{-1}, k_1' = 0.116 sec^{-1}. Curve 2, K_c = 176, k_1' = 0.

that the plots of Figure 5 are not congruent shows that the nature of the aggregates depends on the dye concentration as well as the surfactant concentration.

Discussion

The results of the present study show that the colloids formed by interaction of oppositely charged dyes and surfactants are considerably more complex than when either is uncharged or when both have the same charge. One important difference is the possibility of forming suspensions of the insoluble crystalline dye-surfactant salts, a fact pointed out by Mukerjee and Mysels.[2] In the present system and that studied earlier,[10] however, the crystalline salts appear to make up a small fraction of freshly prepared dispersions, even at S/D ratios where the salts should predominate. The insolubility of the salts may contribute to the apparent instability of the amorphous aggregates. The second important difference is that colloidal species that are neither salts nor micelles of conventional structure are formed at surfactant concentrations far below the cmc's for the surfactant homomicelles. The kinetic probe enables us to detect such species. In the discussion to follow, we will use the term "micelle" in a broad sense without assuming a fixed structure or composition and without assuming the stability of surfactant homomicelles.

The plots of hydrolysis rate as a function of surfactant concentration in Figure 2 are qualitatively consistent with either of two models. The first is a three-species model involving equilibria between free ester, a 1:1 salt or complex, and a normal micelle. The rate depressions at low S/D correspond to the salt formation. The accelerations correspond to the solubilization of the salt into the micelle. Such a model was suggested earlier.[5] The second involves a multispecies model in which a continuum of mixed micelles having differing compositions form over the entire range where kinetic changes are observed. The appropriate relationships for a 1:1 complex in the first model are given by eq 2-4,

$$\begin{tikzcd} D^- + S^+ \arrow[r, shift left, "K_c"] \arrow[d, "k_0'"] & DS \arrow[l, shift left] \arrow[d, "k_1'"] \\ P & P \end{tikzcd} \tag{2}$$

where D^-, DS, and P represent free dye ester, complexed dye ester, and hydrolyzed dye, respectively.

$$K_c = \frac{[DS]}{[D^-][S^+]} = \frac{[DS]}{([D]_T - [DS])([S]_T - [DS])} = \frac{F_c}{[D]_T(1 - F_c)\left(\frac{[S]_T}{[D]_T} - F_c\right)} \tag{3}$$

where F_c is the fraction of the ester complexed

$$\frac{-d \ln [D]_T}{dt} = k_{obsd} = k_0'(1 - F_c) + k_1'F_c \tag{4}$$

where k_0' and k_1' are the pseudo-first-order rate constants for hydrolysis of free and complexed ester, respectively. Sufficient data were available from the descending portion of the rate profiles in DTAB dispersions to test this model. The experimental rate constant at the minimum was used as an estimate of k_1'. The only adjustable parameter is K_c, and we were only interested in whether the data approaching the minimum could be fitted by assuming a single value of K_c. A value was assumed such that the model fitted the data at the lowest S/D ratios where a 1:1 complex was expected to predominate. Equation 3 was solved for F_c in terms of S/D ($=[S]_T/[D]_T$) and K_c and the computed values were used in eq 4 to calculate values of k_{obsd}. Figure 6 shows the comparison of the experimental rate constants with computed plots of k_{obsd} as a function of S/D, assuming that k_1' is equal to the experimental value at the minimum (curve 1) and that $k_1' = 0$ (curve 2). It is clear that the simple model given by eq 2-4 is inconsistent with the data. By eq 3, $F_c = f(S/D)$ is a quadratic function, whereas the data require higher-order terms arising from the presence of at least three species. If several kinetically distinguishable species are required at S/D ratios approaching the rate minima, then the multispecies model is reasonable for the entire range of surfactant concentrations. We propose that the interaction of these anionic dyes with cationic surfactants gives a continuum of mixed micelles of varying compositions, structures, and stabilities. At surfactant concentrations near the cmc for surfactant homomicelles, the structures are those of normal surfactant micelles containing a small fraction of solubilized dye. In such a system, a cmc has no meaning. The various micellar structures are easily interconverted by small changes in solution composition, amphiphile concentration, and concentration of electrolytes.[23] For this reason, properties such as the most probable micellar size and shape are only defined for carefully specified concentration conditions. Conventional methods such as light scattering seem inappropriate for measuring these properties.

