# The Effects of Single- and Twin-tailed Ionic Surfactants upon Aromatic Nucleophilic Substitution

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Reactions of $OH^-$ with 2,4-dinitro-1-chloro-benzene and -naphthalene have been examined in solutions of didodecyldimethylammonium chloride and hydroxide. Rate effects were analysed quantitatively in terms of distribution of reactants between water and the colloidal particles. Second-order rate constants at the surface of the particles are very similar to those in normal aqueous micelles of cetyltrimethylammonium hydroxide, chloride, and bromide and *p*-octyloxybenzyltrimethylammonium bromide and are slightly higher than in water. Similar observations were made on the reaction of $OH^-$ with 2,4-dinitro-1-fluorobenzene.

Single-chain surfactants spontaneously form micelles in water.[1] With dilute surfactant micelles appear to be approximately spherical, but with increasing concentration of surfactant, and especially in the presence of added salt, micelles grow and become ellipsoidal.[2] Growth is very dependent upon the nature of the counterion, for example with quaternary ammonium surfactants growth occurs very readily with the bromide,[2,3] less readily with chloride,[4] and with the hydroxide[5] and sulphate[6] there seems to be little growth above some minimum size.

Surfactants can assemble in a variety of ways and Ninham, Evans, and their co-workers have emphasized the importance of monomer packing.[7] In their view the tendency of surfactants to form micelles or bilayers, either vesicular or lamellar, depends upon the relations between the volume of the hydrophobic part of the surfactant, its length, and the area occupied by the surfactant head group. On this criterion twin-chain surfactants should have a strong tendency to form vesicles.[7b]

Dioctadecyldialkylammonium salts are insoluble in water, but give vesicles on sonication,[8] and large vesicles can also be formed by evaporation.[9] These vesicles are unstable, although relatively stable vesicles can be made by cross-linking the monomers.[8a,10]

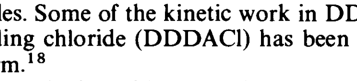
Evans and his co-workers showed that didodecyldimethylammonium hydroxide (DDDAOH) is soluble in water, although the corresponding bromide is almost insoluble.[7b,11] They pointed out that DDDAOH could form vesicles spontaneously, based on packing considerations,[7] and provided support for this hypothesis from various physical measurements. They also suggested that the colloidal assemblies of DDDAOH could have an inside, as well as an outside, surface.[7b] However, with increasing [DDDAOH], the solutions became viscous, which is inconsistent with the existence of spherical particles, and it was assumed that extended structures were present, but solutions were clear, isotropic, and have low to moderate viscosities up to *ca.* 0.1M.

Hydroxide ion surfactants give micelles which are highly charged,[5] because high charge-density, hydrophilic ions have little tendency to associate specifically with a quaternary ammonium colloid. Ions such as fluoride and formate behave similarly[12] and Evans and his co-workers postulate vesicle formation with didodecyldimethylammonium surfactants with these counterions.[11]

An important point is that DDDAOH, and similar surfactants, assemble spontaneously, thus their colloidal particles should be thermodynamically stable, unlike the dioctadecyl systems.

We are interested in the way in which self-assembling ionic colloids influence reaction rates and equilibria, and their relation to colloidal structure. This problem is well studied with micelles and the effects depend upon the ability of micelles to bind reactants and provide a medium in which reaction can take place.[13] Reactivity in dioctadecyl vesicles has also been studied and in many respects these systems are similar to micelles in their rate effects.[9,14] However, there is evidence for reaction at both the interior and exterior surface of the vesicle.[8a,15] In addition, although rate effects seem to follow the quantitative treatments which have been developed for aqueous micelles, the derived parameters depend upon the extent of sonication and age of the solution.

