Modelling of Micellar Effects upon Substitution Reactions with Moderately Concentrated Hydroxide Ion

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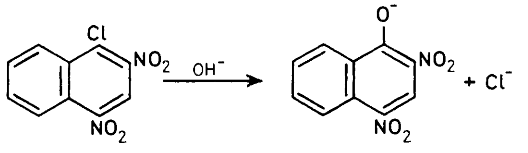
Cationic micelles of cetyltrimethylammonium chloride and bromide (CTACl and CTABr) speed reactions of 2,4-dinitro-1-naphthyl chloride (DNNC) and *p*-nitrophenyl diphenyl phosphate (*p*NPDPP) with OH^-. The pseudophase ion-exchange model fits the data for reaction with $[OH^-] < 0.05$ mol dm^{-3}, but the reaction is faster than predicted at higher ratios of $[OH^-]$. The deviations from theory are largest with high ratios of $[OH^-]$ to $[Cl^-]$ or $[Br^-]$ and are larger in CTABr than in CTACl. A mass-action-like model with each anion binding independently to the micelle fits the data for 10^{-3}–0.5 mol dm^{-3} OH^-.

The pseudophase model of micellar effects upon rate and equilibrium constants is based on the assumption that normal aqueous micelles bind reactants and provide a reaction medium distinct from that of bulk solvent.[1–5] Quantitative applications of this model require estimation of reactant concentrations in the micellar pseudophase. Concentrations of non-ionic solutes in micelles can generally be measured directly, and there is satisfactory agreement between equilibrium binding constants estimated kinetically and by various physical methods. The concentrations of some inorganic ions in micellar pseudophases can, in princicple, be estimated directly, for example electrochemically[6] or spectrally,[7] but these methods cannot be used for some important ionic reagents, *e.g.* OH^-. Concentrations of OH^-, or other reactive hydrophilic ions, at ionic micellar surfaces are often calculated by assuming that reactive and inert ions compete for the micellar surface, and that it is saturated by counter-ions, *i.e.* that the fractional coverage, β, is constant.[3–5] This pseudophase ion-exchange model fits a great deal of data for reactions in dilute electrolyte[3–5,8] although its validity has been questioned on experimental and theoretical grounds.[9,10]

An alternative theoretical treatment involves the assumption that micellar binding of each counter-ion is governed by a mass-action-like equation and that β increases with increasing ionic concentration.[11,12] Alternatively coulombic contributions to counter-ion binding to ionic micelles can be estimated by solving the Poisson–Boltzmann equation,[12c,13–17] and micellar rate effects have been analysed by separating the non-specific, coulombic effects, and the specific effects which depend on dispersive and hydration forces. This method is more complicated than the simpler treatments.

All these models assume that the micelle can be regarded as a pseudophase distinct from the bulk solvent, but a recent treatment, based on transition-state theory, relates micellar rate effects to the variation of the fractional ionization, $\alpha = 1 - \beta$, with changes in the hydrophilic counter-ions.[10]

The various pseudophase treatments are reasonably satisfactory for reactions with dilute ionic reagents, but the ion-exchange model fails for elimination from DDT and related chlorides in moderately concentrated OH^-.[18] The fit with theory is satisfactory for dilute OH^-, but rates increase faster than predicted with increasing $[OH^-]$. Ionescu *et al.*[18a] postulated incursion of a reaction path across the Stern layer for the attack of OH^- in the aqueous pseudophase upon micellar-bound substrate.[18] These apparent failures of the simple pseudophase model may be characteristic of eliminations, or may represent a breakdown of the ion-exchange equations in moderately concentrated OH^-. Rates of micellar reactions in moderately concentrated OH^-, in the absence of inert anions, fit a mass-action-like model,[11a] and this treatment has also been applied to reactions of OH^- in the presence of inert anions.[11b,12a] We have tested a similar treatment for reactions of 2,4-dinitro-1-naphthyl chloride (DNNC) and *p*-nitrophenyl diphenyl phosphate (*p*NPDPP) in mixtures of OH^- and Cl^- or Br^-, with up to 0.5 mol dm^{-3} OH^-. The reactions are:



