some multiphase systems, it is conceivable that the presence of a large volume of compositionally nonequilibrium material at the interfaces may be desirable for maximum catalytic performance. This would be particularly true of systems where the mutual solubility of the key catalytic components is small or nonexistent, such as the mixed Co–Fe–Bi–Mo–O_x catalyst system which initially consists of separate, immiscible $Bi_2(MoO_4)_3$, $Fe_2(MoO_4)_3$, and $CoMoO_4$ phases.[8b] In such a case, all the necessary catalytic components which apparently cannot coexist in an equilibrium crystalline phase can be present in the compositionally nonequilibrium region between the separate phases. This interfacial region will then be the active and selective "phase" of the catalyst.[11,19]

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Dephosphorylation and Aromatic Nucleophilic Substitution in an Alkoxide Functionalized Micelle

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Dephosphorylation of *p*-nitrophenyl diphenyl phosphate (pNPDPP) and aromatic nucleophilic substitution on 2,4-dinitrochlorobenzene and -naphthalene (DNCB and DNCN, respectively) have been examined in aqueous micelles of the functional surfactant hexadecyl(2-hydroxyethyl)dimethylammonium hydroxide, $n\text{-}C_{16}H_{33}N^+Me_2CH_2CH_2OHOH^-$ (**2**). The variation of the first-order rate constant, k_ψ, with concentration of **2** and OH^- can be fitted to equations which describe the distributions of substrate and OH^- between aqueous and micellar pseudophase. The first-formed products of aromatic nucleophilic substitution are ethers formed by attack of alkoxide zwitterion, $n\text{-}C_{16}H_{33}N^+Me_2CH_2CH_2O^-$ (**2a**). The ethers react with micellar-bound OH^- giving aryl oxide ion, and the rate constants for these slower reactions in relatively dilute OH^- can be fitted to a model which describes the distribution of OH^- between aqueous and micellar pseudophases. The second-order rate constants for reactions with **2a** and OH^- in the micellar pseudophase can be estimated and compared with reactions of OH^- and a model alkoxide zwitterion, $Me_3N^+CH_2CH_2O^-$, in water. The rate constants in the micelles are larger than in water for aromatic nucleophilic substitution, but smaller than in water for dephosphorylation. The electrical conductivity of solutions of **2** is consistent with formation of the zwitterion **2a**.

Functionalized surfactants contain a reactive group in the hydrophilic head group, and micelles or comicelles of these surfactants are effective bases or nucleophiles.[2] Typically the reactive center is amino, sulfhydryl, or hydroxy, and in many systems its deprotonation generates the reagent.

Micelles of 2-hydroxyethyl surfactants, **1**, are effective nucleophiles at high pH in dephosphorylation,[7] deacylation,[8] and nucleophilic addition and substitution,[9] and the deprotonated species (**1a**) is the reagent.

$$\underset{\textbf{1}}{RN^+Me_2CH_2CH_2OH} \rightleftharpoons \underset{\textbf{1a}}{RN^+Me_2CH_2CH_2O^-} + H^+$$

But these surfactants contained a counterion, for example, Br^-, which competes with OH^- for the surface of the micelle, complicating analysis of the effect of OH^- on reaction rate in micelles of **1**.

Interionic competition for ionic sites at micellar surfaces is a general phenomenon and has been considered in great detail for nonfunctional micelles where external reagents are involved in bimolecular reactions.[10–12] One approach

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(1) Present address: Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia.

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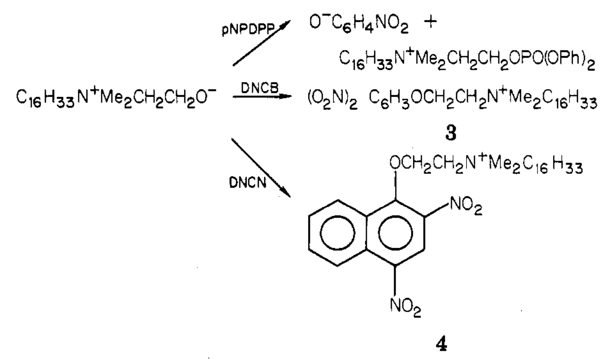
Scheme I



is to eliminate the unreactive ion by using a reactive counterion micelle,[13] and we now apply this approach to reaction in a functional micelle of **2** using OH^- as the counterion. The deprotonation is

$$\underset{\mathbf{2}}{C_{16}H_{33}N^+Me_2CH_2CH_2OHOH} \rightleftharpoons \underset{\mathbf{2a}}{C_{16}H_{33}N^+Me_2CH_2CH_2O^-}$$

For many ionic micelles the degree of counterion dissociation from the surface, α, appears to be approximately independent of variations in the nature, or total concentration, of the counterions.[10,14] When reaction occurs in these reactive counterion micelles the first-order rate constant, k_ψ, increases with [surfactant] as substrate becomes micellar bound, and eventually becomes independent of [surfactant]. Under these conditions k_ψ is given by[13]

$$k_\psi = k_M\beta \tag{1}$$

where k_M is the second-order rate constant in the micellar pseudophase, written in terms of concentration in mole ratio, i.e., as the ratio of the concentration of bound counterion to micellized surfactant. The value of $\beta = 1 - \alpha$ is generally 0.7–0.9.[10,14]

However, for reactions with hydrophilic anions, e.g., OH^- or F^-, we do not see this simple behavior.[13a,b,15] Instead k_ψ increases with [surfactant], even when substrate is fully bound, and addition of reactive counterion increases k_ψ.

This variation of k_ψ with [surfactant], and the effect of added ion, can be explained by assuming that for these micelles β and the concentration of bound counterion, $\bar{X}$, increase with [surfactant] and [counterion] according to eq 2, where the quantities in squared brackets are molar

$$K'_x = [\bar{X}_M]/[\bar{X}_W]([D_n] - [\bar{X}_M]) \tag{2}$$

concentrations in terms of total solution volume, D_n is micellized surfactant, and subscripts W and M denote aqueous and micellar pseudophases, respectively.

