Micellar Effects upon Dephosphorylation in Water and Aqueous 1,2-Diols

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Cationic micelles of cetyltrimethylammonium bromide and chloride (CTABr and CTACl) in aqueous ethaneand propane-1,2-diol speed reaction of OH⁻ with *p*-nitrophenyl diphenyl phosphate (pNPDPP). Reaction with F^- was examined in aqueous ethane-1,2-diol. The rate-surfactant profiles have been treated quantitatively by use of the ion-exchange pseudophase model and, for reaction with OH⁻, direct comparison has been made with the profile for reaction in aqueous CTABr. Reaction with OH⁻ in aqueous CTABr has also been treated quantitatively by use of a mass-action model, and the conclusions of the two treatments are compared. The functional surfactant, N.N-dimethyl-N-(2-hydroxyethyl)-N-hexadecylammonium bromide is an effective dephosphorylating agent in aqueous ethanediol containing NaOH.

Solvophobic interactions are of key importance in the formation of normal micelles in highly ordered inorganic solvents such as water^{2,3} or sulfuric acid.⁴ Organic solvents having three-dimensional structure, e.g., 1,2-diols, triols, and formamide, can also promote micellization,⁵ and micelles form in mixtures of these solvents and water.⁶ The behavior of these solvents is very different from that of monohydric alcohols which generally disrupt water structure and hinder micellization.

Cationic micelles effectively promote bimolecular attack by anionic or nonionic bases or nucleophiles in water, and these reactions have been studied widely.^{2,7,8} Our aim was to study kinetic micellar effects in aqueous 1,2-diol using either the nonfunctional surfactants cetyltrimethylammonium chloride and bromide (CTACl and CTABr, respectively) or the functional surfactant, N,N-dimethyl-N-(2-hydroxyethyl)-N-hexadecylammonium bromide (1).^{8,9}

$$n-C_{16}H_{33}N^{+}Me_{2}CH_{2}CH_{2}OH \Rightarrow 1 \\ n-C_{16}H_{33}N^{+}Me_{2}CH_{2}CH_{2}O^{-} + H^{+} 1a$$

This micellized surfactant is partially deprotonated at high pH and the zwitterion (1a), and similar zwitterions, are effective nucleophiles in dephosphorylation,⁹ (Scheme I), and in deacylation,¹⁰ nucleophilic aromatic substitution,¹¹ and addition to carbocations.¹²

Scheme I

$$C_{16}H_{33}N^{+}Me_{2}CH_{2}CH_{2}O^{-} + (PhO)_{2}PO \cdot OC_{6}H_{4}NO_{2} \rightarrow C_{16}H_{33}N^{+}Me_{2}CH_{2}CH_{2}OPO(OPh)_{2} + O^{-}C_{6}H_{4}NO_{2}$$

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With a chemically inert micelle, of, e.g., CTACl or CTABr, the nucleophile at high pH can be either OH⁻ or the anion of the diol:¹³

$$OH^- + CH_2(OH)CH_2OH \Rightarrow CH_2(OH)CH_2O^-$$

and at lower pH fluoride ion can be used as a nucleophile.¹⁵

The substrate was *p*-nitrophenyl diphenyl phosphate (pNPDPP) and the various reactions are shown in Scheme II.

All these reactions can be followed via formation of the p-nitrophenoxide ion, and a phosphorylated intermediate may react further giving diphenyl phosphate.

Most of our experiments were made in ethane diol:H₂O 1.127:1 w/w, but we also used ethane diol: H_2O 99:1 w/w, and propane-1,2-diol: H_2O 1.11:1 w/w, and we compared the behavior in these solvents with that in water.^{15,16,18}

Experimental Section

Materials. The preparation and purification of the reagents have been described.⁹ The mixed solvents were made up by weight, and molarities are quoted in terms of the total volume of the solution.

Products. Two methods were used to show that at high pH ethanediolate is a dephosphorylating agent.