DNNC

$$(PhO)_2P(O)OC_6H_4NO_2\text{-}p + OH^- \longrightarrow (PhO)_2PO_2^- + {}^-OC_6H_5NO_2\text{-}p$$

*p*NPDPP

These substrates are hydrophobic, and bind strongly to micelles.[11a] This factor is important, because OH^- can 'salt-out' solutes from water and drive them into micelles,[11a] so that with hydrophilic substrates, it may be difficult to distinguish between the rate enhancements due to increasing micellar concentration of OH^- and 'salting-out' of substrate into the micelle.

The reaction of OH^- with DNNC is a multistep process,[19] but we are concerned only with a comparison of the rate constants of formation of the naphtholate ion in water and in cationic micelles rather than with the detailed mechanism.

The cationic surfactants were cetyltrimethylammonium† chloride and bromide (CTACl and CTABr). Both surfactants give micelles which are approximately spherical in dilute surfactant and electrolyte, but growth is important with CTABr and its micelles become rod-like, especially in high $[Br^-]$.[20]

Results and Discussion

2,4-Dinitro-1-naphthyl Chloride.—Reaction of DNNC with OH^- in CTACl or CTABr was followed over a wide range of $[OH^-]$, up to 0.5 mol dm^{-3}, with both NaOH and KOH

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† Cetyl = hexadecyl ($C_{16}H_{33}$).

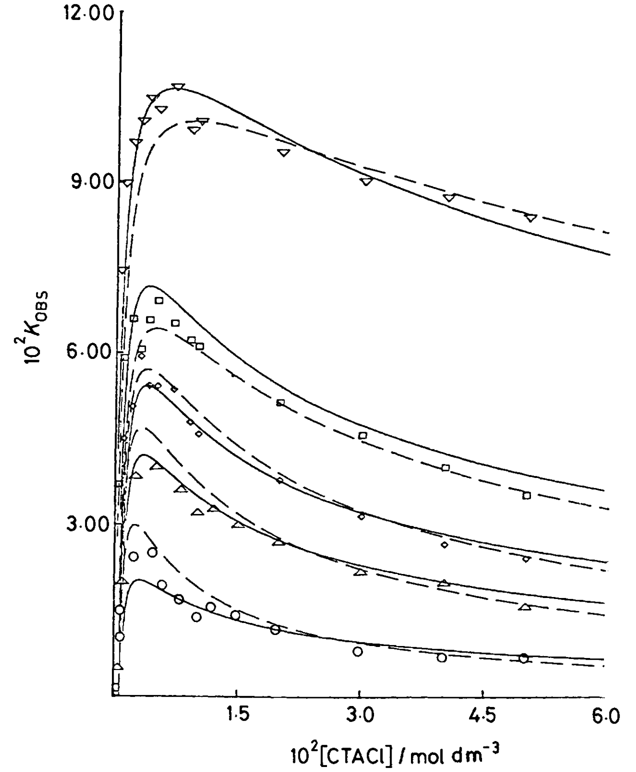


Figure 1. Variation of k_{obs} for reaction of DNNC in CTACl. The dashed lines were calculated by using the ion-exchange model and the solid lines by using the mass-action-like model.