Equation 2 predicts that β will be essentially independent of [surfactant] if $K'_x > 10^3$, but, if the counteranion is very hydrophilic, e.g., OH^- or F^-, the variations of rate constant with cetyltrimethylammonium hydroxide or fluoride (CTAOH or CTAF, respectively) can be interpreted with values of K'_{OH} and K'_F of 55 and 40 M^{-1}, respectively.[13b]

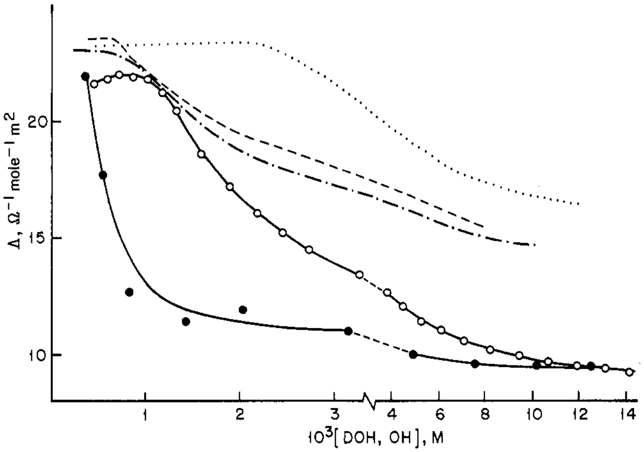


Figure 1. Molar conductance of hexadecyl(2-hydroxyethyl)dimethylammonium hydroxide (**2**): (○) no NaOH; (●) 10^{-2} M NaOH. The plots for CTAOH are from ref 13b: (···) no NaOH; (- - -) 5×10^{-3} M NaOH; (-·-) 10^{-2} M NaOH.

We now apply this treatment to the dephosphorylation of *p*-nitrophenyl diphenyl phosphate (pNPDPP) and reactions of 2,4-dinitrochlorobenzene and -naphthalene (DNCB and DNCN, respectively) in micelles of hexadecyl(2-hydroxyethyl)dimethylammonium hydroxide (**2**) (Scheme I). For reactions with the haloarenes we can also follow the second, slower, reactions of the intermediate ethers, **3** and **4**, with OH^-, giving dinitrophenolate or -naphtholate ion.

Reactions with pNPDPP and DNCB with the bromide ion surfactant corresponding to **2** have been examined,[7,9a] but elimination of Br^- as counterion simplifies estimation of second-order rate constants in the micelle pseudophase and their comparison with rate constants for model reactions in water.

Experimental Section

Materials. The hydroxyethyl surfactant was prepared, in solution, by the method used for the preparation of cetyltrimethylammonium hydroxide.[13b] The bromide ion surfactant was converted into the sulfate by treatment with Ag_2SO_4 in MeOH. It was converted into the hydroxide ion surfactant by treatment with $Ba(OH)_2$, in the absence of CO_2 under N_2. The precipitate of $BaSO_4$ was removed by high-speed centrifugation and the supernatant was tested for Ba^{2+}, SO_4^{2-}, and Br^-. The aqueous solution (ca. 0.25 M) was stored in a refrigerator, in the absence of CO_2. Solutions kept for 2 weeks at room temperature showed no sign of decomposition and gave reaction rates which were the same as those in new solution. Generally we used fresh samples for kinetics.

The preparation or purification of the other reagents has been described.

The kinetic solutions were made up, under N_2, in redistilled, deionized, H_2O.

Kinetics. The formation of *p*-nitrophenoxide ion from pNPDPP at 25.0 °C was followed at 405 nm, by using a Beckman or Gilford spectrophotometer for the slower, and a Durrum stopped-flow spectrophotometer for the faster, reactions, with $<2 \times 10^{-5}$ M substrate. The first-order rate constants, k_ψ, are in reciprocal seconds.

The first step of the reaction of DNCB (Scheme I) was followed at 322 nm (the isosbestic point for the products). Formation of 2,4-dinitrophenoxide ion was followed at 358 nm. The substrate concentration was ca. 6×10^{-5} M. The first step of reaction of DNCN was followed at the isosbestic point, 364 nm, and formation of 2,4-dinitronaphtholate ion was followed at 390 nm. The substrate

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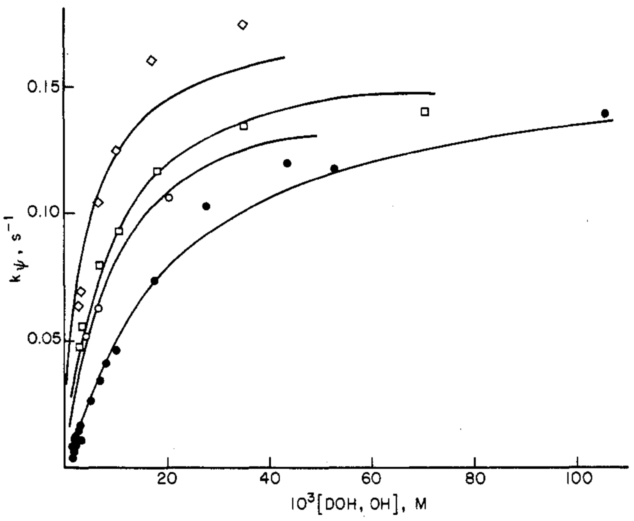

Figure 2. Reaction of DNCB in **2**: (●) no NaOH; (○) 0.07 M OH_T^-; (□) 0.1 M OH_T^-; (◇) 0.3 M OH_T^-. The curves are predicted.