(i) Diphenyl chlorophosphate $(5 \times 10^{-4} \text{ M})$ was allowed to react with 0.01 M NaOH in the presence and absence of 0.05 M CTABr in ethane diol:H₂O 1.127:1 w/w, ethanediol, and in aqueous NaOH.¹⁹ For reaction in H₂O we observed a peak at 265 nm, a shoulder at 270 nm, and a

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OH⁻ with pNPDPP were made with a Gilford spectrophotometer and 0.01 M OH^{-,15} Mixing might have been a problem with some of these relatively fast reactions, so the system was reinvestigated with a Durrum stopped-flow spectrophotometer. We used 0.05 M OH to obtain convenient rate constants

(19) We used the chlorophosphate rather than pNPDPP in these experiments because the strong absorbance of p-nitrophenol obscures that

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Scheme II



 $\mathbf{R} = \mathbf{H}, \mathbf{M}\mathbf{e}$

TABLE I: Reactions in the Absence of Sur	rfactant ^a
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[NaX], M	$X = OH^{-}$	$X = F^{b}$
0.005	(2.26)	**************************************
0.01	4.03	0.95
0.03	10.9(13.6)	2.45
0.05	17.9(24.2)	4.02
0.075	26.5 (37.8)	5.93
0.10	35.2	7.85
0.12	(60.4)	
0.15	(76.5)	

^a Values of $10^3 k_{\psi}$, s⁻¹ at 25.0 °C in aqueous ethanediol; values in parentheses are in aqueous propane-1,2-diol. ^b In 0.015 M borate buffer, pH 8.75.

minimum at 236 nm. Authentic sodium diphenyl phosphate gave a similar spectrum. When the reaction solution contained ethanediol there was a pronounced maximum at 238 nm in ethanediol and 240 nm in the ethanediolwater mixture and a small peak at 263 nm with a shoulder at 268 nm.

(ii) The products of the reaction of pNPDPP in ethanediol and 0.05 M CTABr and 0.01 M NaOH were separated by TLC (silica gel, EtOH:CHCl₃, 15:85 v/v). The surfactant and *p*-nitrophenol stayed at the origin and a spot was observed with $R_f = 0.33$. A similar experiment in water gave diphenyl phosphate with $R_f = 0.12$, which cochromatographed with an authentic sample. The spot with $R_f = 0.33$ was also found in the products of reaction in ethanediol:water 1.127:1 w/w.

Nucleophilic attack upon pNPDPP by the hydroxyl group of the hydroxyethyl surfactant (1) was demonstrated spectrophotometrically. Reaction of 5×10^{-4} M p-NPDPP was carried out in ethanediol:H₂O 1.127:1 w/w containing 10^{-3} M NaOH and 0.05 M 1. After complete reaction NaClO₄ was used to precipitate surfactant (1) and its phosphorylated derivative (2) (Scheme I). The precipitate was washed quickly (H₂O) to remove any *p*-nitrophenoxide ion and diphenyl phosphate ion, and was then treated with EtOH to decompose 2. The EtOH solution adsorbed at 265 nm showing the presence of an aromatic chromophore derived from 2.

Kinetics. Reactions were followed spectrophotometrically at 25.0 °C by using the λ_{max} of the *p*-nitrophenoxide ion at 400 nm. The substrate, in 5 μ L of MeCN, was added to 3 mL of reactant solution so that its concentration was (1–5) × 10⁻⁵ M.^{9,15} The first-order rate constants, k_{ψ} , are in reciprocal seconds.

Reaction of pNPDPP with 0.05 M NaOH in aqueous CTABr was followed with a Durrum stopped-flow spectrometer. The substrate, in CTABr solution, was in one syringe, and NaOH in the other.⁹

Results

Products. Reaction in aqueous ethanediol containing NaOH involves predominant attack by the ethanediolate ion in the presence and absence of CTABr (Experimental Section). This result is understandable because 1,2-diols are more acidic than water,¹⁴ and alkoxide ions are typically much better nucleophiles than $OH^{-.9-12}$ Consistently the zwitterion (1a) is the nucleophile in solutions of 1.

	solvent		
10 ² [CTABr], M	ethanediol ^b	aqueous EtOH ^c	
	3.35	1.50	
0.63		1.82	
1.25		1.82	
2.50		1.86	
5.00	3.35	2.22	
10.0	3.40	2.27	
15.0	3.90		
20.0	6.20		
25.0	6.45	2,48	
30.0	5.84		
40.0	4,91		
50.0	3.77	2.54	

TABLE II: Reaction in the Presence of NaOH^a

^a Values of $10^{3}k_{\psi}$, s⁻¹ with 0.01 M NaOH at 25.0 °C. ^b Ethanediol:H₂O 99:1 w/w. ^c EtOH:H₂O 1:1 w/w.