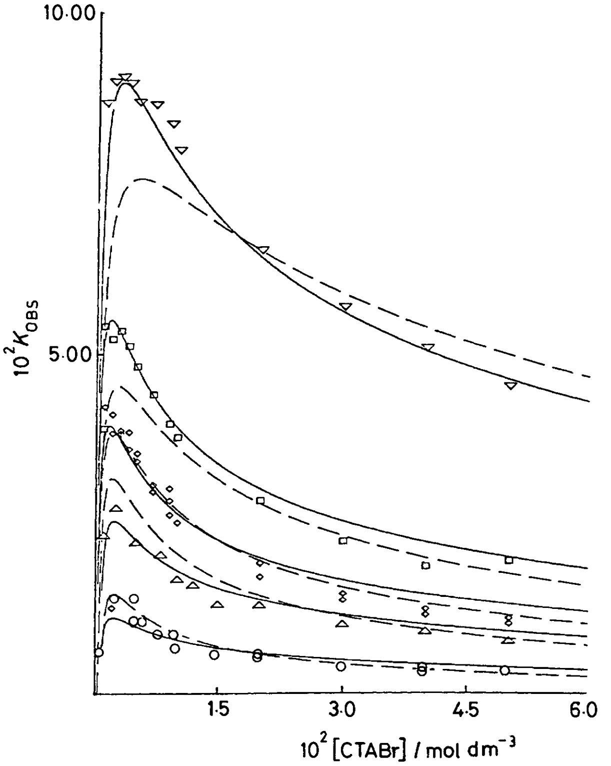


Figure 2. Variation of k_{obs} for reaction of DNNC in CTABr. Key as in Figure 1.

(Figures 1 and 2). Some first-order rate constants, k_{obs}, for the reaction in dilute OH^-, are from earlier work,[21] and values of k_{obs} are similar in NaOH and KOH.

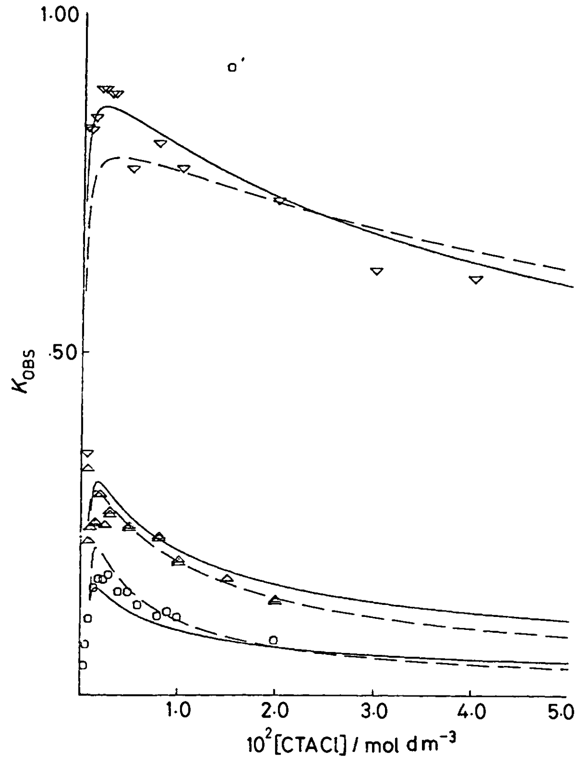


Figure 3. Variation of k_{obs} for reaction of *p*NPDPP in CTACl. Key as in Figure 1.

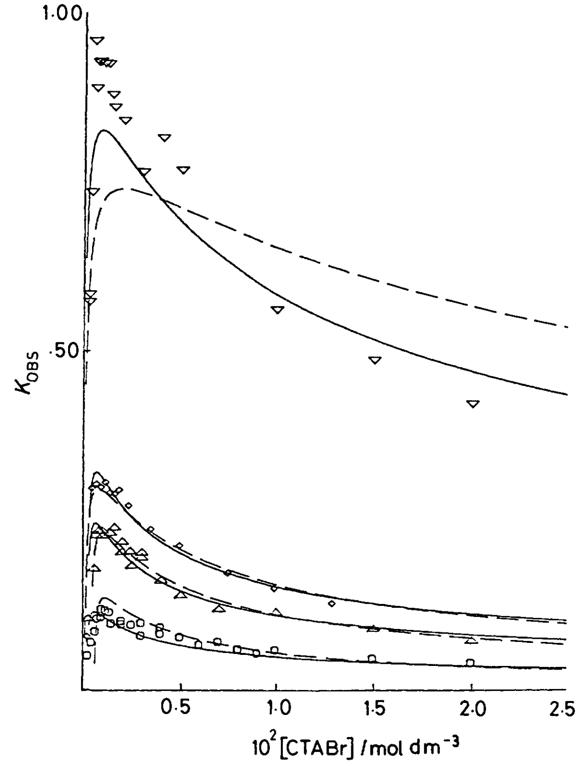


Figure 4. Variation of k_{obs} for reaction of *p*NPDPP in CTABr. Key as in Figure 1.