TABLE I: Effect of OH^- upon Reaction of DNCB in DOH, OH[a]

[NaOH], M	k_ψ, s^{-1}	[NaOH], M	k_ψ, s^{-1}
0.04	0.023	0.40	0.076
0.08	0.030	0.48	0.085
0.12	0.037	0.60	0.097
0.17	0.043	0.76	0.115
0.24	0.055	0.97	0.134
0.32	0.065		

[a] At 25.0 °C in 3.5 × 10^{-3} M DOH, OH (**2**).

concentration was ca. 2 × 10^{-5} M. Substrates were added in MeCN and for reactions of DNCB and pNPDPP the reaction solution contained 0.2% MeCN and 3% MeCN for reaction of DNCN to avoid precipitation of the ether.

Conductivity. The electrolytic conductance of **2** was measured at 25 °C under N_2 by using bright Pt electrodes (Figure 1). The hydroxide ion form of **2** is designated as DOH, OH in this figure which also includes a plot of Λ against [surfactant] in 10^{-3} M NaOH, where Λ is corrected for the conductance of NaOH, assuming that it is not affected by the surfactant. The molar conductance of cetyltrimethylammonium hydroxide (CTAOH)[13b] in the absence and presence of NaOH is included in Figure 1 for purpose of comparison.

Results

Reaction of 2,4-Dinitrochlorobenzene. Attack of micellized **2** upon DNCB is very much faster than attack of OH^- upon ether **3** (Scheme I), and in analyzing the kinetics we neglect the contributions of reaction with OH^- in aqueous and micellar pseudophases.[9a]

The variations of k_ψ upon DNCB are shown as a function of [surfactant] and [NaOH] in Figure 2 and Table I, where here, and elsewhere, D ≡ $C_{16}H_{33}N^+Me_2CH_2CH_2$, and the corresponding results for decomposition of ether **3** are given in Figures 3 and 4. Figure 4 also has data on decomposition of the ether in the bromide ion form of the surfactant, DOH, Br (**5**). Competition between Br^- and

$C_{16}H_{33}N^+Me_2CH_2CH_2OHBr^-$
5

OH^- decreases the extent of deprotonation of the hydroxy group and slows reaction.[9a]

Reaction of 2,4-Dinitrochloronaphthalene. The variation of k_ψ with [surfactant] (Figures 5 and 6) for reaction of DNCN is consistent with DNCN being more reactive than DNCB and binding more strongly to micelles. Reaction is inhibited by Br^-. The subsequent reaction of the first-formed ether (**4**) is shown in Figure 7.

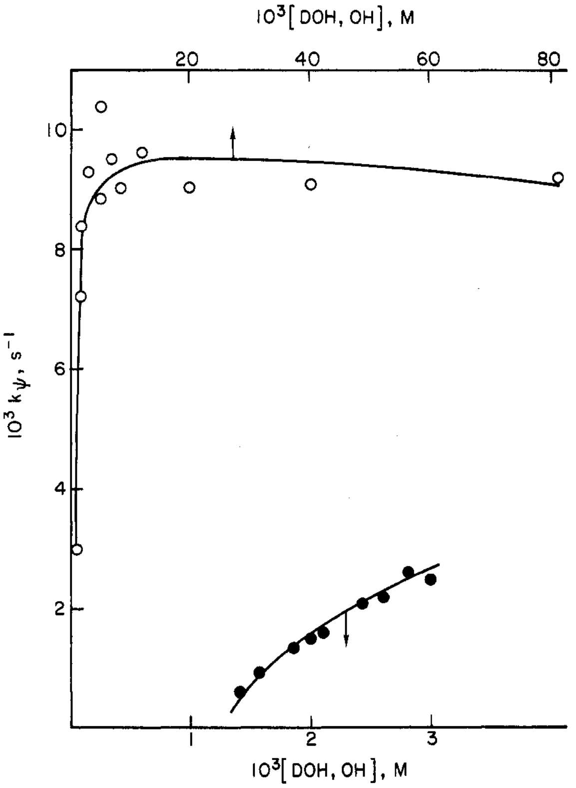

Figure 3. Reaction of DNCB in **2**, decomposition of ether: (●) no NaOH; (○) 0.1 M OH_T^-. The curves are predicted, with k_M = 0.025 s^{-1} and 10^4(cmc) = 10 and 4 M in absence and presence of NaOH.

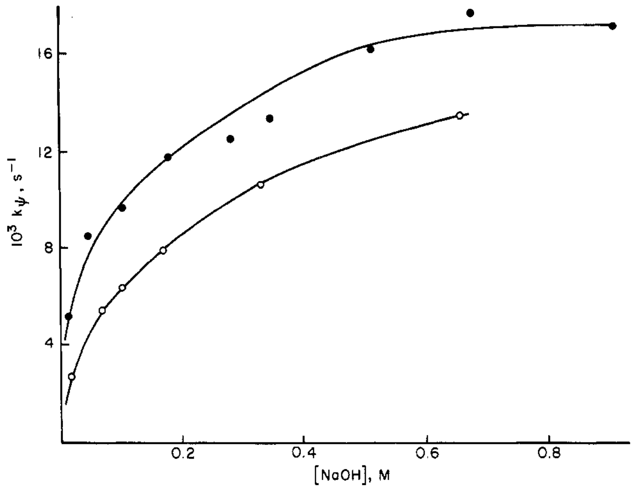

Figure 4. Effect of NaOH upon reaction of DNCB, decomposition of ether: (○) in 5.5 × 10^{-3} M **5** (DOH, Br); (●) in 12.1 × 10^{-3} M **2** (DOH, OH).

Reaction of p-Nitrophenyl Diphenyl Phosphate. Micelles of **2** react readily with pNPDPP (Scheme I). The substrate is very hydrophobic so that reactions in the aqueous pseudophase or with OH^- can be neglected.[16,17] The dependence of k_ψ on the concentrations of surfactant and OH^- is shown in Figure 8. Replacement of OH^- in the surfactant by Br^- slows reaction (Figure 8 and ref 16).