Figure 1. Reaction of pNPDPP with 0.05 M NaOH in CTABr: (i) solid line calculated by use of the mass action model; (ii) and (iii) broken lines, calculated by use of the ion-exchange model, see text and Table V.

Reaction in the Absence of Surfactant. Reactions in aqueous 1,2-diols are second order in solutions containing NaOH or NaF (Table I), and the respective second-order rate constants in ethanediol:H₂O 1.127:1 w/w are 0.36 and 0.079 M⁻¹ s⁻¹. For reaction in propane-1,2-diol:H₂O 1.11:1 w/w containing NaOH the second-order rate constant is 0.5 M⁻¹ s⁻¹. For reaction in ethanediol:H₂O 99:1 w/w and 0.01 M NaOH the second-order rate constant is 0.34 M⁻¹ s⁻¹ and in EtOH:H₂O 1:1 w/w it is 0.15 M⁻¹ s⁻¹ (Table II). In water at 25.0 °C the second-order rate constants are 0.48 and 0.11 M⁻¹ s⁻¹ for reaction of OH⁻ and F⁻, respectively.¹⁵

Reaction in Aqueous CTABr. The values of k_{ψ} for reaction of pNPDPP with 0.05 M OH⁻ go through maxima with increasing [CTABr] (Figure 1). These results are in qualitative agreement with earlier observations in 0.01 M NaOH.¹⁵

Reactions in Micelles in Mixed Solvents. The variation of k_{ψ} with [surfactant] in aqueous 1,2-diols follows the typical pattern in that k_{ψ} goes through maxima with increasing [surfactant] at constant OH⁻ or F⁻ (Figures 2-4).



Figure 2. Reaction of pNPDPP in ethane diol:H₂O 1.127:1 w/w containing NaOH: Solid points, 0.01 M NaOH; open, 0.1 M NaOH; \bullet , O in CTABr; \bullet , \diamond in CTACI. The solid lines are for CTABr and the broken lines are for CTACI, calculated by use of the ion-exchange model.



Figure 3. Reaction of pNPDPP with F⁻ in ethanediol 1.127:1 w/w containing CTABr: ■, 0.01 M F⁻; □, 0.05 M F⁻. The lines are calculated by use of the ion-exchange model, see text and Table V.



Figure 4. Reaction of pNPDPP in propane-1,2-diol containing NaOH and CTABr. • and O in 0.01 and 0.1 M KOH, respectively. The lines are calculated by use of the ion-exchange model. In 0.01 M KOH, n = 3, and in 0.1 M KOH, n = 2.

As is generally found the reactions are less than first order with respect to the nucleophilic anion.²¹

TABLE III: Salt Effects of NaBra

[NaBr], M	NaOH ^b	NaF^{c}
	28.7 (29.5)	9.9
0.01	21.1(13.8)	7.6
0.02	15.0(7.4)	6.1
0.03	11.6 (5.6)	5.1
0.04	10.8 (3.6)	4.1

^a Values of $10^3 k_{\psi}$, s⁻¹ at 25.0 °C and 0.025 M CTABr, in ethanediol:H₂O 1.127:1 w/w. Values in parentheses are for reaction in aqueous CTABr. ^b 0.01 M NaOH. ^c 0.01 M NaF, pH 8.75.

TABLE IV: Reaction in the HydroxyethylSurfactant $(1)^a$

10 ³ [1], M	$10^{3}k_{\psi}, \mathrm{s}^{-1}$	10 ³ [1], M	$10^{3}k_{\psi}, s^{-1}$
3.1 6.3 12.5 15.0	$\begin{array}{c} 35.2\ (4.03)\\ 38.2\ (4.08)\\ 269\ (37.7)\\ 387\ (87.1)\\ 388\ (89.5) \end{array}$	$25.0 \\ 50.0 \\ 70.0 \\ 100$	376 (81.5) 345 (64.6) 320 (58.1) 286 (40.2)

 a At 25.0 °C in ethanediol:H_2O 1.127:1 w/w and 0.1 M NaOH. The values in parentheses are for reaction in 0.01 M NaOH.