The self-assembling didodecyl system is therefore attractive for quantitative study of reaction rates and equilibria, and we compare these results with those with single-chain surfactants. The single-chain surfactants were cetyltrimethylammonium chloride and bromide (CTACl and CTABr respectively), and *p*-octyloxybenzyltrimethylammonium bromide[16] (1). The rates of reaction of $OH^-$ with 2,4-dinitro-1-chloro-benzene and -naphthalene (DNCB and DNCN, respectively) were examined (Scheme 1). Reactions of DNCB and DNCN in CTAOH have been analysed quantitatively,[5b] and micellar effects upon reaction of $OH^-$ with DNCB have been followed in halide ion surfactants,[17] but not treated quantitatively by the ion-exchange model. We used (1) because it has a bulky phenyl group in the hydrophobic moiety[16] and therefore may pack differently from the C-16 micelles. Some of the kinetic work in DDDAOH and the corresponding chloride (DDDACl) has been published in preliminary form.[18]

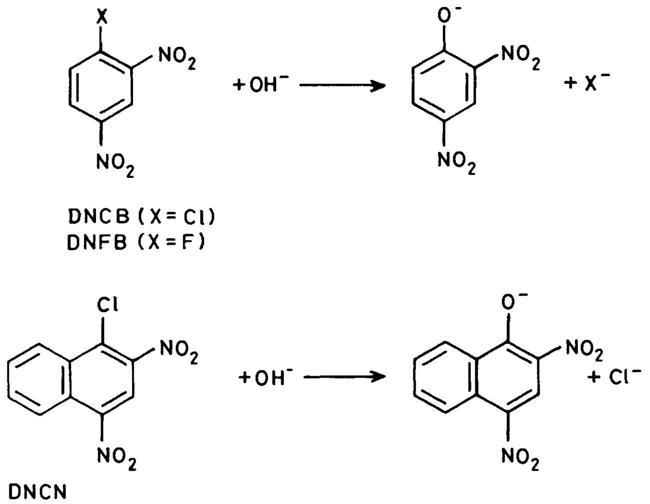


(1)

We did not use the bromide (DDDABr) because of its very low solubility, and we could only use a limited range of [DDDACl]. In all our experiments we used dilute surfactants. A few experiments were also carried out with 2,4-dinitro-1-fluorobenzene (DNFB) (Scheme 1).

## Results and Discussion

*Reactions in Halide Ion Surfactants.*—Reactions of DNCB, DNFB, and DNCN give rate maxima when concentrations of CTACl, CTABr, or (1) are increased at constant $[OH^-]$



**Scheme 1.**

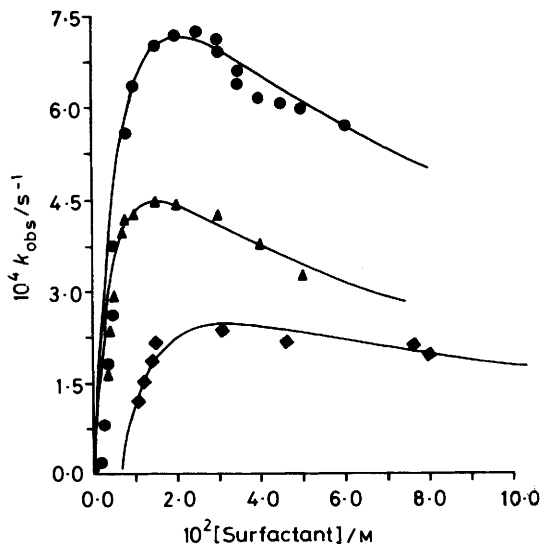


**Figure 1.** Reaction of DNCB, 0.05M-OH$_T^-$: (◆) in (1); (▲) in CTABr; (●) in CTACl

(Figures 1—3). Low concentrations of DDDACl had to be used and rate maxima were not well defined (Figures 4 and 5).