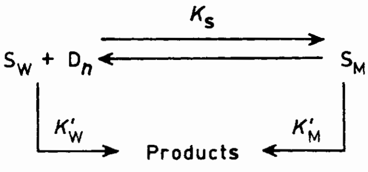
p-*Nitrophenyl Diphenyl Phosphate*.—Micellar effects upon the reaction of *p*NPDPP with OH^- are shown in Figures 3 and 4. Some of the data in dilute OH^- are from earlier work.[22]

Table 1. Fitting parameters: ion-exchange model.[a]

Surfactant	Substrate	$[OH^-]$/ mol dm^{-3}	10^4 c.m.c./ mol dm^{-3}	k_M/s^{-1}
CTABr	*p*NPDPP	0.01	6	0.47
CTABr	*p*NPDPP	0.03	4	0.48
CTABr	*p*NPDPP	0.05	1	0.51
CTABr	*p*NPDPP	0.5	0	1.02
CTACl	*p*NPDPP	0.01	5	0.54
CTACl	*p*NPDPP	0.03	5	0.54
CTACl	*p*NPDPP	0.5	0	1.15(1.3)[b]
CTABr	DNNC	0.01	7	0.080
CTABr	DNNC	0.03	3	0.085
CTABr	DNNC	0.05	1	0.092
CTABr	DNNC	0.1	0.7	0.092
CTABr	DNNC	0.5	0	0.12
CTACl	DNNC	0.01	6	0.1
CTACl	DNNC	0.03	5	0.1
CTACl	DNNC	0.05	5	0.12
CTACl	DNNC	0.1	4	0.12
CTACl	DNNC	0.5	1	0.16(0.12)[c]

[a] At 25 °C and fitted taking the following parameters unless specified: $\beta = 0.8$ and 0.72 for CTABr and CTACl, respectively; $K_{Br}^{OH} = 14$; $K_{Cl}^{OH} = 4$; $K_s = 10^4$ and 1 600 mol dm^{-3} for *p*NPDPP and DNNC, respectively; $k_W = 0.48$ and 0.006 dm^3 mol^{-1} s^{-1} for *p*NPDPP and DNNC, respectively. [b] $K_{Cl}^{OH} = 8$. [c] $\beta = 0.9$.

Analysis of Kinetic Data.—Ion exchange. The overall reactions are illustrated in the Scheme, where S is the substrate, D_n is the micellized surfactant and k'_W and k'_M are first-order rate constants for reaction in the aqueous and micellar pseudophases, respectively.



Scheme.

This scheme leads to equation (1).[23]

$$k_{obs} = \frac{k'_W + k'_M K_s([D] - \text{c.m.c.})}{1 + K_s([D] - \text{c.m.c.})} \tag{1}$$

where K_s is the substrate binding constant to micellized surfactant, the concentration of which is that of total concentration ([D]) less that of monomeric surfactant, *i.e.* $[D_n] = [D] - \text{c.m.c.}$ (The critical micelle concentration, c.m.c., is taken as the concentration of monomeric surfactant[23]).

The first-order rate constants can be written as second-order rate constants, k_W and k_M, with the concentration of OH^- in the micellar pseudophase written as a mole fraction[4,5] (the

$$k'_W = k_W[OH_W^-] \tag{2}$$

$$k'_M = k_M[OH_M^-]/[D_n] = k_M m_{OH}^s \tag{3}$$

quantities [ ] denote molar concentrations in terms of total solution volume).