The rate enhancements of reaction in NaOH are larger with CTACl than with CTABr, because Br^- is more effective than Cl⁻ at excluding the nucleophilic anion from the cationic micelle.²²

The micellar rate enhancement in ethane-1,2-diol: H_2O 99:1 w/w is only by a factor of two (Table II) and is smaller than in the more aqueous solvents (Figures 1 and 2 and ref 15). There is little or no micellar effect in aqueous ethanol, which is understandable because ethanol disrupts water structure and with it micellization.^{2,3}

The micellar rate enhancements in aqueous propane-1,2-diol (Figure 4) are smaller than in aqueous ethanediol.

For reactions with 0.01 M NaOH the maximum rate enhancements by CTABr are by factors of approximately 15 in water, 10 in aqueous ethanediol, 3 in aqueous propane-1,2-diol, and 2 in ethanediol: H_2O (99:1). These rate enhancements depend on the binding of the reactants to the micelle and on the second-order rate constant in the micellar pseudophase.

Salt Effects on Reaction in CTABr. Added salts typically reduce micellar rate enhancements of bimolecular reactions of hydrophilic ions.^{21,22a} The main source of the inhibition is competition between a reactive and an unreactive counterion for the micelle. The inhibition of reactions in solutions of OH⁻ or F⁻ and CTABr by Br⁻ is qualitatively similar to that observed for reaction in aqueous CTABr (Table III and ref 15), except that in solutions of OH⁻ inhibition is larger in water than in aqueous ethanediol. This difference is understandable, because the ethanediolate ion should be more strongly micellar bound than is OH⁻, and therefore less readily displaced by Br⁻. (In aqueous cationic micelles OH⁻ is readily displaced from the micelle by Br^{-,22})

Reactions in Micelles of 1. Micelles of hydroxyethyl surfactant, 1, are effective nucleophiles at high pH where the hydroxyl group is partially deprotonated, and the apparent pK_a of micellized 1 is ca. 12.4 in water.^{8,9}

We see a similar behavior in solutions of ethanediol: H_2O (Table IV) and reaction is considerably faster than that

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TABLE V: Quantitative Treatment Using the Ion-Exchange Model

medium ^a	cmc, M	K _X OH	$K_{\mathbf{X}}^{\mathbf{F}}$	β	$K_{\rm S}, {\rm M}^{-1}$	$k_{\rm M}, {\rm s}^{-1}$
aqueous CTABr, 0.05 M OH-	$2 \times 10^{-4} b$	15.5 ^b		0.8 ^b	104	0.55
	3×10^{-4} c	120		0.75	10-	0.55
aqueous diol, CTABr, 0.01 M OH	6 X 10 ⁻³	1.5		0.75	110	0.26
aqueous diol, CTABr, 0.1 M OH	5 X 10 *	1.8		0.75	300	0.33
aqueous diol, CTACI, 0.01 M OH	4×10^{-3}	1.1		0.85	200	0.37
aqueous diol, CTABr. 0.01 M F	7 × 10-4		3 ^d	0.75	110	0.11
• , , ,	7×10^{-4}		3.5^{e}	0.75	110	0.11
aqueous diol, CTABr, 0.05 M F	5×10^{-4}		5.5	0.75	110	0.08
aqueous diol, CTABr, 0.01 M OH ^{-f}	10-2	3		0.5	25	0.5
aqueous diol, CTABr, 0.1 M OH-7	5×10^{-3}	4		0.6	60	0.5

^a Diol is ethanediol, unless specified. ^b Fitted to line - - (Figure 1). ^c Fitted to line - - (Figure 1). ^d Fitted to broken line (Figure 3). ^e Fitted to solid line (Figure 3). ^f Aqueous propane-1,2-diol.

Scheme III

in 1,2-diol:H₂O solutions of CTABr (Figure 2), probably because 1 is a stronger acid than ethane- or propane-1,2diol.¹⁴ These observations are consistent with the product being formed by reaction of 1a with pNPDPP (Experimental Section).

