

TABLE I: Orientational Data for 4,4'-Dibromobenzophenone

	$x(N)$	$y(L)$	$z(M)$
<i>a</i>	0.9993	0.0349	0.0
<i>b</i>	-0.0349	0.9993	0.0
<i>c</i>	0.0	0.0	1.0

cessible from the zero-field absorption spectrum.

4,4'-Dibromobenzophenone. The experimental results of the electric field effect on single crystals of 4,4'-dibromobenzophenone are presented in Figures 4 and 5 for the lowest ${}^3n\pi^*$ state located at 4178.0 Å. In these experiments the electric field is along the *c* axis while the incident light is directed normal to the *ac* plane. The orientation matrix which we have calculated from the available crystallographic data⁴ is given in Table I where the molecular *y* and *z* axes are in the C-(CO)-C plane with *z* collinear with the carbonyl axis. The zero-field absorption spectrum has the appearance of two bands that are incompletely resolved and separated by 1.14 cm^{-1} . The lower energy band is about four times the intensity of the higher energy band. Our study shows this transition to be polarized in the *yz* molecular plane, strongly but not exclusively along the *c* axis. In an ODMR investigation, Mucha and Pratt⁶ suggest that the ordering of the zero-field triplet sublevels is $Z > 0 > Y > X$ with $|T_z\rangle$ being radiatively dominant over $|T_x\rangle$ in agreement with other studies on benzophenone.^{13,14} This would mean that the local C_{2v} carbonyl 3A_2 state would correlate directly to the 3A_2 factor group state (C_{2v}) since the carbonyl axial symmetry is preserved by the C_2 site group. Thus we would

expect that the *c*-polarized ${}^3A_2 \leftarrow {}^1A_1$ transition would be the most intense exciton band.

The energy of each of the observed bands is linearly dependent on the dc field strength and increases or decreases in the crystal domain which we studied according to the polarity of the field. This behavior is in agreement with the predicted pyroelectric nature of this crystal.⁴ Assuming that these bands are exciton states, we find that within experimental error the overall modulation spectra are identical in intensity profile at various dc field strengths confirming that the field does not mix these optically accessible states. Since there appears to be only two states it is not unreasonable to classify them by invoking the C_s interchange group¹⁵ chosen from the C_{2v} factor group; with reference to the σ_{ac} (glide) A_1 correlates with $A'(x,y)$, A_2 with $A_2''(z)$, B_1 with A' , and B_2 with A'' . Invoking an Ewald-Kornfeld point-dipole lattice summation, using intercarbonyl distances⁴ between the molecules in the unit cell of $d_{12} = 13.82$ Å, $d_{13} = 13.65$ Å, and $d_{14} = 4.79$ Å, we find that predicted ordering of the interaction energies is $V_{14} > V_{12} > V_{13}$. Based on these observations, and with reference to the C_s interchange classification, we assign the values of 1.14 ± 0.05 cm^{-1} to V_{14} and 0.95 ± 0.05 D to the crystal dipole moment change. The dipole moment change was calculated by using the correction $E_{loc} = 1.60E_{app}$.

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(13) R. M. Hochstrasser and T.-S. Lin. *J. Chem. Phys.*, **49**, 4929 (1968).
 (14) M. S. Sarnoff, *J. Chem. Phys.*, **51**, 451 (1969).

(15) R. Kopelman, *J. Chem. Phys.*, **47**, 1684 (1969).

Micellar Effects upon the Reaction of Betaine Esters with Hydroxide Ion

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The reaction of hydroxide ion with methyl *N,N,N*-trimethylglycinate (1a) is inhibited by cationic micelles of $C_{14}H_{29}NMe_3Cl$ and $C_{16}H_{33}NMe_3Cl$ (MTACl and CTACl) because the substrate is largely in the aqueous pseudophase which is depleted in OH^- by the cationic micelles. Added Cl^- displaces OH^- from the micelles and decreases micellar inhibition. The corresponding reaction of methyl *N*-dodecyl-*N,N*-dimethylglycinate (1b) is catalyzed by both MTACl and CTACl which bind both reactants, but this catalysis is reduced by NaCl. Self-micellization of methyl *N*-hexadecyl-*N,N*-dimethylglycinate (1c) speeds reactions with OH^- , and the rate constants reach plateau values with increasing substrate concentration and are independent of OH^- . But addition of either CTACl or NaCl slows reaction because Cl^- displaces OH^- from the micelle. These diverse rate effects can be accounted for quantitatively in terms of the pseudophase ion-exchange model, which considers reactions in both the aqueous and micellar pseudophases and the distribution of both reactants between the pseudophases.

The rates of many reactions are affected by micellized aqueous surfactants,¹ and it is generally accepted that incorporation of reactants into the micelles is of major importance. For example, cationic micelles catalyze bimolecular reactions of nucleophilic or basic anions by incorporating both reactants into the small volume of the micellar pseudophase.²⁻⁷ Micelles can also affect the rates

of spontaneous, unimolecular, reactions, but here they exert only a medium effect.³

For a number of bimolecular reactions the relation between reaction rate and [surfactant] can be interpreted

(1) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975.
 (2) Cordes, E. H. *Pure Appl. Chem.* **1978**, *50*, 617.
 (3) Bunton, C. A. *Pure Appl. Chem.* **1977**, *49*, 969.

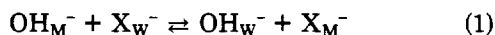
(4) Martinek, K.; Yatsimirski, A. K.; Levashov, A. V.; Berezin, I. V. In "Micellization, Solubilization and Microemulsions"; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 2, p 489.
 (5) Quina, F. H.; Chaimovich, H. *J. Phys. Chem.* **1979**, *83*, 1844.
 Chaimovich, H.; Bonilha, J. B. S.; Politi, M. J.; Quina, F. H. *Ibid.* **1979**, *83*, 1851.
 (6) Almgren, M.; Rydholm, R. *J. Phys. Chem.* **1979**, *83*, 360.
 (7) Sudhölter, E. J. R.; van de Langkruis, G. B.; Engberts, J. B. F. N. *Rec., J. Roy. Neth. Chem. Soc.* **1980**, *99*, 73.

quantitatively by estimating the concentration of the two reactants in the micellar pseudophase.⁴⁻⁹ It is usually easy to measure directly the concentration of a nonionic reactant in the micellar pseudophase,¹⁻⁴ but it is often more difficult to do this with ionic reagents.