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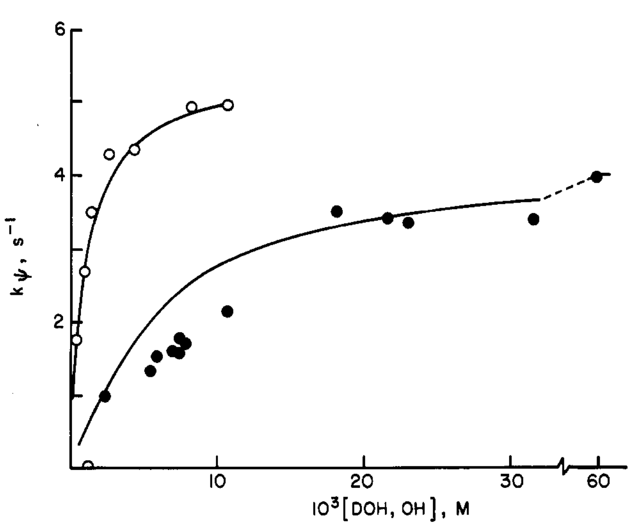


Figure 5. Reaction of DNCN in **2**: (●) no NaOH; (O) 0.05 M OH_T^-. The curves are predicted with K_s = 1100 M^{-1}, k_M = 8.5 s^{-1}, and 10^4(cmc) = 10 and ca. 0 M in absence and presence of NaOH.

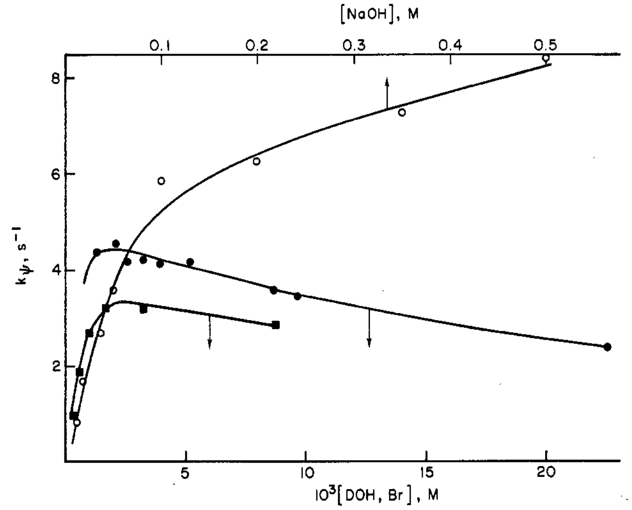


Figure 6. Reaction of DNCN in the bromide form of the surfactant (**5**): (●, O) for 3 wt % MeCN; (■) for 0.2 wt % MeCN; (■, ●) 0.05 M NaOH; (O) 8.7 × 10^{-3} M **5**.

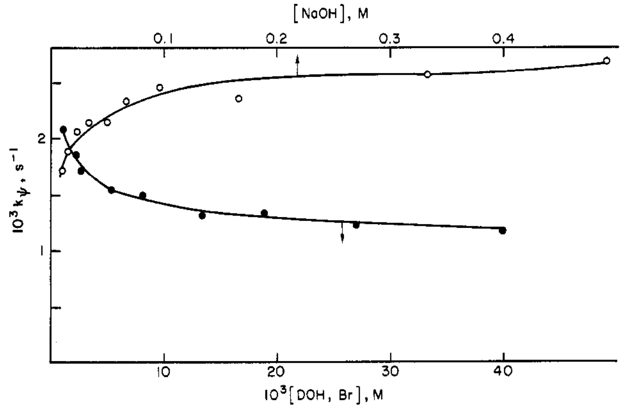


Figure 7. Reaction of DNCN, decomposition of ether in the bromide form of the surfactant (**5**): (●) in 10^{-2} M NaOH; (O) in 2.7 × 10^{-3} M **5**.

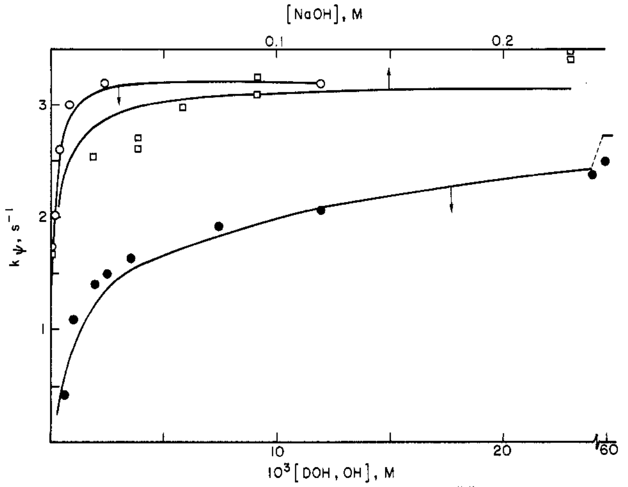
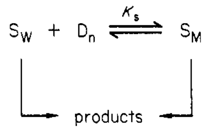


Figure 8. Reaction of pNPDPP in **2**: (●) no NaOH; (O) 0.1 M OH_T^-; (□) in 4.75 × 10^{-3} M **2** (DOH, OH). The curves are predicted, with K_s = 10^4 M^{-1}, k_M = 5.6 s^{-1}, and cmc = 2 × 10^{-4} M and ca. 0 in presence of NaOH.

Scheme II



Conductivity. Our kinetic data and observation of ether formation from DNCB and DNCN show that the hydroxyethyl group in micellized **2** is partially deprotonated. Consistently the molar conductivity of a solution of the hydroxyethyl surfactant is decreased by addition of NaOH, when allowance is made for the contribution of NaOH to the conductivity (Figure 1). In addition, the conductivity of CTAOH, with and without added NaOH,[13b] is much larger than that of the hydroxyethyl surfactant (DOH, OH, **2**) in comparable conditions (Figure 1). Formation of the zwitterion, **2a**, should sharply reduce conductivity of the solution, but we have not attempted to analyze the conductance data quantitatively because we do not know the mobilities or charges of the various surfactant species which may be present in solution. There is an ill-defined break in a plot of Λ against [surfactant] at ca. 10^{-3} M, indicating onset of micellization (cf. ref 13b).