Competition between OH^- and halide ion (X^-) is written as:

$$K_x^{OH} = \frac{[OH_W^-]\,[X_M^-]}{[OH_M^-]\,[X_W^-]} \tag{4}$$

and

$$\beta = m_x^s + m_{OH}^s = \text{constant} \tag{4'}$$

By combining (4) and (4′), the concentration of micelle-bound OH^- is given by equation (5):[4,21]

$$(m_{OH}^s)^2 + m_{OH}^s\left(\frac{[OH_T^-] + K_x^{OH}[X_T^-]}{(K_x^{OH} - 1)[D_n]} - \beta\right) - \frac{[OH_T^-]\beta}{(K_x^{OH} - 1)[D_n]} = 0 \tag{5}$$

where T denotes total concentration.

Equations (1), (2), (3), and (5) can be combined and a simple computer program allows simulation of the overall rate–surfactant profiles. The parameters used in the fitting are given in Table 1. The values of the c.m.c. are as in ref. 21, except that for 0.5 mol dm^{-3} OH^- the c.m.c. ≃ 0.

The variation of k_{obs} with [CTAX] for various $[OH^-]$ was fitted on the assumption that k_W would be unaffected by surfactant, that β and K_x^{OH} are constant for a given surfactant and that k_M would not change markedly with [surfactant] (Tables 1 and 2). The quality of the fit between the calculated and experimental values is not a sensitive test of the validity of the fitting parameters. For example, values of k_{obs} for the reaction of OH^- with *p*NPDPP in CTACl can be fitted with values of K_{Cl}^{OH} that differ by a factor of 2. The fits are shown in Figures 1 and 2.

The fits are good for dilute OH^-, in agreement with earlier experiments,[3–5,21,22] but there are marked deviations between the experimental and theoretical values of k_{obs} at higher $[OH^-]$, and estimated values of k_M increase with $[OH^-]$, *cf.* ref. 18. These observations agree with earlier evidence that the ion-exchange model fails for eliminations when $[OH^-]$ is large.[18a] The fits shown in Figures 1–4 for reactions in 0.5 mol dm^{-3} OH^- required a large increase in k_M relative to the value in dilute OH^- (Table 1).

Mass-action-like Model.—Micellar binding of X^- and OH^- is assumed to follow equations (6) and (7):[11,12a]

$$K'_x = [X_M^-]/[X_W^-]([D_n] - [X_M^-] - [OH_M^-]) \tag{6}$$

$$K'_{OH} = [OH_M^-]/[OH_W^-]([D_n] - [X_M^-] - [OH_M^-]) \tag{7}$$

For reactions in CTAOH, fits of rate–surfactant profiles were satisfactory with $K'_{OH} = 55$ dm^3 mol^{-1}, and we use that value.[11a] We took $K'_{Cl} = 450$ dm^3 mol^{-1} and $K'_{Br} = 3\,000$ dm^3 mol^{-1}. Equations (1)–(3), (6), and (7) were combined and the predicted rate–surfactant profiles are given in Figures 1 and 2.

The fit of theory and experiment is reasonably good and fitted values of k_M are within ±8% for reaction of DNNC, although the variations of k_M are larger for reaction of *p*NPDPP (Table 2). The values of K'_{OH}, K'_{Cl}, and K'_{Br} are similar to those used earlier,[11,24] but differ slightly from those used by Rodenas and co-workers.[12a] Equally good fits could probably be obtained with other combinations of these ion-bonding parameters.

Comparison of rate constants for reactions in CTACl and CTABr illustrates the importance of the ratio of OH^- to inert anion. With 0.5 mol dm^{-3} OH^-, values of k_{obs} at the rate maximum, where substrates are extensively bound, are similar in CTACl and CTABr but as the ratio of OH^- to inert anion decreases, either by addition of surfactant or decrease in $[OH^-]$, the difference in the values increases (Figures 1–4). Values of k_{obs} in 0.5 mol dm^{-3} OH^- at the rate maxima are similar to those in CTAOH with added 0.5 mol dm^{-3} OH^-.[11a]

This model fits the data reasonably well even for reactions in

Table 2. Fitting parameters: mass-action-like model.[a]