In favorable cases the concentrations of hydrophobic anions can be measured spectrophotometrically.¹⁰ Electrochemical methods, e.g., specific ion electrodes or conductivity, can be used with some hydrophilic inorganic ions, e.g., bromide¹¹ or hydrogen¹² ions, but these methods are often not applicable, as for example, to the hydroxide ion.

An indirect approach to this problem is to assume that the interaction of two (or more) counterions with an ionic micelle is governed by an ion-exchange equilibrium¹³ similar to that which governs interaction with ion-exchange resins. This approach explains qualitatively a number of micellar effects upon reactions rates and equilibria and leads to equations which describe the competition between counterions for an ionic micelle.

This approach is illustrated by eq 1, for micellar binding



of OH⁻ to a cationic micelle having X⁻ as counterion, where the subscripts M and W denote the micellar and aqueous pseudophases, respectively. The ion-exchange constant K_X^{OH} is given by

$$K_X^{\text{OH}} = [\text{OH}_W^-][\text{X}_M^-] / ([\text{OH}_M^-][\text{X}_W^-]) \quad (2)$$

It can readily be shown that, if eq 2 is used to describe the distribution of OH⁻, the first-order rate constants of bimolecular reactions at constant [OH⁻] should go through maxima with increasing surfactant concentration,¹³ as is generally observed. But it is another question to estimate K_X^{OH} from the relation between rate constant and [surfactant].^{5,6,13} For example, one has to assume that K_X^{OH} is independent of concentrations of surfactant and reactants, that the rate constant in the micellar pseudophase is independent of counterion and surfactant concentration, and that the ratio of counterions to ionic headgroups in the micelle, β , is independent of these concentrations. The equations which relate the ion-exchange parameters, e.g., K_X^{OH} , to overall rate constants therefore depend on a number of assumptions, and certain parameters, e.g., β , whose values are uncertain.

The assumption that β is constant implies that the micelle is effectively saturated with counterions. This assumption is supported experimentally and theoretically,^{13,14} although recent measurements of micellar charge by quasielastic light scattering suggest that it is decreased by added counterions,¹⁵ i.e., β increases on addition of counterions. There are also problems when only hydrophilic counterions, e.g., OH⁻ or F⁻, are present in micellar solutions. The pseudophase model predicts that, if β is constant, the rate constants of reactions in these solutions should be independent of [surfactant] once all the sub-

strate is micellar bound, but rate constants increase with [surfactant] and with added OH⁻ or F⁻.¹⁶ The predicted behavior is, however, observed for reactions of H₃O⁺ in micellized alkanesulfonic acids,^{16a} and when the reactive counterions are CN⁻¹⁷ or Br⁻.¹⁸ Thus one can ask whether the model should be generally applicable to reactions of OH⁻ in solutions of micellized quaternary ammonium halides.

To date there have been several estimations of K_X^{OH} . For the reaction of *p*-nitrophenyl acetate, in micellized cetyltrimethylammonium bromide (CTABr), the estimated value was ca. 40, but it was very sensitive to the assumptions made in the treatment of the data.⁵ An alternative approach is to use a substrate which does not bind to the micelles, so that reaction occurs wholly in the aqueous pseudophase.⁵ Such a substrate is the *N*-methyl-4-cyanopyridinium ion, and analysis of the rate data gave values of K_X^{OH} of 7 for C₁₄H₂₉NMe₃Cl and 13 for CTABr.⁵ Unfortunately, the micellar ion-exchange effect upon the binding of OH⁻, and therefore upon the observed rate constants, is similar in magnitude to the kinetic salt effect upon the reaction in water. The estimated ion-exchange constants depend upon assumptions about the magnitude of the salt effects exerted by micelles and their counterions upon reactions in the aqueous pseudophase. Nonetheless, the treatment is self-consistent and explains the variation of rate constant with [surfactant]. Recently, Funasaki and Murata have interpreted micellar catalysis and inhibition of the reactions of OH⁻ with benzocaine and related esters in terms of the pseudophase ion-exchange model, taking $K_{\text{Br}}^{\text{OH}} = 10$.¹⁹ Measurements of the equilibrium deprotonation of benzimidazole have given values of K_X^{OH} of 4, 12, and 14 for CTACl, CTABr, and CTANO₃, respectively.²⁰

Another approach is to compare the abilities of OH⁻ and X⁻ in expelling an indicator anion, e.g., an arenesulfonate ion, from the cationic micelle.²¹ This method gave values of K_X^{OH} of 4, 21, and 23 for CTACl, CTABr, and CTANO₃, respectively. However, it was necessary to assume that, despite its relatively high concentration, the arenesulfonate ion does not perturb the micellar structure.

Although these estimated ion-exchange parameters agree reasonably well they depend upon unproven assumptions, and in some cases are very sensitive to changes in parameters such as β .

Our aim was to examine micellar effects upon reaction of hydroxide ion with a series of chemically similar substrates of different hydrophobicities chosen so that reaction would occur either largely in the aqueous pseudophase or with a more hydrophobic substrate largely in the micellar pseudophase. If the pseudophase ion-exchange model is correct consistent values of such parameters as β and K_X^{OH} should be applicable to reactions of structurally similar substrates occurring in either micellar or aqueous pseudophase.

We used a series of betaine esters (1) whose hydrophobicities could be changed without affecting the reaction mechanism.