Discussion

The variation of k_ψ with [surfactant] is superficially similar to that observed for reactions in solutions of reactive ion surfactants, e.g., cetyltrimethylammonium hydroxide and fluoride.[13,15] The values of k_ψ do not become constant when all the substrate is micellar bound but continue to increase toward a limiting value at high [surfactant], and added OH^- (or F^-) increases k_ψ up to this limiting value.

These variations of k_ψ with [surfactant] can be treated by using a mass action model, eq 2, which assumes that β increses with [counterion], either because the micellar Stern layer gradually becomes saturated with counterion or because the micelles grow with increasing [counterion] and become better able to bind counterion.[18]

The generally accepted treatment of reactivity in normal micelles in water follow Scheme II, where k'_W and k'_M are respectively first-order rate constants in the aqueous and micellar pseudophases.

The first-order rate constant for the overall reaction is given by[19]

$$k_\psi = \frac{k'_W + k'_M K_S[D_n]}{1 + K_S[D_n]} \qquad (3)$$

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[18] For discussion of the physical significance of this apparent variation of β see ref 13b.

[19] Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* **1967**, *89*, 4698.

The approach for bimolecular reactions is to establish the value of the binding constant, K_S, and to write the first-order rate constants, k'_W and k'_M, in terms of second-order rate constants and reactant concentrations in the micellar and aqueous pseudophases.

The binding constants of DNCB and DNCN in a variety of surfactants are ca. 10^2 and 10^3 M^{-1}, respectively, but for pNPDPP they are greater than 10^4 M^{-1}, and we assume that similar values will apply in solutions of **2**.[13a,16,17,20,21]

We assume that conversion of micellized surfactant (DOH) into the reactive zwitterion can be written as a two-step process (Scheme III). In aromatic substitution the product is an ether which may react further to give phenolate or naphtholate ion (Figures 3, 4, and 7).

Scheme III

$$DOH_M + OH_W^- \overset{K'}{\rightleftharpoons} OH_M^- \overset{K_D}{\rightleftharpoons} DO_M^-$$

$$S_M + DO_M^- \xrightarrow{k_M} \text{products}$$

The concentration of DO_M^- is given by

$$[DO_M^-] = K'K_D[OH_W^-]([D_T] - \text{cmc} - [OH_M^-] - [DO_M^-]) \quad (4)$$

where D_T is total surfactant and the concentration of monomeric surfactant (D_n) is assumed to be given by the critical micelle concentration, cmc.[19]

Equation 4 and Scheme III give

$$[DO_M^-] = \frac{K'K_D[OH_W^-]([D_T] - \text{cmc}])}{1 + K'[OH_W^-](1 + K_D)} \quad (5)$$

However, we can also write

$$[D_T] = [OH_W^-] + [OH_M^-] + [DO_M^-] \quad (6)$$

in the absence of added OH^-.

Combining eq 5 and 6 gives

$$K'(1 + K_D)[OH_W^-]^2 + \{1 - K'(1 + K_D)(\text{cmc})\}[OH_W^-] - [D_T] = 0 \quad (7)$$

Reaction in **2** is so much faster than that in water that we neglect this latter reaction and write

$$k_\psi = k_M[DO_M^-][S_M]/\{([D_T] - \text{cmc})[S_T]\} \quad (8)$$

where k_M is a second-order rate constant written in terms of the mole ratio of DO_M^- to total micellized surfactant, D_T.

Equation 5, 7, and 8 give

$$k_\psi = \frac{k_M K_S K_D([D_T] - [OH_W^-])}{(1 + K_D)(1 + K_S([D_T] - \text{cmc}))} \quad (9)$$

where $[OH_W^-]$ can be calculated from the quadratic eq 7 by using assumed values of K' and K_D.

The equations for the distribution of OH^- are modified when NaOH is added. In this case the treatment outlined above and mass balance give the quadratic

$$K'(1 + K_D)[OH_W^-]^2 + (1 + K'(1 + K_D))([D_T] - \text{cmc} - [OH_T^-])[OH_W^-] - [OH_T^-] = 0 \quad (10)$$

$$k_\psi = \frac{k_M K_S K' K_D[OH_W^-]([D_T] - \text{cmc})}{\{(1 + K_S([D_T] - \text{cmc}))(1 + K'[OH_W^-] + K'K_D[OH_W^-])\}} \quad (11)$$

TABLE II: Formation of Ether from DNCB in Micelles of DOH, OH (**2**)[a]

$[OH_T^-]$, M	$10^4\cdot$(cmc), M	K_S, M^{-1}	k_M, s^{-1}
0-0.1[b]	8	90	0.3
0.07[c]	2	90	0.3
0.1[c]	2	110	0.3
0.3[c]	2	200	0.3

[a] At 25.0 °C, taking $K_D = 1.5$ and $K' = 120$ M^{-1}. [b] No NaOH. [c] Variable DOH, OH.

We treated eq 7 and 8 (for reaction without added NaOH) or eq 10 and 11 (with added NaOH) using computer simulation with the requirement that K' and K_D be independent of the nature of the substrate.

Decomposition of first-formed ether (Scheme I) can be treated by assuming that it is completely micellar bound and reacts only with micellar-bound OH^-, i.e., with OH_M^-, so that

$$k_\psi = k_M^E[OH_M^-]/([D_T] - \text{cmc}) \quad (12)$$

The second-order rate constant for this reaction, k_M^E, is written in terms of the mole ratio of OH_M^- to micellized surfactant, and $[OH_M^-]$ is related to $[OH_W^-]$ by the reactions shown in Scheme III, i.e.

$$[OH_M^-] = \frac{K'[OH_W^-]([D_T] - \text{cmc})}{1 + K'[OH_W^-](1 + K_D)} \quad (13)$$

so that

$$k_\psi = \frac{k_M^E K'[OH_W^-]}{1 + K'[OH_W^-](1 + K_D)} \quad (14)$$

The variations of k_ψ with concentration of **2** can be fitted to these various equations for reactions in micellized **2**, and for some, but not all, reactions in solutions containing NaOH. Added electrolytes reduce the cmc, and we assume that the effect will be similar to that on ionic surfactants.[10,13] In addition reactions of hydrophobic substrates are often mediated by surfactants at concentration below the cmc in water. In our experiments [surfactant] was generally such that uncertainties in the magnitude of the cmc were unimportant.