Surfactant	Substrate	[OH$^-$]/mol dm^{-3}	k_M/s^{-1}
CTABr	*p*NPDPP	0.01	1.00
CTABr	*p*NPDPP	0.03	0.75
CTABr	*p*NPDPP	0.05	0.75
CTABr	*p*NPDPP	0.5	1.00
CTACl	*p*NPDPP	0.01	0.7
CTACl	*p*NPDPP	0.03	0.70
CTACl	*p*NPDPP	0.5	0.95
CTABr	DNNC	0.01	0.14
CTABr	DNNC	0.03	0.14
CTABr	DNNC	0.05	0.14
CTABr	DNNC	0.1	0.14
CTABr	DNNC	0.5	0.14
CTACl	DNNC	0.01	0.12
CTACl	DNNC	0.03	0.12
CTACl	DNNC	0.05	0.12
CTACl	DNNC	0.1	0.12
CTACl	DNNC	0.5	0.13

[a] Fitting parameters as in Table 1, except for K'_{OH}, K'_{Cl}, and K'_{Br} = 55, 450, and 3 000 l mol^{-1}, respectively.

0.5 mol dm^{-3} OH$^-$ (Figures 1–4). The increases in k_M are much smaller than those based on the ion-exchange model (Tables 1 and 2).

Comparison of Ion-binding Models.—The ion-exchange and mass-action-like models fit the experimental data equally well in dilute OH$^-$. These data can also be fitted by a model in which coulombic interactions are calculated by solving the Poisson–Boltzmann equation and specific interactions are written in terms of a Volmer isotherm.[16b,c]

Micellar rate enhancements in bimolecular reactions can be explained in terms of the concentration of reactants at the micellar surface. Comparison of second-order rate constants in aqueous and micellar pseudophases requires that concentrations in the latter be expressed as molarity rather than a mole ratio. The reactive molar volume in the micellar pseudophase, V_M, can be taken either as that of the micelle, or of some reaction region on its surface, and estimates of V_M range from 0.14–0.37 dm^3.[3–5,8] The second-order rate constant, k_2^m/dm^3 mol^{-1} s^{-1}, is given by:

$$k_2^m = V_M k_M \qquad (8)$$

and we used a value of V_M = 0.14 l.[4,5]

In agreement with earlier work [11a] values of k_2^m for DNNC are larger than k_W, with $k_2^m/k_W \simeq 2$, and for *p*NPDPP they are smaller, with $k_2^m/k_W \simeq 0.2$. Results are similar if k_2^m is calculated by solving the Poisson–Boltzmann equation and assuming that reaction occurs in a 2.4 Å shell at the micellar surface.[16] The widely observed differences in k_2^m/k_W for various reactions may be due to a dependence of V_M upon the reactants.[25] The recent treatment of Hall [10] depends upon estimation of the extent to which micelles change the difference of free energies of initial and transition states, and does not depend explicitly upon reactant concentrations in the micellar pseudophase or upon the second-order rate constant in that pseudophase. This model and the pseudophase models are therefore calculating the incremental free energy of reaction to the micellar interaction in different ways.

The ion-exchange model is based on an assumed constance of β,[3–5,8] which is probably reasonable when a strongly binding ion, such as Br$^-$, is in relatively high concentration, but it fails when this condition is not satisfied. In addition, the exchange constant, K_x^{OH}, equation (4), may vary with extensive changes in [counter-ion] because non-specific coulombic and specific dispersive interactions will have different dependences upon [counter-ion] and their relative importance depends upon the counter-ion.[16b,c] The ion-exchange model has been applied to micellar reactions in solutions of mixed inert ions,[4,8] but the simple exchange equation (4) fails when applied to reactions in mixtures of very hydrophilic anions, *e.g.* OH$^-$ and F$^-$, based on their competition with Br$^-$ as calculated by fluorescence quenching. These experiments showed that OH$^-$ did not directly displace Br$^-$ from the surface of a cationic micelle. This conclusion is consistent with n.m.r. line widths of Br$^-$ in CTABr + OH$^-$.[26]