The maximum first-order rate constants of reaction in solutions of 1 in aqueous ethanediol are 0.09 and 0.39 s^{-1} in 0.01 and 0.1 M NaOH, respectively (Table IV), whereas in water the corresponding values are 1.45 and 2.8 s⁻¹, and the optimum surfactant concentrations are much higher in aqueous ethanediol, being ca. 0.015 M, as compared with 0.0015 M in water.9

These results are consistent with pNPDPP binding less strongly to micelles in aqueous 1,2-diol, as compared with water. In addition, reaction depends upon deprotonation of 1, which is probably less in aqueous ethanediol than in water because of the higher acidity of ethanediol.¹⁴

Discussion

Qualitatively the different rate effects of micelles in aqueous 1.2-diol and in water can be due to several factors, e.g., reduced binding of the substrate because of its greater solubility in aqueous 1,2-diol than in water, or decreased uptake of reactive anion, or to a lower rate constant in the micelles in aqueous 1,2-diol. We have to analyze the rate-surfactant profiles to separate these factors, and we use treatments which have been applied to ionic reactions in aqueous micelles.²³

Ion-Exchange Model and Micellar Rate Enhancements. The treatment of micellar catalysis and inhibition is based on the assumption that reaction occurs in the micellar and aqueous pseudophases, and that equilibrium is maintained between reactants in the two pseudophases.^{2,7,8,24} In scheme III D_n is micellized surfactant, i.e., $[D_n] = [CTAX]$ - cmc, where the critical micelle concentration, cmc, is assumed to give the concentration of monomeric surfactant.24

The binding constant is given by

$$K_{\rm S} = [S_{\rm M}] / [S_{\rm W}] [D_{\rm n}] \tag{1}$$

where S_M and S_W are, respectively, substrate in the micellar

and aqueous pseudophase. The overall first-order rate constant is given by

$$k_{\psi} = \frac{k'_{\rm W} + k'_{\rm M} K_{\rm S}[{\rm D_n}]}{1 + K_{\rm S}[{\rm D_n}]} \tag{2}$$

and the first-order rate constants are given by

$$k'_{\rm W} = k_{\rm W} [\rm OH^-_{\rm W}] \tag{3}$$

$$k'_{\rm M} = k_{\rm M} m^{\rm s}_{\rm OH} = k_{\rm M} [{\rm OH}_{\rm M}^{-}] / [{\rm D}_{\rm n}]$$
 (4)

where $k_{\rm M}$, s⁻¹, the second-order rate constant in the micellar pseudophase, is defined in terms of the mole ratio of OHto surfactant head groups in the micelle.

The binding constant $K_{\rm S} \approx 10^4 {\rm M}^{-1}$, for pNPDPP in aqueous cationic micelles,²⁵ and we use this value for aqueous CTABr or CTACl, and k_W is known. The problem is therefore that of estimating $[OH_M]$.

A widely used approach is to assume that counterions bind to a micelle according to an ion-exchange equation²¹

$$OH_{M}^{-} + X_{W}^{-} \rightleftharpoons OH_{W}^{-} + X_{M}^{-}$$
(5)

$$K_{\rm X}^{\rm OH} = [OH_{\rm W}^{-}][X_{\rm M}^{-}]/[OH_{\rm M}^{-}][X_{\rm W}^{-}]$$
 (6)

where subscripts W and M denote the aqueous and micellar pseudophases, respectively.

The value of $[OH_M]$ can be estimated in terms of K_X^{OH} , assuming that β , the ratio of bound counterions to head groups, is independent of the nature and concentration of counterions:²¹

$$\beta = ([OH_{M}^{-}] + [Br_{M}^{-}]) / [D_{n}]$$
(7)

Generally values of $\beta\approx 0.75$ have been used in these treatments, 21,22c,d,23,26 in accord with independent estimates of β for ionic micelles in water.

Equations 2-4 give

$$k_{\psi} = \frac{k_{\rm W}[\rm OH_{W}^{-}] + k_{\rm M}K_{\rm S}[\rm OH_{M}^{-}]}{1 + K_{\rm S}[\rm D_{n}]}$$
(8)

Thus if $[OH_M]$ (and $[OH_w]$) are calculated (eq 6 and 7) the variation of k_{ψ} with $[D_n]$ (eq 8) can be used to estimate $k_{\rm M}$. In practice computer simulation is usually used to fit the variation of k_{ψ} with $[D_n]$ in terms of the various parameters in eq 8.