(8) Bunton, C. A.; Wolfe, B. *J. Am. Chem. Soc.* **1973**, *95*, 3742. Bunton, C. A.; Romsted, L. S.; Smith, H. J. *J. Org. Chem.* **1978**, *43*, 4299.

(9) Bunton, C. A. *Catal. Rev. Sci. Eng.* **1979**, *20*, 1.

(10) Bunton, C. A.; Sepulveda, L. *J. Phys. Chem.* **1979**, *83*, 680.

(11) Larsen, J. W.; Magid, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 5664.

1975, *97*, 1988.

(12) Bunton, C. A.; Ohmenzetter, K.; Sepulveda, L. *J. Phys. Chem.* **1977**, *81*, 2000.

(13) Romsted, L. S., in ref 4, p 509.

(14) (a) Stigter, D., *Prog. Colloid Polym. Sci.* **1978**, *65*, 45. (b)

Romsted, L. S., Thesis, University of Indiana, Bloomington, 1975.

(15) Rohde, A.; Sackmann, E. *J. Colloid. Interface Sci.* **1979**, *70*, 494.

J. Phys. Chem. **1980**, *84*, 1598. Cf. Kratochvil, J. P. *J. Colloid Interface Sci.* **1980**, *75*, 271.

(16) (a) Bunton, C. A.; Romsted, L. S.; Savelli, G. *J. Am. Chem. Soc.* **1979**, *101*, 1253. (b) Bunton, C. A.; Frankson, J.; Romsted, L. S. *J. Phys. Chem.* **1980**, *84*, 2607.

(17) Bunton, C. A.; Romsted, L. S.; Thamavit, C. *J. Am. Chem. Soc.* **1980**, *102*, 3900.

(18) Cowell, C., unpublished results.

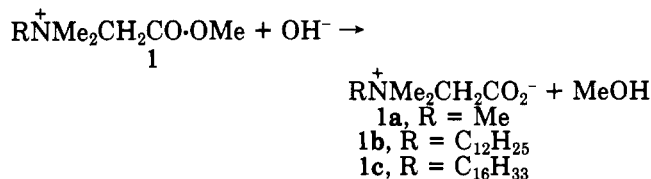
(19) Funasaki, N.; Murata, A. *Chem. Pharm. Bull.* **1980**, *28*, 805.

(20) Bunton, C. A.; Romsted, L. S.; Sepulveda, L. *J. Phys. Chem.* **1980**,

84, 2611. Bunton, C. A.; Hong, Y.-S.; Romsted, L. S. "Solution Behavior of Surfactants"; Fendler, E. J., Ed.; Plenum Press: New York, 1981.

(21) Bartet, D.; Gamboa, C.; Sepulveda, L. *J. Phys. Chem.* **1980**, *84*,

272.



As surfactants we used cetyltrimethylammonium chloride (C₁₆H₃₃NMe₃Cl, CTACl) and tetradecyltrimethylammonium chloride (C₁₄H₂₉NMe₃Cl; MTACl).

The reaction of betaine esters with hydroxide ion has been studied extensively in water in the absence of surfactant.²²

Experimental Section

Materials. The betaine esters were prepared as the chloride salts by heating ClCH₂CO₂Me with the tertiary amine under reflux in MeOH for 48 h.²² We used equimolar amounts of ClCH₂CO₂Me and C₁₂H₂₅NMe₂ or C₁₆H₃₃NMe₂, but because of the high volatility of Me₃N we used it in excess and added it in the course of reaction. The betaine esters were recrystallized from MeOH/Et₂O.

The surfactants MTACl and CTACl were prepared from alkyl chloride and Me₃N in *i*-PrOH and were recrystallized from MeOH/Et₂O. The critical micelle concentrations (cmc) were 1.3 × 10⁻³ and 6.9 × 10⁻³ M for CTACl and MTACl, respectively, in agreement with literature values.²³ The cmc of C₁₂H₂₅N⁺Me₂CH₂CO₂MeCl⁻ was 7.9 × 10⁻³ M and that of C₁₆H₃₃N⁺Me₂CH₂CO₂MeCl⁻ was 6.2 × 10⁻⁴ M, which is somewhat lower than that of CTACl,²³ probably because of the introduction of extra hydrophobicity into the head groups. There were no minima in plots of surface tension against log concentration.

The reactions were carried out in CO₂-free distilled deionized water.

Kinetics. All the reactions were run at 25.0 °C with a Durrum stopped-flow spectrophotometer. Reaction was followed at 215 nm where ε = 33 for 1a. The change in absorbance during reaction was small and we were restricted to the range of reactant concentrations. We used 0.003 M ester, except where specified, and either 0.02 or 0.04 M NaOH, so that the individual runs were first order for most of the reaction. The first-order rate constants, *k*_ψ, are expressed in reciprocal seconds. The inert counterion was Cl⁻ in all the experiments because absorbance by Br⁻ causes problems at these low wavelenghts. We generally made 6–8 independent kinetic runs for each set of reaction conditions.

Substrate Binding to Micelles. The binding of the esters (1a,b) to micelles of CTACl was examined by ultrafiltration, using an Aminco 202 cell with PM 10 membrane.¹⁷ The transport number of the trimethyl ester (1a) in water is 1.01, and that of the dodecyl dimethyl ester (1b) is 1.05 and the concentrations of ester in filtrate and filtrand were determined spectrophotometrically. Hydrolysis of the esters under these conditions is sufficiently slow to be neglected.²²

Results

Reaction in the Absence of Surfactant. Our values of the second-order rate constants for reactions of the trimethyl ester (1a) and the (nonmicellized) dodecyl dimethyl ester (1b) are 77 and 79 M⁻¹ s⁻¹, respectively, and are similar to the value of 66 M⁻¹ s⁻¹ for reaction of ethyl

TABLE I: Salt Effects on Reaction with No Added Surfactant^a

[salt], M	LiCl	NaCl	KCl
0.01	1.50	1.53 (1.44)	1.52
0.02		(1.39)	
0.03	1.46		1.46
0.04		1.45 (1.33)	
0.06	1.42	1.41	1.41
0.07		(1.20)	
0.08		1.36	
0.09	1.31		1.32
0.10		1.30 (1.05)	
0.13	1.28		1.28
0.15		1.26 (1.03)	
0.16	1.25		
0.20	1.23	1.22 (0.98)	1.23

^a Values of *k*_ψ, s⁻¹ at 25.0 °C with 0.02 M NaOH and 0.003 M 1a. Values in parentheses are for reaction of the dodecyl dimethyl ester (1b). In the absence of added salt *k*_ψ = 1.54 s⁻¹ for reaction of 1a and 1.58 s⁻¹ for reaction of 1b.