The mass-action-like model [equations (6) and (7)] makes the unreasonable prediction that the limits of β are 0 and 1 at low and high [counter-ion], respectively, although these limits will not be approached within reasonable concentrations of added electrolyte.[11] We can assign arbitrary limits to β, and data can also be fitted on this basis.[27] However, K'_{OH} and K'_x may represent changes in the physical structure of the micelle, *e.g.* size or surface charge density, which affect ion binding. Despite the uncertainties in the theoretical significance of the various parameters, this model provides a simple and convenient way of treating micellar effects upon ionic reactions, and the ion-exchange model is satisfactory if the counter-ions are in low concentration.

Values of k_2^m/k_W inevitably depend upon assumed values of V_M, and some workers have estimated V_M on the assumption

Table 3. Supplementary data. Reactions with 0.5 mol dm^{-3} OH$^-$.[a]

*p*NPDPP													
10^3[CTABr]/mol dm^{-3}	0.3	0.4	0.5	0.6	0.7	0.8	1.0	1.2	1.4	1.5	2.0	3.0	
kψ/s^{-1}	0.58	0.74	0.96	0.89	0.93	0.93	0.92	0.92	0.88	0.86	0.84	0.72	
10^3[CTABr]/mol dm^{-3}	4.0	5.0	10.0	15.0	20.0								
kψ/s	0.82	0.77	0.56	0.49	0.43								
10^3[CTACl]/mol dm^{-3}	0.45	0.6	0.7	1.0	2.0	3.0	5.0	7.5	10.0	20.0	30.0	40.0	
kψ/s^{-1}	0.22	0.33	0.92	0.94	0.91	0.94	0.85	0.81	0.78	0.68	0.63	0.63	
DNCN													
10^2[CTABr]/mol dm^{-3}	0.1	0.2	0.3	0.4	0.5	0.7	0.9	1.0	2.0	3.0	4.0	5.0	
10^2kψ/s^{-1}	8.71	9.02	9.09	9.00	8.72	8.68	8.40	8.02	6.55	5.72	5.12	4.56	
10^2[CTACl]/mol dm^{-3}	0.05	0.1	0.2	0.3	0.4	0.5	0.7	0.9	1.0	2.0	3.0	4.0	5.0
10^2kψ/s^{-1}	7.48	9.01	9.72	10.1	10.5	10.3	10.7	9.94	10.1	9.57	9.07	8.79	8.44

[a] At 25.0 °C.

that $k_2^m = k_W$.[25b] There is no obvious way of testing the validity of the various assumptions regarding V_M, and in any event, molarity is justified as a unit of concentration in solution kinetics by virtue of convenience rather than exactitude. In addition the hypothesis that micellar reactions are localized within the Stern layer is almost certainly an oversimplification.

Experimental

Materials.—The preparation and purification of reagents and surfactants have been described.[11,21,22] There were no minima in plots of surface tension against logarithm of surfactant concentration. Reactions were carried out in CO_2-free water and the most dilute OH^- solutions were made up in an atmosphere of N_2.

Kinetics.—Reactions were followed spectrophotomerically at 25.0 °C by using Beckman, Perkin-Elmer, Gilford, or HP diode array spectrometers for the slower, and a Durrum stopped-flow spectrometer for the faster reactions. Reaction of DNNC was followed at 390 nm and *p*NPDPP at 405 nm. Substrates were added in MeCN so that the final solution contained *ca.* 0.3 vol% MeCN and *ca.* 10^{-5} mol dm^{-3} substrate. First-order rate constants, k_{obs}/s^{-1} were calculated using a simple first-order least-squares program.[21]

Data Simulation.—Variations of k_{obs} with [surfactant] were simulated using HP 300 or 9840 or IBM XT desk-top computers.[11,21,22]

Values of β (Table 1) for the ion-exchange treatment are consistent with physical measurement,[3–5,20c,d] but equally good fits can be obtained with a range of β values.

Acknowledgements

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