The occurrence of inhibition followed by catalysis is readily explained by the continuum model. Molecular scale models show that the distance from the center of charge in the sulfo group of the dye esters to the carbonyl carbon is about 14 Å. The distances from the quaternary nitrogen to the ends of the C_{12} and C_{16} alkyl chains of DTAB and CTAB in the all-gauche conformations are 16 and 22 Å, respectively. Any reasonable structure of a mixed micelle that has the oppositely charged head groups in proximity and oriented toward the aqueous phase will put the site of reaction well within the core of the micelle. Mixed micelles having only a small excess of surfactant will have low surface potential and hydroxide ion will not be concentrated appreciably near the surface. Reduced charge repulsion of head groups should give a tighter surface structure than with ionic homomicelles. With only one reactant of the bimolecular reaction concentrated, the unfavorable location of the reaction site within the micelle will be the predominant factor and inhibition results. As the S/D ratio is increased, the micelles become progressively richer in surfactant with a corresponding increase in surface potential. The resulting concentration of hydroxide in the micelle domains permits the favorable concentration effect to overcome the unfavorable geometric effect. Increased surfactant content of the micelles or increased counterion binding[23] appears to loosen the surface structure and make the reactive site more accessible.

The spectral shifts would conventionally be thought to mark the first appearance of micelles. These shifts, however, reflect only a change in the microenvironment of the dye. They merely mark the point in changing micellar compositions where the mixed micelle becomes sufficiently rich in surfactant that the dye recognizes a new microenvironment. This point also corresponds to the micellar composition where there is sufficient potential to concentrate hydroxide ion enough to overcome the steric retardation. There is apparently a high degree of cooperativity in the process since the spectral change occurs over a small concentration range of surfactant. The formation of homomicelles from monomeric surfactant is also highly cooperative, so that the spectral-change method is not a good one for distinguishing the two processes. The fact that the spectral shifts become saturated at surfactant concentrations below the concentrations of maximum catalysis indicates that the continuing changes in composition that are detectable kinetically do not further alter the microenvironment of the dye ester. In fact, the absorptivity of the dye does continue to increase with surfactant concentrations above those at which the absorption maximum becomes constant. In systems of oppositely charged dyes and surfactants, the surfactant concentration at which the largest spectral changes occur does not necessarily mark a cmc. It is fortunate that in other dye-surfactant systems where micellization and solubilization occur normally the spectral changes do appear close to the cmc.

Bunton and his coworkers[21] have investigated the effects of arene sulfonates as added hydrophobic counterions on the structures of CTAB micelles and on the rates of unimolecular reactions of solubilizates in the micelles. Their kinetic and NMR evidence show that the sulfonates do not function merely as counterions but are incorporated into the micelles with accompanying structural changes. They depict the incorporation in the same way as we believe our dye sulfonates form mixed micelles with cationic surfactants.

It is interesting to speculate on the intrinsic stability of mixed micelles containing only a small excess of surfactant. The possibility of forming insoluble crystalline salts makes the mixed micelles studied here appear unstable because the micellar equilibrium is shifted by precipitation. The question is whether the micelles would reorganize spontaneously to dye-surfactant ion pairs under conditions where the salts are soluble. In our earlier study using the indicator dye whose absorption curve is very different in micelles and in ion pairs, we showed that at concentrations where the salts were soluble, micelles with DTAB at low S/D ratios gave no measurable reorganization in 3 days. This suggests that surfactant-poor mixed micelles from oppositely charged colloidal electrolytes can be stable. The methods used in the present study give no insight into the nature of the particle reorganization which we detect by the kinetic probe during times when there appears to be little crystallization or increase in particle size. This is apparently a structural change accompanying the conversion from a micellar aggregate to a crystal nucleus.

Our results differ somewhat from those of Mukerjee and Mysels, who studied the interaction of sodium lauryl sulfate with a cationic cyanine dye, pinacyanol. They found that at low S/D ratios, the principal colloidal species were suspensions of the insoluble dye-surfactant salt. The difference in the nature of the dispersions in the two systems is a result of the difference in the nature of the dyes. The positive charge in cyanine dyes is not localized in a head group as in our dyes, but is delocalized through much of the dye structure. The cyanine dyes are not amphiphiles in the same sense as the azo dye sulfonates and lack the structure requirements necessary to form mixed micelles at low concentrations and low S/D ratios.

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