All these rate–surfactant profiles show certain common features. (i) The steepness of plots of first-order rate constants, $k_{obs}$, against concentrations of surfactant, D, are greater for reaction of DNCN compared with DNCB, and rate maxima are observed at lower [surfactant]. These differences are due to differences in substrate hydrophobicities and therefore of substrate binding to the colloidal assemblies. (ii) Rate enhancements tend to be larger with a chloride than with a bromide ion surfactant, because of differences in the competitive abilities of these ions towards OH$^-$.[13]

*Reactions in DDDAOH.*—Variations of $k_{obs}$ with DDDAOH are shown in Figures 4 and 5. They are similar to those observed for reactions in CTAOH in that limiting rate constants are reached only with the more hydrophobic substrate, DNCN, and then only in the presence of added NaOH.[5b]

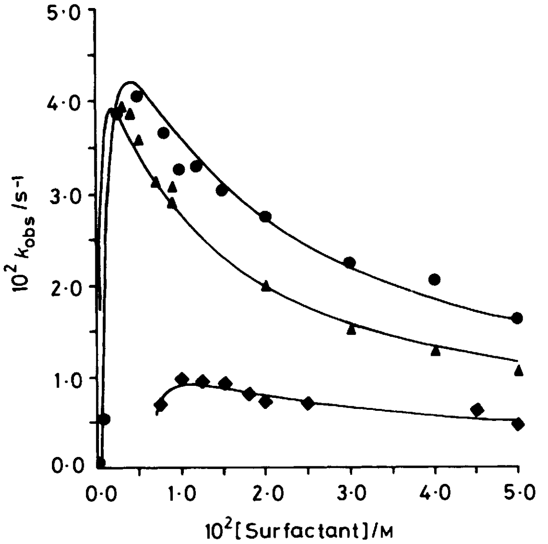


**Figure 2.** Reaction of DNCN: (◆) in (1), 0.05M-OH$_T^-$; (▲) in CTABr, 0.05M-OH$_T^-$; (●) in CTACl, 0.03M-OH$_T^-$

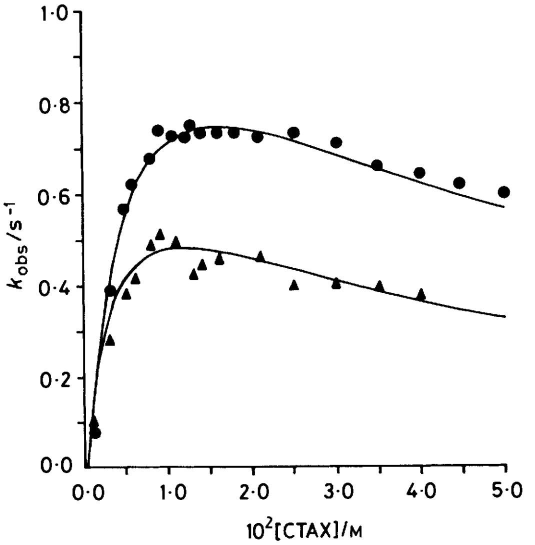
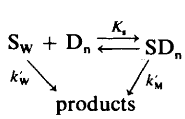


**Figure 3.** Reaction of DNFB, 0.03M-OH$_T^-$: (▲) in CTABr; (●) in CTACl

*Quantitative Treatment.*—Overall rate enhancements of bimolecular reactions by micelles, or similar colloids, are due largely to the bringing together of the two reactants in the small volume of the micelles, *i.e.* there is a concentration, rather than a medium, effect, although the latter is all important in spontaneous reactions.[13]

We analyse our data using the ion-exchange, pseudophase model although we recognize its imperfections and its failure at high concentrations of some ionic reagents.[13,17b,19–22] Other treatments which have been used to analyse micellar rate effects are discussed in ref. 13*c*.

Substrate, S, is distributed between water and micelles, and can react in either medium[23] (Scheme 2).