Reaction in Aqueous CTABr. The variation of k_{ψ} with [CTABr] for reaction of pNPDPP in aqueous NaOH can be fitted by using the ion-exchange pseudophase model. The values of the parameters used to calculate the broken

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lines in Figure 1 are given in Table V. The value of $K_{\rm S} \approx 10^4 \,{\rm M}^{-1}$ is in reasonable agreement with the experimental value,²⁵ but because pNPDPP is very strongly micellar bound in aqueous CTABr, the treatment is insensitive to the value of $K_{\rm S}$, and we can neglect the contribution of reaction in the aqueous pseudophase. As is often the case the rate-surfactant profile can be fitted by various combinations of the parameters,^{23,27} and two sets of them are illustrated in Figure 1 and Table V. The values of $K_{\rm Br}^{\rm OH}$ and β are similar to those estimated earlier.^{22b-d} The cmc is lower than that in aqueous CTABr,²⁸ but the "kinetic" cmc is often low for reactions of very hydrophobic substrates.

Reactions in Aqueous 1,2-Diol. Reaction in aqueous ethanediol containing NaOH involves attack by diolate monoanion (Results). However, the variation of k_{ψ} with [surfactant] can be fitted to the ion-exchange pseudophase model (Figures 2 and 4), although now the ion-exchange constant is written as

$$K_{\rm X}^{\rm RO} = [{\rm RO}_{\rm W}^{-}][{\rm X}_{\rm M}^{-}]/[{\rm RO}_{\rm M}^{-}][{\rm X}_{\rm W}^{-}]$$
 (9)

where RO⁻ denotes the diolate ion as the dominant nucleophile.

A similar treatment can be applied to reaction with F^- (Figure 3). The parameters used in these calculations are in Table V, and some of these are very different from those estimated for reaction in aqueous CTABr (Table V). In particular $K_{\rm S}$ is much smaller in aqueous 1,2-diol than in water,²⁵ which is understandable because the solubility of pNPDPP is increased by the 1,2-diol, especially with propane-1,2-diol, so that there is less substrate bound to the micelles. Also $K_{\rm Br}^{\rm OR}$ is smaller than $K_{\rm Br}^{\rm OH}$ (Table V), because the diolate monoanion should be less hydrophilic than OH⁻ and therefore bind more strongly to a cationic micelle. Although the ion-exchange model fits the kinetic data direct comparison of the values of $K_{\rm Br}^{\rm OR}$ and $K_{\rm Br}^{\rm OH}$ is complicated because $K_{\rm Br}^{\rm OR}$ is a complex quantity which involves the extents of deprotonation of ethanediol in both the aqueous and micellar pseudophases. However, our results are consistent with nucleophilic attack by the diolate ion.

It appears that K_s in aqueous ethanediol increases with increasing [NaOH] (Table V), possibly because NaOH "salts-out" pNPDPP and therefore increases its binding to the micelle, cf. ref 22d and 29.

Critical micelle concentrations are increased by addition of 1,2-diols to water,⁶ and our values of the "kinetic" cmc are also larger in aqueous 1,2-diol than in water. The value of β is apparently lower in aqueous propane-1,2-diol than in the other solvents. The micellar effects are small in this solvent, so there are considerable uncertainties in the parameters used to fit the rate data. Organic solutes which bind to micelles typically reduce β ,³⁰ because they reduce the surface charge of the micelle, and propane-1,2-diol may be sufficiently hydrophobic to show this effect.

Alternative Treatment of Ion Exchange. The widely used ion-exchange pseudophase model based on eq 6 involves the assumption that β does not change as reactive counterion, e.g., OH^- , is added or the surfactant concentration changed.²¹ This assumption appears to fail when the only anions in the solution are very hydrophilic, e.g., OH⁻ or F^{-.29,31} In these systems the data can be fitted by a mass-action model which assumes that β increases with increasing [OH⁻] or [F⁻], eq 10.³²

$$D_n + OH_W \xrightarrow{K'_{OH}} OH_M \xrightarrow{}$$
 (10)

The binding of inert counterion, e.g., Br^- , could similarly follow eq 11

$$D_n + Br_W \xrightarrow{K'_{Br}} Br_M$$
 (11)

so that

$$K'_{OH} = [OH_{M}^{-}]/([D_{n}] - [OH_{M}^{-}] - [Br_{M}^{-}])([OH_{T}^{-}] - [OH_{M}^{-}])$$
(12)

 $K'_{Br} =$

$$[Br_{M}^{-}]/([D_{n}] - [OH_{M}^{-}] - [Br_{M}^{-}])([Br_{T}^{-}] - [Br_{M}^{-}])$$
 (13)

where the subscript T denotes the total concentration.