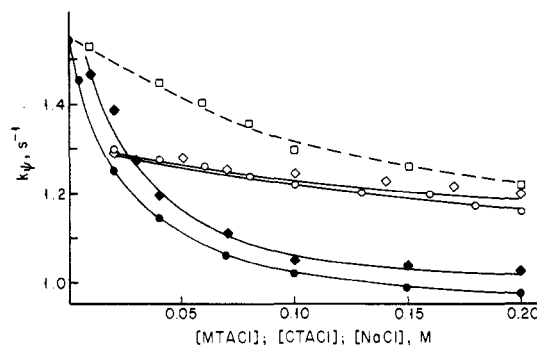


Figure 1. Reactions of the trimethyl ester (1a) in 0.02 M NaOH and 0.003 M ester. The solid lines are predicted: (■) in MTACl; (□) in MTACl + 0.1 M NaCl; (●) in CTACl; (○) in CTACl + 0.1 M NaCl; (■) in NaCl.

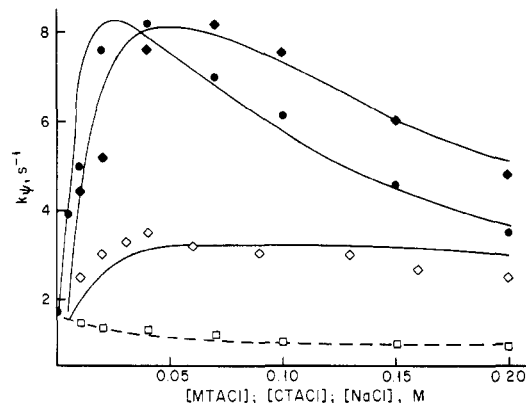


Figure 2. Reaction of 0.003 M dodecyl dimethyl ester (1b) in 0.02 M NaOH. The solid lines are predicted, symbols as in Figure 1.

N,N,N-trimethylglycinate with OH⁻ at 25 °C.²² Added salts inhibit reaction of 1a with OH⁻, cf. ref 22, and the effect is independent of the nature of the added cation (Table I). The kinetic salt effects are slightly larger for 1b than for 1a (Table I).

Reaction of the Trimethyl Ester (1a) in Surfactant Solution. The reaction rate is decreased by addition of either MTACl or CTACl (Figure 1), and the inhibition changes when the reaction is carried out in 0.1 M NaCl.

Reaction of the Dodecyl dimethyl Ester (1b). Both MTACl and CTACl modestly speed the reaction (Figure 2). The maximum rate constants are similar for the two surfactants, but the optimum surfactant concentration is lower for CTACl than for MTACl, and the rate decrease

(22) Bell, R. P.; Lindars, F. J. *J. Chem. Soc.* 1954, 4601. Bell, R. P.; Collier, B. A. W. *Trans. Faraday Soc.* 1964, 60, 1087.

(23) Mukerjee, P.; Mysels, K. J. "Critical Micelle Concentrations of Aqueous Surfactant Systems"; National Bureau of Standards; U.S. Government Printing Office: Washington, D.C., 1970.

TABLE II: Reaction of the Hexadecyldimethyl Ester (1c) in Aqueous Solution

$10^3[\text{ester}], \text{M}$	[NaOH], M	
	0.02	0.04
1	15	13
2	32	29
3	41	48
4	48	49
6		54
8		57
10		57

^a Values of k_{ψ} , s^{-1} at 25.0 °C.

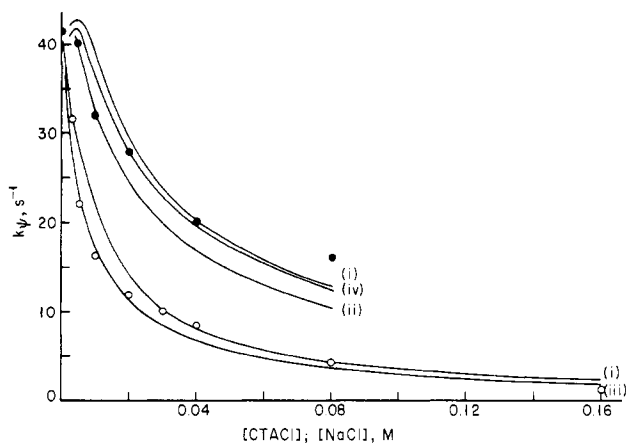


Figure 3. Reaction of the hexadecyldimethyl ester (1c) in 0.02 M NaOH and 0.003 M ester: (●) in CTACI; (○) in NaCl. The lines are predicted: (i), (ii), and (iii) $k_M^E = 105, 95,$ and 85 s^{-1} , respectively, and $K_{\text{Cl}^{\text{OH}}} = 4$ and $\beta = 0.75$; (iv) $k_M^E = 85 \text{ s}^{-1}$, $K_{\text{Cl}^{\text{OH}}} = 3.5$ and $\beta = 0.8$.

from the maximum is steeper with CTACI. Qualitatively these observations are consistent with CTACI having a lower cmc and stronger substrate binding than MTACI.

Reaction of the Hexadecyldimethyl Ester (1c). The hexadecyl moiety makes 1c sufficiently hydrophobic to self-micellize, and the rate constants increase with increasing ester concentration (Table II). The rate constants are independent of the hydroxide ion concentration, which suggests that the micelles of the substrate become saturated with hydroxide ion.