**Scheme 2.**

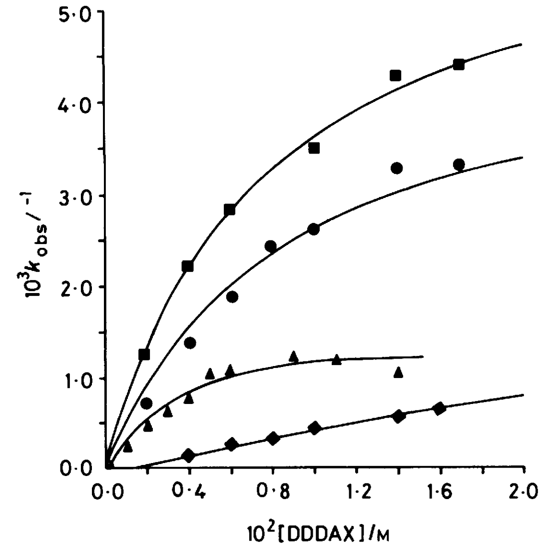


**Figure 4.** Reaction of DNCB: (▲) in DDDACl, 0.05M-$\mathrm{OH_T^-}$; (◆) in DDDAOH, no NaOH; (●) in DDDAOH, 0.1M-$\mathrm{OH_T^-}$; (■) in DDDAOH, 0.2M-$\mathrm{OH_T^-}$

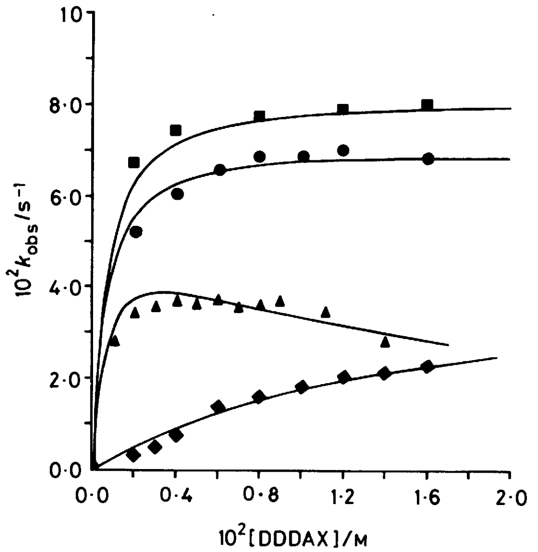


**Figure 5.** Reaction of DNCN: (▲) in DDDACl, 0.05M-$\mathrm{OH_T^-}$; (◆) in DDDAOH, no NaOH; (●) in DDDAOH, 0.1M-$\mathrm{OH_T^-}$; (■) in DDDAOH, 0.2M-$\mathrm{OH_T^-}$

In Scheme 2 $K_s$ is a binding constant, and $k'_W$ and $k'_M$ are first-order rate constants in water and micelles respectively. Micellized surfactant is written as $D_n$ and its concentration is that of total surfactant, D, less that of monomeric surfactant, which will be approximately that of the critical micelle concentration (c.m.c.) under kinetic conditions.

Scheme 2 leads to equation (1). The first-order rate constants

$$k_{obs} = (k'_W + k'_M K_s[D_n])/(1 + K_s[D_n]) \quad (1)$$

are given by equations (2) and (3). In equation (3) concentration

$$k'_W = k_W[OH^-] \quad (2)$$

$$k'_M = k_M m^s_{OH} = k_M[OH^-_M]/[D_n] \quad (3)$$

of bound $OH^-$ is written as a mole ratio,[13a,c,24] which evades the question of the appropriate volume element of the micellar reaction.

We assume that $OH^-$ and inert anion $X^-$ (X = Cl, Br) compete for the micelle according to equation (4).[13,25] The fraction

$$K_X^{OH} = [OH^-_W][X^-_M]/([OH^-_M][X^-_W]) \quad (4)$$

of head groups neutralized by counterions, β, is given by $1 - \alpha$, where α is the fractional ionization of the micelle. Equation (4), with the mass-balance condition, gives $m^s_{OH}$ in terms of various parameters characteristic of the micelle [equation (5)].[13a,c]

$$(m^s_{OH})^2 + m^s_{OH}\left(\frac{[OH^-_T] + K_X^{OH}[X^-_T]}{(K_X^{OH} - 1)[D_n]} - \beta\right) - \frac{[OH^-_T]\beta}{(K_X^{OH} - 1)[D_n]} = 0 \quad (5)$$

Equations (1)—(5) can be combined, allowing simulation of rate–surfactant profiles using a simple computer program.[26]