Reaction of pNPDPP. This reaction involves only nucleophilic attack upon a substrate which binds so strongly to micelles that the fit is little affected by the precise value of K_S. The directly measured value of K_S is ca. 16000 M^{-1} in CTABr,[17] but, for reactions in solutions of cationic surfactants, the kinetic data can be fitted by taking $K_S \approx 10^4$ M^{-1} (Figure 8). Values of $K_D = 1.5$ and $K' = 120$ M^{-1} (Scheme III) were used in fitting all the kinetic data.

Formation of Ether from DNCB. 2,4-Dinitrochlorobenzene does not bind very strongly to cationic micelles, for example, $K_S \approx 75$ M^{-1} in CTABr.[20] However, added electrolytes may "salt-out" apolar solutes from the aqueous pseudophase and into the micelles.[13b] Therefore, we assume that K_S may increase on addition of NaOH. The calculated curves based on the parameters in Table II are in Figure 2. The agreement between observed and predicted rate constants is satisfactory except in the most concentrated NaOH.

We were unable to fit the variation of k_ψ with [NaOH] (Table I). Our treatment based on Scheme III predicts that k_ψ should level off at high $[OH^-]$, but it does not. Thus, the treatment fails in these concentrated electrolyte solutions for both initial reaction of DNCB and subsequent decomposition of the ether (Figure 4).

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(21) Added electrolytes, especially those having hydrophilic ions, may increase solute binding to micelles by "salting-out" the substrate from the aqueous pseudophase. This effect should become important only in relatively concentrated electrolyte solutions.[12b,13b]

Formation of 2,4-Dinitrophenoxide Ion. The intermediate ether (**3**) should be essentially fully micellar bound, and, if it reacts only with OH^- bound in the Stern layer, eq 12–14 should be followed (Figure 3). We were not able to account for the variation of k_ψ with [NaOH] at constant [DOH, OH] (Figure 4). We did not attempt to treat variations of rate constant with [surfactant] in solutions containing OH^- and Br^- (Figure 4).

Reaction of 2,4-Dinitrochloronaphthalene. These reactions were generally carried out in water/MeCN 97:3 v/v, and the added MeCN should decrease binding of DNCN to the micelle by increasing its solubility in the aqueous pseudophase. In CTABr and CTAOH[13b] $K_S \approx 1600$ M^{-1}, and added MeCN should decrease K_S. The rate constants calculated by using eq 7–11 agree reasonably well with experimental values (Figure 5).

Reactions in Relatively Concentrated NaOH. Our quantitative treatments are satisfactory except for aromatic nucleophilic substitution in the more concentrated solutions of NaOH (Table I and Figure 4). These failures could be related to the (relatively low) hydrophobicity of DNCB, the least hydrophobic substrate studied, so that there might be a major effect of OH^- on the micellar binding of DNCB. However, ether **3** should be fully micellar bound and the equations fail here also.

Another possibility is that OH^- in the aqueous pseudophase reacts with DNCB in the micelle (cf. ref 13a and 22). This explanation is satisfactory for conversion of ether **3** into 2,4-dinitrophenoxide ion, but not for conversion of DNCB into ether **3**, which involves nucleophilic attack by alkoxide zwitterion **2a** (Scheme I).

The relatively high concentrations of NaOH used in these experiments could modify the structure of the micelle, and deprotonation of the hydroxyl group, by changing the activity of OH^- in the aqueous pseudophase, a factor which is not taken into account in our treatment, but we note that the failure is less acute for reaction of pNPDPP than for the reactions of DNCB. These differences may be related to the fact that the relatively hydrophilic dinitrophenyl moiety may be in the water-rich region of the micellar surface whereas the hydrophobic pNPDPP may, on the average, be located in a less aqueous region of the micelle. But the failure of the treatment in relatively concentrated NaOH suggests that the simple equations based on the distribution of solutes between aqueous and micellar pseudophases are not applicable to systems of high electrolyte content, and this question is considered later.

Rate and Equilibrium Constants in the Micellar Pseudophase. The equations based on Scheme III fit the variation of k_ψ with concentration of **2** and OH^- for reactions of several substrates under various conditions, using substrate binding constants, K_S, similar to those found for other micellized surfactants.

It is more difficult to relate the value of K' to similar parameters for the binding of OH^- to other micelles, for example, of CTAOH,[13b] where $K' \approx 55$ M^{-1}. The apparent variable charge neutralization of the cationic head groups in a CTA^+, or other, micelle may in actuality be the result of a changing size distribution of the micelles. With dilute surfactant the micelles may be very small and therefore bind little OH^-, although they could bind apolar solutes (cf. ref 24). But with increasing concentration of surfactant or OH^- the micelles could grow, and become more effective at binding OH^-, and therefore **2** would become more deprotonated. However, our treatment is essentially empirical because it does not take into account the different micellizing abilities of cationic and zwitterionic surfactants, or the extent to which high concentrations of OH^-, or other anion, in the aqueous pseudophase may perturb the micelle. For example, zwitterionic, and nonionic, surfactants have lower critical micelle concentrations than otherwise similar ionic surfactants because of differences in the Coulombic repulsions between the micellar head groups.[3,25]

TABLE III: Comparison of Second-Order Rate Constants in Aqueous and Micellar Pseudophases

substrate	k_2^m, M^{-1} s^{-1}	k_2^m/k_W[a]	k_2^m/k_{ch}
DNCB	0.04	290 (47)	15[b]
ether 3	0.0035		
DNCN	1.2	190 (63)	
pNPDPP	0.8	1.6 (8)	0.05[c]