Surfactant Effects on the Reaction of the Hexadecyldimethyl Ester (1c). Typically reactions of hydrophobic substrates with OH^- are catalyzed by cationic micelles.¹ At first sight the effect of CTACI upon reaction of self-micellized 1c is an exception to this generalization, because CTACI decreases the rate (Figure 3). However, the reaction is much faster than those of the nonmicellizing substrate 1a, or of 1b below its cmc.

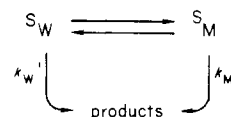
Salts Effects on the Reaction of the Hexadecyldimethyl Ester (1c). Sodium chloride strongly inhibits reaction of the self-micellized ester (Figure 3). This inhibition is understandable because added Cl^- displaces OH^- from the surface of micellized 1c.

Substrate Binding to Micelles. The trimethyl ester (1a) binds weakly at most to cationic micelles, but binding is increased by added salt. The salt effect on coion binding can be ascribed to micellar binding of an ion pair,²⁴ or one can assume that the micelle has a constant charge which is maintained by entry of both cationic substrate and chloride ion.

The binding constant, K_s , is given by

$$K_s = [\text{S}_M] / [\text{S}_W][\text{D}_n] \quad (3)$$

Scheme I



where S_W and S_M are substrate in aqueous and micellar pseudophase, respectively, and D_n is micellized surfactant. For the binding of 1a to MTACI with added salt the substrate binding constant is given by

$$K_s = A[\text{Cl}_W^-] \quad (4)$$

with $A = 3 \text{ M}^{-2}$. We assumed that this empirical relation would also apply to binding of 1a to CTACI.

The binding constants, K_s , of the dodecyl dimethyl ester (1b) to MTACI is 19 M^{-1} , and it is increased to 22 M^{-1} by 0.1 M NaCl, and it is 28 M^{-1} in CTACI.

Discussion

In developing a quantitative model for the kinetic results we make certain key assumptions: (i) that reaction occurs independently in the micellar and aqueous pseudophases, and that rate constants can be estimated for these reactions; and (ii) that the distribution of counterions between aqueous and micellar pseudophases is governed by an ion-exchange equilibrium.¹³ We also assume that β is an adjustable parameter within narrow limits, e.g., between 0.6 and 0.8, but is constant for any given set of experiments; that added ions may affect micellar binding of the cationic substrates;²⁴ and that the salt effect of surfactant ions on reaction in the aqueous pseudophase will be similar to that of NaCl (Table I), cf. ref 5. We also make some ad hoc assumptions in discussing reactions of the hydrophobic esters which are considered in context.

Rate Constants in Aqueous and Micellar Pseudophases. The pseudophase model for bimolecular reactions of substrates in aqueous micelles is shown in Scheme I, where k_W' and k_M' , the first-order rate constants in the aqueous and micellar pseudophases, are given by eq 5 and 6.¹⁶

$$k_W' = k_W[\text{OH}_W^-] \quad (5)$$

$$k_M' = k_M m_{\text{OH}^{\ominus}} = k_M[\text{OH}_M^-] / [\text{D}_n] \quad (6)$$

In eq 6 k_M is written in terms of the mole ratio, $m_{\text{OH}^{\ominus}}$, of micellar bound OH^- to micellar head groups, i.e., for a mixture of OH^- and Cl^- , β is identical with $m_{\text{OH}^{\ominus}} + m_{\text{Cl}^{\ominus}}$. The concentrations $[\text{OH}_W^-]$ and $[\text{OH}_M^-]$ are molarities expressed in terms of total solution volume, so that $[\text{OH}_T^-]$, the total concentration of OH^- , is given by

$$[\text{OH}_T^-] = [\text{OH}_W^-] + m_{\text{OH}^{\ominus}}[\text{D}_n] \quad (7)$$

The first-order rate constant, k_{ψ} , is given by⁹

$$k_{\psi} = \frac{k_W[\text{OH}_W^-] + k_M K_S m_{\text{OH}^{\ominus}}[\text{D}_n]}{1 + K_S[\text{D}_n]} \quad (8)$$

$$= \frac{k_W[\text{OH}_W^-] + k_M K_S[\text{OH}_M^-]}{1 + K_S[\text{D}_n]} \quad (8a)$$

Equations 8 and 8a take into account the distribution of both the substrate and hydroxide ion between the aqueous and micellar pseudophases.⁹

The concentrations of OH^- in the aqueous and micellar pseudophases can in principle be estimated by using the ion-exchange eq 2, and our approach is to fit the kinetic data to eq 2, 4, and 8.

It is convenient to write eq 8 in terms of $[\text{OH}_T^-]$ giving

$$k_{\psi} = \frac{k_W[\text{OH}_T^-] + (k_M K_S - k_W) m_{\text{OH}^{\ominus}}[\text{D}_n]}{1 + K_S[\text{D}_n]} \quad (9)$$

TABLE III: Estimated Micellar Parameters

substrate ^a	surfactant	[NaCl], M	K_{Cl}^{OH}	β	k_M, s^{-1}	$k_2^m, M^{-1} s^{-1}$	K_s, M^{-1}
Me ₃ N ⁺ Y	MTACl		3.5	0.8			
Me ₃ N ⁺ Y	MTACl	0.1	4	0.75	160	22	
Me ₃ N ⁺ Y	CTACl		4	0.8			
Me ₃ N ⁺ Y	CTACl	0.1	4	0.75	130	18	
C ₁₂ H ₂₅ N ⁺ Me ₂ Y	MTACl		4	0.75	180	25	19
C ₁₂ H ₂₅ N ⁺ Me ₂ Y	MTACl	0.1	4	0.75	160	22	22
C ₁₂ H ₂₅ N ⁺ Me ₂ Y	CTACl		4	0.75	130	18	26
C ₁₆ H ₃₃ N ⁺ Me ₂ Y	CTACl		4	0.8	<i>b</i>		

^a Y = CH₂CO₂Me. ^b In self-micellized ester $k_M \approx 10^2 s^{-1}$.

and in some systems reaction occurs largely in only one of the pseudophases.