Assumptions and approximations in this treatment have been discussed.[13c] In particular, the pseudophase model may fail at high ionic concentrations,[21] and there are questions as to values of $K_X^{OH}$[22] and β.[3–5,27] In our calculations we use values of β for CTACl and CTABr from dynamic light scattering.[4] Values of $K_s$ used in the data fitting are consistent with independent estimates.[5b,13]

**Table 1.** Fitting parameters for reaction of DNCB in single-chain micelles

| Surfactant | $[OH^-]$/M | $10^4$C.m.c. (M) | β | $K_X^{OH}$ | $K_s$/ l mol$^{-1}$ | $10^3k_M$/s$^{-1}$ |
|---|---|---|---|---|---|---|
| CTACl | 0.05 | 4 | 0.72 | 4 | 60 | 3.94 |
| CTABr | 0.05 | 6 | 0.8 | 14 | 70 | 3.5 |
| (1) | 0.05 | 70 | 0.8 | 14 | 55 | 3.0 |

**Table 2.** Fitting parameters for reaction of DNCN in single-chain micelles

| Surfactant | $[OH^-]$/ M | $10^4$C.m.c. (M) | β | $K_X^{OH}$ | $K_s$/ l mol$^{-1}$ | $10^3k_M$/s$^{-1}$ |
|---|---|---|---|---|---|---|
| CTACl | 0.01 | 6 | 0.72 | 4 | 1 000 | 110 |
| | 0.03 | 5 | 0.72 | 4 | 1 000 | 100 |
| CTABr | 0.01 | 7 | 0.8 | 14 | 1 600 | 80 |
| | 0.03 | 3 | 0.8 | 14 | 1 600 | 85 |
| | 0.05 | 1 | 0.8 | 14 | 1 600 | 92 |
| (1) | 0.05 | 62 | 0.8 | 14 | 1 000 | 47 |

**Table 3.** Fitting parameters for reactions of DNFB in single-chain micelles

| Surfactant | $[OH^-]$/M | $10^4$C.m.c. (M) | β | $K_X^{OH}$ | $K_s$/ l mol$^{-1}$ | $k_M$/s$^{-1}$ |
|---|---|---|---|---|---|---|
| CTACl | 0.01 | 4 | 0.72 | 4 | 40 | 4.45 |
| CTACl | 0.03 | 4 | 0.72 | 4 | 70 | 4.90 |
| CTABr | 0.01 | 6 | 0.8 | 14 | 70 | 4.30 |
| CTABr | 0.03 | 4 | 0.8 | 14 | 80 | 4.60 |

Despite problems the pseudophase, ion-exchange model gives reasonable fits of rate–surfactant profiles and leads to consistent values of $k_M$, provided that high electrolyte concentrations are avoided, and we apply it under these conditions (Tables 1—4).

**Table 4.** Rate and equilibrium constants for reactions in DDDACl and DDDAOH[a]

| Substrate | Surfactant | $[OH^-]/\text{M}$[b] | $K_s$/l mol$^{-1}$ | $10^3k_M$/s$^{-1}$ |
|---|---|---|---|---|
| DNCB | DDDACl | 0.05 | 100 | 5.5 |
| DNCB | DDDAOH | | 100 | 3 |
| DNCB | DDDAOH | 0.1 | 110 | 6 |
| DNCB | DDDAOH | 0.2 | 130 | 7 |
| DNCN | DDDACl | 0.05 | 1 600 | 82 |
| DNCN | DDDAOH | | 1 600 | 65 |
| DNCN | DDDAOH | 0.1 | 1 600 | 86 |
| DNCN | DDDAOH | 0.2 | 1 600 | 80 |

[a] Based on $K'_{OH}$ 55 l mol$^{-1}$, $K_{Cl}^{OH}$ 4, β 0.7, and c.m.c. $10^{-4}$M and zero with $[OH^-] \geqslant 0.1$M. [b] Added as NaOH.