[a] Values in parentheses are based on reaction of OH^- in CTAOH.[13b] [b] Based on $k_{ch} = 2.7 \times 10^{-3}$ M^{-1} s^{-1}.[9a] [c] Based on $k_{ch} = 17$ M^{-1} s^{-1}.[7a]

Comparison with Nonmicellar Reactions. Alkoxide ions are effective nucleophiles and, in water, are considerably more reactive than OH^- in deacylation, dephosphorylation, nucleophilic aromatic substitution, and addition to carbocations.[9a,26]

A major problem in relating reactivity of nucleophiles in aqueous and micellar pseudophases is the concentration units in the two pseudophases. We have defined k_M in terms of concentration as a mole ratio. These constants cannot be compared directly with second-order rate constants in water and units of M^{-1} s^{-1}, but the comparison can be made on the basis of assumed volume elements of reaction in the micellar pseudophase. This volume could be that of the total micelle, whose molar volume should be ca. 0.3 L;[11,27] alternatively it could be that of the Stern layer which is approximately half that of the micelle.[28]

If the volume element of reaction is that of the Stern layer eq 15 gives, for reaction in a micelle of cetyltrimethylammonium bromide

$$k_2^m = 0.14 k_M \tag{15}$$

where k_2^m has the dimensions M^{-1} s^{-1}. If this conversion factor can be applied to reactions in micelles of **2**, we obtain the values of k_2^m in Table III which can be compared with second-order rate constants for reactions of substrates with other nucleophiles in water and in micelles.

Approximate second-order rate constants, k_M, for reactions of DNCB and pNPDPP with micellized **2a** were estimated earlier from rate constants in micelles of the hydroxyethyl surfactant (**5**), assuming complete incorporation of the substrate, and using an apparent acid dissociation constant of the hydroxyl group.[29] The agreement

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[23] Reaction could be written as attack of the hydroxyethyl group of the surfactant, catalyzed by OH^- acting as a general base. However, such reactions are generally regarded as involving attack of preformed alkoxide ion.

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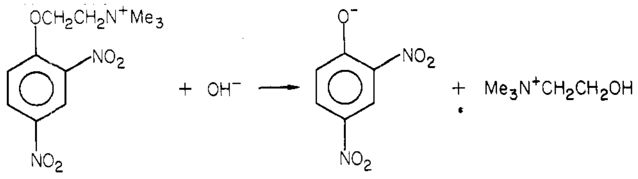
Scheme IV



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is reasonable for reaction of pNPDPP where the original value of k_M was 3.7 s^{-1}, as compared with 5.6 s^{-1} (Figure 8) but the earlier value for reaction of DNCB of k_M = 0.063 s^{-1} (ref 29) was too small (Table II) because we did not take into account partial incorporation of the substrate.

The second-order rate constants, k_2^m, i.e., $k_M/7$, for reactions of micellized alkoxide zwitterion, **2a**, with the various substrates can be compared with rate constants for reactions of a model alkoxide zwitterion in water, e.g., the cholinate zwitterion (**6**), whose second-order rate

$$Me_3N^+CH_2CH_2OH \rightleftharpoons \underset{\mathbf{6}}{Me_3N^+CH_2CH_2O^-} + H^+$$

constants for reactions in water with DNCB and pNPDPP have been estimated,[7a,9a] based on the pK_a of 13.9 for choline.[30]

The second-order rate constants (M^{-1} s^{-1}) are compared in Table III where k_{ch} is the second-order rate constant for reaction of the cholinated zwitterion in water and for reaction of DNCB $k_2^m/k_{ch} \approx 15$, so that reaction is faster in the micelles (taking cholinate ion as the model compound), but for reaction of pNPDPP $k_2^m/k_{ch} \approx 0.05$ and reaction is slower in the micelles.

We can also compare the nucleophilicity of micellized **2a** toward the various substrates with that of OH^- in water, given by k_2^m/k_W (Table III), and in *micelles of CTAOH.*[13b] These latter relative nucleophilicities are given in parentheses in Table III. The alkoxide is a better nucleophile than OH^- under all conditions, but the relative reactivities depend upon substrate and reaction medium.

Halonitronaphthalenes are more reactive toward nucleophiles than the corresponding halobenzenes,[31] and the approximate relative reactivities of DNCN and DNCB toward OH^- are 50 and 20 in water and CTAOH, respectively,[13b] and 30 toward micellized zwitterion (**2a**) (Table III), suggesting that reactions in micelles slightly disfavor the more hydrophobic substrate.

We can also compare the reactivities of DNCB and ethers toward OH^- in water and in cationic micelles, using the choline derivative (**7**) as the model compound (Scheme IV).

For reaction with OH^- in water the reactivity of **7** relative to that of DNCB is 6.4.[9a] In a micelle of **2** the second-order rate constant, k_2^m, for reaction of OH^- with ether **3** in the Stern layer is 0.0035 M^{-1} s^{-1} (Table III) and for reaction of OH^- with DNCB in CTAOH micelles $k_2^m \approx 10^{-3}$ M^{-1} s^{-1},[13b] so that in both water and micelles the ethers are somewhat more reactive than DNCB toward OH^-. We can also compare the second-order rate constant for reaction of the choline derivative (**7**) with OH^- in water, which is 9.1×10^{-4} M^{-1} s^{-1},[9a] with that of OH^- with ether **3** in micelles of **2** (Table III), and for this aromatic substitution reaction in micelles is faster than a similar reaction in water by a factor of ca. 4.