In water the salt effect upon reaction of the trimethyl ester (1a) is unaffected by the nature of the cation (Table I), and in dilute salt (<0.1 M) the rate concentration varies linearly with [salt], eq 10, where k_W^0 is the second-order rate constant in the absence of added salt.

$$k_W = k_W^0 - 120[NaCl] \quad (10)$$

We assume that the rate constant for that part of the reaction which occurs in the aqueous pseudophase will depend upon the ions generated by dissociation of counterions from the micelle (assuming that the salt effect of the micelle is similar to those of uni- or divalent ions)^{5,25} plus the critical micelle concentration so that

$$k_W = k_W^0 - 120\{\alpha[D_n] + cmc\} \quad (11)$$

where α is the degree of counterion dissociation from the micelle, i.e.

$$\alpha = 1 - \beta$$

Although the trimethyl ester (1a) does not bind to cationic micelles added NaCl induces binding, eq 4. We assume that the increased binding will depend upon the concentration of chloride ions in the aqueous pseudophase, $[Cl_T^-]$, eq 4, and the binding constant under the experimental conditions will be given by

$$K_S = A([Cl_T^-] - (\beta - m_{OH_s})[D_n]) \quad (12)$$

where $[Cl_T^-]$ is the total concentration of Cl⁻. This salt correction is small, and the results are little affected by small changes in the value of A, eq 4. For example, with $A = 3 M^{-2}$ (Experimental Section) we estimate that addition of 0.1 M NaCl to 0.2 M CTACl would give ca. 8% micellar binding of 1a. Under these conditions most of the added hydroxide ion will be in the aqueous pseudophase, and the micelle would have only a small catalytic effect.

Distribution of Hydroxide Ion. On the assumption that the ion-exchange parameter, k_{Cl}^{OH} , and β are independent of the nature or concentration of the counterions eq 2 and mass balance equations give

$$K_{Cl}^{OH} = \frac{([OH_T^-] - m_{OH_s}[D_n])(\beta - m_{OH_s})}{m_{OH_s}([Cl_T^-] - (\beta - m_{OH_s})[D_n])} \quad (13)$$

Equation 13 leads to the quadratic eq 14:

$$(m_{OH_s})^2 + m_{OH_s} \left(\frac{[OH_T^-] + K_{Cl}^{OH}[Cl_T^-]}{(K_{Cl}^{OH} - 1)[D_n]} - \beta \right) - \frac{\beta[OH_T^-]}{(K_{Cl}^{OH} - 1)[D_n]} = 0 \quad (14)$$

Equation 14 has the same general form as that used elsewhere,⁴⁻⁷ except that we express the concentration of micellar bound OH⁻ as a mole ratio, m_{OH_s} .

Equation 9 and 11-14 were combined by using a computer program which allowed us to simulate the variation of k_ψ with surfactant or salt concentration using the various parameters in these equations. Wherever possible we used experimental values, e.g., of k_W or K_s , with a correction for the salt effect where necessary, eq 11. The concentration of micellized surfactant $[D_n]$ is generally assumed to be given by eq 15, i.e., the concentration of monomeric surfactant is given by the cmc.

$$[D_n] = [CTACl] - cmc \quad (15)$$

The second-order rate constant of reaction in the micellar pseudophase, k_M , was treated as an adjustable parameter, although its value should be similar to that of $k_M \approx 10^2 s^{-1}$ for reaction of micellized hexadecyldimethyl ester (1c) estimated from the data in Table II.²⁶

We assumed that β would be ca. 0.8 and all our data could be fitted with $\beta = 0.75 - 0.8$. Initially we assumed that the ion-exchange parameter, K_{Cl}^{OH} , would be ca. 4, cf. ref 5, 20, and 21, and in fitting the data we allowed it to vary between 3.5 and 5. In all cases we allowed for the contribution of Cl⁻ from the substrate.

Reaction of the Trimethyl Ester (1a). The fit between theory and experiment using the parameters given in Table III is shown in Figure 1 for reaction of the trimethyl ester (1a). In fitting the results in the absence of salt we assumed that no substrate was bound to the micelle at low surfactant concentration, and that as the chloride ion builds up in the aqueous pseudophase the binding is given by eq 12. Therefore, the inhibition was the result of binding of OH⁻ to the micelle plus a negative kinetic salt effect of the surfactant ions in the aqueous pseudophase, cf. ref 5.

The rate increase on addition of 0.1 M NaCl to MTACl or CTACl is the result of opposing factors: (i) Cl⁻ displaces OH⁻ from the micelle and speeds reaction; (ii) the substrate binds to the micelle in the presence of NaCl, (eq 12), and there is then a contribution from reaction of micellar bound substrate and OH⁻; (iii) there is a negative salt effect of NaCl upon reaction in the aqueous pseudophase (eq 11). The effect of added salt in MTACl or CTACl fits the model without introduction of further adjustable parameters (cf. ref. 4 and 6), but including a contribution of reaction in the micellar pseudophase. The values of the various parameters are in Table III.

Reaction of the Dodecyldimethyl Ester (1b). When the reactions were followed at substrate concentrations below the cmc in water comparison of the rate constants of the dodecyldimethyl and the trimethyl esters 1b and 1a confirms that monomeric substrate is reacting.

(25) Mysels, K. J.; Dulin, C. I. *J. Colloid Sci.* 1955, 10, 461. Hoyer, H. W.; Greenfield, A. *J. Phys. Chem.* 1957, 61, 735.

(26) The values of k_ψ with 0.04 M NaOH are independent of [1c] when it is $8 \times 10^{-3} M$ (Table II). If $K_{Cl}^{OH} \approx 4^{5,20,21}$ and $\beta = 0.75$ $m_{OH_s} = 0.46$ and $k_M \approx 10^2 s^{-1}$.