Hydroxide ion appears to bind very weakly to cationic micelles,²² so that in CTABr $[OH_T^-] >> [OH_M^-]$. With this assumption and eq 12 and 13, and mass balance, the value of $[OH_M^-]$, is given by

$$(K'_{Br} + K'_{OH}K'_{Br}[OH_{T}^{-}])[OH_{M}^{-}]^{2} + (1 + K'_{OH}[OH_{T}^{-}] + K_{Br}'[Br_{T}^{-}] - K'_{Br}[D_{n}])(K'_{OH}[OH_{T}^{-}])[OH_{M}^{-}] - (K'_{OH}[OH_{T}^{-}])[D_{n}] = 0$$
(14)

assuming that $K' o_{H}$ and K'_{Br} are independent parameters.

The quadratic eq 14 can be solved for given concentrations of OH⁻ and CTABr, assuming values of K'_{OH} and K'_{Br} .³³ For reaction of pNPDPP with OH⁻ we can neglect the contribution of reaction in the aqueous pseudophase so that

$$k_{\psi} = k_{\rm M} K_{\rm S} [\rm OH_{\rm M}^{-}] / (1 + K_{\rm S} [\rm D_{\rm n})]$$
 (15)

using values of $[OH_M]$ calculated from eq 14.

For reactions of pNPDPP and other substrates we fitted the kinetic data taking $K'_{OH} = 55 \text{ M}^{-1}$, and $K_{\rm S} \approx 10^4 \text{ M}^{-1}$, and we use these values here.²⁹ The variation of k_{ψ} with [CTABr] in aqueous 0.05 M NaOH (Figure 1) can be fitted to eq 14 and 15 taking $K'_{\rm Br} = 2200 \text{ M}^{-1}$, $k_{\rm M} = 0.75 \text{ s}^{-1}$, and cmc = $3 \times 10^{-4} \text{ M}$. The fit is insensitive to the values of $K_{\rm s}$ and cmc, although the values are similar to those used with the ion-exchange model.

This treatment makes no assumptions regarding the value of β , which in principle can range from 0 to 1, although the lower limit cannot be reached because of counterion due to the presence of monomeric surfactant, and the upper limit could only be reached at very high [counterion].²⁹

In comparing these two models we note that $K'_{\rm Br}/K'_{\rm OH} \approx 40$ would be equivalent to the ion-exchange constant, $K_{\rm Br}^{\rm OH}$, for the hypothetical situation of $\beta = 1$. In the "conventional" ion-exchange treatment the estimation of $K_{\rm Br}^{\rm OH}$, or other equivalent parameter,²¹⁻²³ is critically dependent upon the assumed value of β . We believe that both the ion-exchange model, eq 6, and the mass action model, eq 10 and 11, are limiting models which fit the kinetic data, but only approximate to reality. In particular, the ion-exchange constants obtained by these fitting pro-

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⁽³³⁾ If both reactive and unreactive ions bind strongly to the micelles the solution of eq 10-13 will involve a cubic equation.

TABLE VI: Second-Order Rate Constants in Micelles and in Bulk Solvents^a

medium	$k_{2}^{m}, M^{-1} s^{-1}$	$k_{W}, M^{-1} s^{-1}$
aqueous CTABr, OH⁻	0.10 ^b	0.48
aqueous CTABr, OH-	0.08	0.48
aqueous diol CTABr, OH-	0.04	0.36
aqueous diol CTACI, OH-	0.05	0,36
aqueous diol CTABr, OH ^{- c}	0.07	0.50
aqueous diol CTABr, F⁻	0.016	0.08

^a From values of $k_{\rm M}$ in Table V, the diol is ethanediol unless specified. ^b Calculated by use of the mass action model. ^c In aqueous propane-1,2-diol.

cedures appear to depend very much on the assumptions made in deriving the various equations.