Reactivities of Micellar and Aqueous Pseudophases. There are many examples of bimolecular reactions of anionic nucleophiles for which second-order rate constants in nonfunctional or functional micelles are very similar to those in water.[5,6,11,12,29,32] The rate enhancements, which are sometimes very large, generally can be explained in terms of an increased concentration of reactants in the micellar pseudophase.[33]

However, in a few reactions second-order rate constants in the micellar pseudophase differ markedly from those in water. This result is not surprising because micelles, as a medium, are less polar than water and may exert a kinetic medium effect.[35]

In our present work it appears that reaction of an alkoxide ion is faster in the micelles than in water for aromatic nucleophilic substitution and slower for dephosphorylation, and other evidence on reactions of hydroxide or alkoxide ion supports this conclusion.[36] The relative reactivities of **2a**, OH^-, and cholinate zwitterion given in Table III depend upon the assumption of our treatment but these uncertainties do not affect the directions of the micellar effects.

Aromatic nucleophile substitution by hydroxide, alkoxide, and especially azide ion[37] is faster in cationic micelles than in water, probably because of favorable interactions between the cationic head groups and the charge-delocalized transition states. On the other hand, a very hydrophobic substrate, such as pNPDPP, may spend less time close to the water–micelle interface, and therefore be less exposed to hydrophilic anions, and its reactions are often slower in a micelle than in water. In addition, nonmicellar solvent effects upon reactions of OH^- with pNPDPP and DNCB are different. Addition of organic solvents strongly assists aromatic nucleophilic substitution but hinders, or only slightly assists, dephosphorylation.[16,38] Thus, micellar effects parallel solvent effects.

The apparent limitations of the pseudophase ion-exchange model for reactions in moderately concentrated solutions of NaOH (Table I, Figure 4, and ref 22) contrast sharply with the success of this model for reactions with less hydrophilic reagents or in dilute OH^-.[5,6,17,27] The model assumes that ionic reagents are distributed between the aqueous pseudophase and the micellar Stern layer depending specifically upon the nature of the ion.[10,11,39] No distinction is made between ions in the aqueous pseudophase and in the diffuse Gouy–Chapman layer, where the ion distribution is governed by Coulombic, rather than specific, interactions. These assumptions will be least satisfactory for ions such as OH^-, which bind weakly in the Stern layer, and with added NaOH the population of OH^- may be high in the diffuse layer. These ions may react with a micellar-bound substrate, but the contribution of this reaction will be significant only when an appreciable

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fraction of reactive ions, e.g., OH$^-$, are in the diffuse layer. The postulated reaction of ions in the diffuse layer may also be important for small cationic aggregates which do not bind hydrophilic anions specifically in a Stern layer.

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Registry No. 2, 87696-35-3; **2a**, 54385-45-4; 3, 61095-52-1; 4, 87696-36-4; 6, 44519-34-8; Br$^-$, 24959-67-9; Me$_3$N$^+$CH$_2$CH$_2$OH, 62-49-7; OH$^-$, 14280-30-9; *p*-nitrophenyl diphenyl phosphate, 10359-36-1; 2,4-dinitrochlorobenzene, 97-00-7; 2,4-dinitrochloronaphthalene, 2401-85-6.

Surface Effects in the Photochemistry of Colloidal Cadmium Sulfide

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Both steady-state and pulsed-laser photoexcitation techniques have been used to investigate photoinduced processes at the surface of CdS colloids. The colloid surfaces have been modified by use of adsorbed reactants and surfactants, the latter conveniently changing the charge of the colloid and lending greater stability to the system. Luminescence of CdS is observed, the spectral quality of which depends on the excitation light intensity, and the nature of the adsorbed species. The CdS luminescence is quenched rapidly ($\tau << 10^{-9}$ s) by various additives either via positive hole or e$^-$ capture. The kinetics of the former process are Perrin, while those of the latter are Stern–Volmer in nature. Photoinduced e$^-$ transfer arises from e$^-$ involved with the luminescence processes, and also from e$^-$ which do not give rise to luminescence; these two processes are quite separate. Pulsed studies show that reduced products of photoinduced e$^-$ transfer readily move on the colloid surface to react with other adsorbed species. They remain on the particle surface for extended periods of time which are greater than 260 μs.

Introduction

The promotion of photochemical reactions by colloidal particles has lately received much attention.[2–5] Quite often an interface, one side of which is water, will strongly promote photoinduced e$^-$ transfer reactions and also serve to inhibit the back-reaction between the ionic products.[6] Over the past decade the concept of interfacial photochemistry has successfully been applied to semiconductor electrodes, powder dispersions, and aqueous colloidal systems.[7–13] The photogenerated e$^-$/hole pair of the semiconductor may undergo redox reactions with adsorbed species by either reduction of an e$^-$ acceptor, e.g., methyl viologen or nitrobenzene, or oxidation of an e$^-$ donor, e.g., I$^-$ or ethylenediaminetetraacetate. It should be stressed that the material undergoing the e$^-$ transfer reaction must be adsorbed on the semiconductor surface in order to react efficiently with the photoproduced e$^-$/hole pair. Thus, it is obvious that the surface of the semiconductor plays a crucial role in this type of interfacial photoprocess.

The present paper deals with the effect of modifying the surface of an aqueous cadmium sulfide colloid with various surfactants which function both to stabilize the colloid and to alter the surface, particularly with respect to charge. These modifications help to identify important features of the photoinduced charge transfer process, e.g.: the degree of adsorption of e$^-$ acceptors to the particle surface, the rate of escape of the reduced acceptor from the surface, and the nature of positive hole repair.

Experimental Section

Pulsed irradiation studies were carried out with either a 337-nm beam (8-mJ energy, 6-ns fwhm) from a Lambda Physik X100 laser, or with 490-nm light (0.1-J energy, 120-ns fwhm) from a Candela SLL-66A dye laser. The short-lived transients produced were monitored by fast spectrophotometry (response ≤ 1 ns) and the data were captured by a Tektronix 7912 A digitizer with subsequent processing by a 4051 minicomputer.[6] Steady-state irradiation studies were performed with a 300-W quartz iodine lamp with cutoff filters interposed between the sample and lamp so that only light of wavelength greater than 400 nm reached the sample. Quantum yield determinations were carried out with light of wavelength 488 nm from a Spectra

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