TABLE IV: Predicted Relation of Micellar Bound to Total Hydroxide Ion^a

β	K_{Cl}^{OH}	$[OH_T^-], M$	
		0.02	0.04
0.6	4	0.36	0.44
0.6	5	0.34	0.42
0.75	4	0.46	0.56
0.75	5	0.43	0.53
0.8	4	0.49	0.60
0.8	5	0.46	0.56

^a Values of m_{OH^s} in 0.004 M $C_{16}H_{33}N^+Me_2CH_2CO_2MeCl^-$.

The variation of rate constant with surfactant concentration fits the model satisfactorily (Figure 2). The values of K_S, M^{-1} which were used are 26 (28) in CTACl, 16 (19) in MTACl, and 22 (22) in MTACl + 0.1 M NaCl. (Those determined by ultrafiltration are in parentheses.)

The values of the various parameters are in Table III.

Reaction of the Hexadecyldimethyl Ester (1c). The similarity of the first-order rate constants of reaction of [1c] at different $[OH^-]$ (Table II) suggests that the concentration of OH^- in the micellar pseudophase, m_{OH^s} , is relatively insensitive to changes in $[OH_T^-]$ from 0.02 to 0.04 M. This hypothesis fits eq 14 for m_{OH^s} (Table IV), taking reasonable values of β and K_{Cl}^{OH} . The relative values of m_{OH^s} are insensitive to changes in β and K_{Cl}^{OH} , but the actual values depend upon β (Table IV).

The variation of k_ψ with $[OH_T^-]$ (Table II) is smaller than that predicted by the estimated variations in m_{OH^s} (Table IV), probably because we neglected reaction of monomeric ester and its contribution to Cl_w^- . We see no simple way of solving this problem because the cmc of 1c will be decreased by OH^- , and we cannot measure this effect.

Addition of either CTACl or NaCl to self-micellized 3×10^{-3} M hexadecyldimethyl ester (1c) sharply retards the reaction, with NaCl being the more effective (Figure 3). The ester concentration was well above the cmc, which should be reduced by both NaOH and NaCl, so we assumed that all the ester was micellized, with no reaction in the aqueous pseudophase. There will be a competition for the substrate micelle between OH^- and Cl^- from the substrate and added NaCl, which will reduce the concentration of bound OH^- .

Because of the low extinction coefficients of 1c its concentration was not very much lower than that of CTACl, and therefore the composition of the micelle changed as [CTACl] was increased. The value of k_M for reaction of 1c at high [CTACl] should be similar to that for reaction of 1b and under these conditions, $k_M = 130 s^{-1}$. However, it appears that for reaction of self-micellized 1c $k_M \approx 10^2 s^{-1}$,²⁶ i.e., the effective value of k_M may depend upon the composition of the micelle. We assume that the relation between k_M and micellar composition will be given by eq 16, where χ is the mole fraction of CTACl, k_M^E is the rate

$$k_M = 130\chi_{CTACl} + k_M^E(1 - \chi_{CTACl}) \quad (16)$$

constant for reaction of self-micellized 1c, and we assume that 1b and 1c have the same rate constant of $130 s^{-1}$ in micelles of CTACl (Table III).

Figure 3 shows that the treatment fits the data in both NaCl and CTACl reasonably well. For reaction in NaCl we get reasonable agreement with experiment taking k_M^E within the limits of 85 and $105 s^{-1}$, $\beta \approx 0.75$, and $K_{Cl}^{OH} \approx 4$, and the rate constants in CTACl can also be fitted reasonably well to parameters in this range. However, Figure 3 shows that the treatment is too insensitive to distinguish between combinations of various values of the

parameters, k_M, K_{Cl}^{OH} , and β , and other combinations of values of these parameters also fit the data. In addition neglect of the contribution of reaction of monomeric 1c creates additional uncertainty.

Consistency of the Model. If the ion-exchange pseudophase model is correct it should predict the variation of rate constant with substrate, surfactant, and salt concentration using the same, or at least similar, values of β, K_{Cl}^{OH} , and k_M . However, we cannot estimate other than approximate values of k_M for reaction of the trimethyl ester (1a) (Table III) which reacts largely in the aqueous pseudophase.

The agreement between the theory and experiment is illustrated in Table III, which gives our "best" values of the various parameters based on subjective fitting of the data, bearing in mind accepted values of β and K_{Cl}^{OH} .^{5,19-21} Although we can fit our experimental results to the relatively simple model represented by Scheme I and eq 9 we are less certain about the reliability of the value of, for examples, K_{Cl}^{OH} , or even its constancy over a range of experimental conditions. Much of our experimental data can be fitted by using various combinations of k_M, K_{Cl}^{OH} , and β , and their values may vary slowly with concentration of surfactant or salt. This problem is a general one whenever one deals with an equation which contains several parameters, and in particular we find that the values of K_{Cl}^{OH} are very sensitive to β . The "salt effect" of the surfactant upon reactions in the aqueous pseudophase also creates a problem in treating reactions of the trimethyl ester (1a), or the reactions discussed in ref 5, but it should be less of a problem for reactions of the hydrophobic esters which occur largely in the micellar pseudophase.

However, β may vary with nature and concentration of counterion, cf. ref 15, and it is difficult to rationalize a situation in which K_X^{OH} depends on the nature of X^- , but at the same time have β constant and independent of the amounts of X^- and OH^- . However, we note that β is generally close to unity, and therefore it may not vary rapidly with changes in concentration of surfactant or counterion.

It seems probable that the postulated constancy of β is reasonable over a limited range of concentration of relatively hydrophobic counterions, e.g., $Cl^-, Br^-,$ or NO_3^- . However, if β varies with counterion concentration, cf. ref 15, our, and other, values of the ion-exchange constants will be incorrect, and direct methods for their determination will be very important.^{21,27}

Despite these questions about the significance of the various parameters used in this treatment the approach is satisfactory in that it explains the ability of micelles and salts to speed some reactions and inhibit others. However, different values of ion-exchange constants are now appearing in the literature,^{5,6,19-21} and it remains to be seen whether these differences are due to the different experimental approaches or are of a more fundamental origin.