Comparison of the Different Models. The variation of k_{ψ} with [surfactant] follows the predictions of the ion-exchange model (eq 5-8), but a problem with the treatment is that the data can be fitted with various combinations of the parameters, in particular β and K_X^{OH} . The values of β and K_X^{OH} which we use in fitting the kinetic data are similar to those estimated independently,^{22b-d,23,27,30} but we do not believe that the kinetic method can be used to estimate these values with any certainty. Despite these uncertainties variations in k_M are not large, so that the treatment is apparently satisfactory for estimation of second-order rate constants in the micellar pseudophase, despite assumptions regarding ion binding to micelles.

Our rate data for reaction with OH⁻ in aqueous CTABr can be fitted equally well to the ion-exchange model (eq 5-8) or the mass action model (eq 10-14), and the two models lead to very similar values of $k_{\rm M}$ (Table V), and these values are similar to those of ca. 0.7 s⁻¹ for reaction in CTAOH and CTAOH + NaOH, estimated by using the mass action model.²⁹

We did not apply the mass-action model (eq 10–14) to reactions in aqueous 1,2-diols, because the treatment involves the assumption that Br⁻ binds much more strongly than the lyate ion to the micelle. This assumption may be valid in water where $K_{\rm Br}^{\rm OH} > 10$, but it would probably fail in aqueous 1,2-diols where the corresponding ion-exchange parameters are much lower, i.e., where lyate ion competes more effectively with Br⁻ (Table V).

Rate Constants in Micelles and in Bulk Solution. The second-order rate constants, $k_{\rm M}$, are calculated by taking concentration as a mole ratio, which can be specified unambiguously. But these constants cannot be compared directly with $k_{\rm W}$ in water, or aqueous 1,2-diol, for which concentration is specified, by convention, as molarity. They can be compared by assuming a volume element of reaction in the micellar pseudophase and estimating the molarity of the reagent, e.g., the lyate ion, in that volume element. Arbitrarily we could assume this volume to be that of the micelles, or of the Stern layer of the micelles. If we assume that the molar volume of the Stern layer of micelles of CTABr is 0.14 L³⁴ we can define a second-order

rate constant, k_2^{m} , M⁻¹ s⁻¹, eq 16.

$$k_2^{\rm m} = 0.14k_{\rm M}$$
 (16)

The rate constants k_W and k_2^m have the same dimensions and can be compared directly. We also apply eq 16 to reactions in micelles in aqueous 1,2-diols (Table VI). Some of the values of k_2^m given in Table VI are the average for reactions in different concentrations of OH⁻ or F⁻, and, except for one of the values for reaction in aqueous CTABr, are calculated by use of the ion-exchange model.

The conversion of the units of $k_{\rm M}$ and $k_2^{\rm m}$ could be carried out by taking the molar volume of the micelles as the volume element of reaction,^{21,22c,26} which would approximately double $k_2^{\rm m}$. The second-order rate constants, $k_{\rm M}$, or $k_2^{\rm m}$ (Table VI) are not very different for reactions of the lyate ions in the various micelles. The second-order rate constants, $k_2^{\rm m}$, and $k_{\rm W}$, M^{-1} s⁻¹ (Table VI), are consistently similar in magnitude, although in all cases $k_{\rm W} > k_2^{\rm m}$ and $k_{\rm W}/k_2^{\rm m}$ varies between 5 and 9.

There are now many examples of bimolecular reactions in aqueous micelles in which second-order rate constants in micellar and aqueous pseudophases are similar in magnitude.^{7,8,23,25,26,35,36} It is generally assumed that the observed overall rate enhancements of bimolecular reactions are due to concentrations of both reactants in the small volume of the micellar pseudophase,³⁷ rather than to different second-order rate constants in micelles and water, and this generalization seems to apply also to reactions in normal micelles in aqueous 1,2-diols. In reactions of pNPDPP with lyate ion the hydrophobic substrate and hydrophilic anion are probably located, on the average, in different regions of the micelle,⁴⁰ which would make k_W larger than k_2^m .

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⁽³⁷⁾ It appears that this generalization does not apply to aromatic substitutions by N_3^- where the second-order rate constants in the micelles are much larger than those in water,³⁸ and typically second-order rate constants for reactions between nonionic reactants,^{25,36} and for hydrogen ion catalyzed reactions,^{31a} are smaller than in water. Some of these differences can be ascribed to the polarity of micelles, which also affects the rate constants of spontaneous unimolecular, or water-catalyzed, reactions.^{8,39}