For reaction in absence of halide ion we write the distribution of $OH^-$ using the mass-action-like equation (6). Equations (1),

$$K'_{OH} = [OH_M^-]/\{[OH_W^-]([D_n] - [OH_M^-])\} \qquad (6)$$

(2), and (6) can be combined to allow prediction by computer simulation of the variation of $k_{obs}$ with [DDDAOH] or added $[OH^-]$. This treatment has been applied successfully to reactions in micelles having $OH^-$, $F^-$, or $HCO_2^-$ as counterions.[5b,12,26] There are major questions as to the physical significance of equation (6), but a more detailed treatment, based on solution of the Poisson–Boltzmann equation in spherical symmetry,[27] give results similar to those given by equation (6), and therefore we use the simple treatment (Table 4).

This treatment has already been applied to reaction of DNCB and DNCN in CTAOH. We fitted the data for reactions in DDDAOH using the value of $K'_{OH}$ [equation (6)] which had been estimated for CTAOH.[5b]

*Variations of Rate Constants with Surfactants.*—The simple distribution models fit the kinetic data reasonably well for reactions in DDDACl and DDDAOH with the parameters given in Table 4 as shown by the agreement between the experimental data and the computed plots in Figures 1—5. Values of $K_s$ for DNCB in DDDAOH increase slightly with increasing $[OH^-]$ as found with CTAOH.[5b] The value of $k_M$ for reaction of DNCB in DDDAOH in absence of NaOH is approximate because $k_{obs}$ varies almost linearly with [DDDAOH] (Figure 4). With this reservation values of $k_M$ are insensitive to concentration of surfactant and $OH^-$.

Values of $K_M$ in aggregates of the didodecyl surfactants are similar to those in micelles of the single-chain surfactants (Tables 1—4). Calculations of $k_M$ involve assumptions about such parameters as β and $K_X^{OH}$, but $k_M$ is insensitive to other than large changes in these parameters, so we believe that uncertainties in values of $k_M$ are not so large as to nullify our qualitative conclusions.

These conclusions also apply to reactions in micelles of the single chain *p*-octyloxy surfactant (1), despite marked differences between its hydrophobic group and those of the other surfactants.

These observations suggest that colloidal particles formed from these surfactants have very similar surfaces, despite marked differences in the hydrophobic groups, because reactions must be taking place in similar environments. There is no evidence for exo- and endo-vesicular reactions with DDDAOH or DDDACl. Thus, if vesicles are present, both reactants must either be excluded from the interior surface, or both must pass freely through the vesicle wall, *cf.* refs. 7*b*, 11.

**Table 5.** Comparison of rate constants in water and colloidal assemblies[a]

| Substrate | Reaction Medium | $10^3k_2^m$/l mol$^{-1}$ s$^{-1}$ | $k_2^m/k_W$ |
|---|---|---|---|
| DNCB | DDDACl + $OH^-$ | 0.8 | 5.6 |
| DNCB | (1) + $OH^-$ | 0.4 | 2.9 |
| DNCB | DDDAOH | 0.43 | 3.1 |
| DNCB | DDDAOH + $OH^-$ | 0.9 | 6.5 |
| DNCB | CTACl + $OH^-$ | 0.55 | 3.9 |
| DNCB | CTABr + $OH^-$ | 0.49 | 3.5 |
| DNCB | CTAOH | 0.7[b] | 5.0 |
| DNCB | CTAOH + $OH^-$ | 1.0[b] | 7.0 |
| DNCN | DDDACl + $OH^-$ | 11.5 | 1.8 |
| DNCN | (1) + $OH^-$ | 6.6 | 1.0 |
| DNCN | DDDAOH | 9.1 | 1.4 |
| DNCN | DDDAOH + $OH^-$ | 11.6 | 1.8 |
| DNCN | CTACl + $OH^-$ | 14.7 | 2.3 |
| DNCN | CTABr + $OH^-$ | 12.0 | 1.9 |
| DNCN | CTAOH | 15[b] | 2.3 |
| DNCN | CTAOH + $OH^-$ | 14[b] | 2.2 |
| DNFB | CTACl + $OH^-$ | 654 | 5.5 |
| DNFB | CTABr + $OH^-$ | 623 | 5.2 |

[a] Based on $10^3k_W = 0.14$, 6.4, and 120 l mol$^{-1}$ s$^{-1}$ for DNCB, DNCN, and DNFB respectively. [b] Ref. 5*b*.