Rate Constants in the Micellar and Aqueous Pseudophase. The second-order rate constants, k_M , in the micellar pseudophase are given in terms of mole ratio rather than molarity as the unit of concentration and cannot be compared directly with the second-order rate constants, k_w , in water whose dimensions are $M^{-1} s^{-1}$. The comparison can be made provided that the volume element of reaction in the micellar pseudophase is specified. We estimated the molar volume of the Stern layer of micelles of CTABr as ca. 0.14 L so that the second-order rate constant, k_2^m , in terms of moles of reagent in 1 L of Stern layer is²⁴

(27) For discussions of the significance of counterion binding to micelles see ref 28.

$$k_2^m = 0.14k_M \quad (17)$$

Alternatively, we could take the volume of the micelle as the volume element, which would approximately double the value of k_2^m .^{4,19}

The values of k_2^m for reaction of the betaine esters are in Table III. The volume element of 0.14 L calculated for CTABr is probably too small for self-micellized hexadecyldimethyl ester (1c), because of its larger head group, so that our value of k_2^m for reaction of this ester may be too small. It appears that for reactions of the various esters in the micellar pseudophase k_2^m is 18–25 M⁻¹ s⁻¹ (Table III) and is smaller than k_w in water which is 77 and 79 M⁻¹ s⁻¹ for reactions of 1a and 1b, respectively.²⁹ These dif-

ferences are not unexpected because there is a negative salt effect on reactions of OH⁻ with betaine esters in water,²² and the high ionic concentration in the Stern layer should inhibit reaction. We do not include in our treatment a term for an assumed electrostatic effect on reaction in the micellar pseudophase. Some workers explicitly include such a term, which then affects the estimated ion-exchange parameters.^{4,6,7} However, all the treatments suggest that concentration of reactants into a small volume at the micelle-water interface is the main factor in rate enhancements of bimolecular reactions.

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(28) Mukerjee, P.; Mysels, K. J.; Kapauuan, P. *J. Phys. Chem.* 1967, 71 4166. Anacker, E. W. In "Solution Chemistry of Surfactants"; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 1, p 247.

(29) The values of k_2^m would be approximately doubled if the total volume of the micelles was used as the volume element of reaction.

Effects of an Aliphatic Tail on the Interactions of an Ionic Dye and a Polyelectrolyte. The System of N-Alkylated Acridine Orange Derivatives and Poly(styrenesulfonic acid)

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The binding equilibria of N-alkylated acridine orange cations (AO⁺-(CH₂)_nH) with poly(styrenesulfonic acid) have been studied with spectrophotometric and electric dichroism measurements. The length of the alkyl chain (-(CH₂)_nH) is varied from $n = 0$ to 18. The following experimental quantities are obtained as a function of n : the interaction parameters of a bound dye with the first and second neighbors (q_1 and q_2 , respectively), the angle between electric field direction and the transition moment due to a bound dye molecule (ϕ), and the rate constants for migration of a bound dye dimer or aggregate to a different polymer chain (k_3 and k_6 , respectively). q_1 and q_2 are compared with previous results for $n = 0$ (ref 9). q_1 , q_2 , k_3 , and k_6 show an appreciable dependence on n , while ϕ is little affected by a change of n . The results are discussed in terms of the hydrophobic effects due to an aliphatic tail on the structures of dye-polyelectrolyte complexes.

Introduction

The interaction of a small molecule with a macromolecule or a molecular aggregate has been a subject of many researchers.¹ Such a system provides basic information on the functions of enzymes or bioaggregates, when they activate a small molecule. Recently, the present authors have investigated the reaction of a cationic dye, N-alkylated acridine orange derivative (AO⁺-C_n), in reversed micellar systems.² The length of an attached aliphatic tail was varied from H to C₁₈H₃₇. It was demonstrated that the dye with a CH₃ group acquired the highest reactivity toward oxidation by the Ce⁴⁺ ion.

In the present study, the investigation has been extended to the interaction of the same dye series with an anionic polyelectrolyte, poly(styrenesulfonic acid) (PSS), in water. In this system, a dye molecule adsorbs along a linear PSS chain with dissociated sulfonate groups.³ From

the electronic spectra, the interaction parameters of bound dye molecules have been determined as a function of the length of the alkyl chain. The orientation angle of the molecular plane of a bound dye has been obtained with respect to the polymer axis by means of transient electric dichroism.⁴ The rate of migration of a bound dye molecule to a different polymer chain has been measured with a stopped-flow apparatus. Among the results, it is found that the length of an aliphatic tail affects the cooperative interaction among bound dye species to an appreciable extent.

Experimental Section

Poly(styrenesulfonic acid) (PSS, mol wt = 3.5×10^5) was kindly donated by Dr. S. Harada of Hokkaido University. Its aqueous solution was neutralized by KOH. A resultant solution of potassium poly(styrenesulfonate) (KPSS) was used as a stock solution. N-alkylated acridine orange derivatives (AO⁺-C_n·X⁻) were synthesized according to Miethke and Zanker's method as previously described.^{2,5}

(1) (a) H. Morawetz, "Macromolecules in Solution", 2nd ed, Wiley, New York, 1974, Chapter VIII. (b) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, 1975, Chapter 4.

(2) A. Yamagishi, T. Masui, and F. Watanabe, *J. Phys. Chem.*, 85, 281 (1981).

(3) V. Vitagliano and L. Constantino, *J. Phys. Chem.*, 74, 197 (1970).

(4) K. Yamaoka and E. Charney, *Macromolecules*, 6, 66 (1973).

(5) E. Miethke and V. Zanker, *Z. Phys. Chem. (Frankfurt am Main)*, 18, 375 (1958).