(Non-ionic solutes move freely through the walls of sonicated synthetic vesicles.[8–10])

The second-order rate constants, $k_M$, have different dimensions from those of $k_W$ [equations (2) and (3)] but rate constants in the colloidal aggregate can be compared with those in water provided that the micellar molar volume of reaction, $V_M$, is defined. Elsewhere we have taken $V_M = 0.14$ dm$^3$ so that we write a second-order rate constant, $k_2^m$, which can be compared

$$k_2^m = 0.14k_M \qquad (7)$$

with $k_W$.[5b,26] Other estimates of $V_M$ range up to *ca.* 0.35 dm$^3$ which introduces an approximately two-fold uncertainty in $k_2^m$.[9,13c,28] Hicks and Reinsborough have suggested that $V_M$ varies with electrolyte concentration.[29]

Values of $k_2^m$, based on equation (7) (Table 5), are consistently slightly larger than in water but the similarities in $k_W$ and $k_2^m$ are consistent with reactions occurring at a water-rich surface[30] with all the colloidal aggregates examined here, regardless of their structure.

Rate constants are lower in micelles of the *p*-octyloxy surfactant (1) than in CTA micelles probably because micellized (1) has a more open surface structure and is therefore less effective at binding counterions.[5b,27] Values of $k_2^m/k_w$ are larger for reaction of DNCB and DNFB compared with DNCN (Table 5). This behaviour is general,[5b] and suggests that the more hydrophobic substrates bind more deeply in the micellar surface further away from bound $OH^-$. These differences suggest that $V_M$ may depend upon the reaction type and probably also upon the surfactant and that for reactions of such hydrophilic ions as $OH^-$ it is unrealistic to make a sharp distinction between reactions involving ions in the so-called Stern layer and those in the diffuse layer.[21,27]

Although didodecyldimethylammonium salts are reported to form vesicles in dilute solution and micelle-like assemblies at higher concentration[7,11] our kinetic data give no evidence for structural changes. However, reactivity depends upon the surfaces of the assemblies, which are probably insensitive to changes in surfactant.

Formation of normal micelles is associated with sharp breaks in plots of surface tension against log [surfactant][31] and the unusual behaviour of the DDDA salts (Experimental section) is consistent with formation of non-micellar species in very dilute solution, and the absence of monomeric surfactant. Our rate measurements were at [surfactant] greater than these break points.

## Experimental

*Materials.*—Didodecyldimethylammonium chloride (DDDACl) was prepared by quaternizing dodecyldimethylamine with dodecyl chloride in EtOH under reflux for 4 days. It was recrystallized from $Et_2O$–EtOAc and had m.p. 130—131 °C (Found: C, 74.7; H, 13.45; N, 3.25; Cl, 8.4. Calc. for $C_{26}H_{56}ClN$: C, 74.7; H, 13.5; N, 3.3; Cl, 8.5%). The bromide, prepared similarly, had m.p. 169—170 °C (Found: C, 67.4; H, 12.2; N, 3.0; Br, 17.2. Calc. for $C_{26}H_{56}BrN$: C, 67.5; H, 12.2; N, 3.0; Br, 17.3%).

The bromide was converted into the sulphate with $Ag_2SO_4$ in MeOH and was recrystallized ($Et_2O$–EtOAc). It contained no $Ag^+$ or $Br^-$. It was converted into the hydroxide (DDDAOH) by treatment with equimolar $Ba(OH)_2$, and $BaSO_4$ was removed by high-speed centrifugation.[5b] The solution was *ca.* 0.1M and contained no $Ba^{2+}$ or $SO_4^{2-}$. All manipulations were carried out under $N_2$ with $CO_2$-free solutions.

Purification of the substrates and the other surfactants has been described.

*Kinetics.*—Reactions were followed spectrophotometrically at 25.0 °C using Beckman, Gilford, or Perkin-Elmer spectrophotometers.[5b] All solutions were made up using $CO_2$-free, redistilled water. Substrate concentrations were generally *ca.* $2 \times 10^{-5}$M except for reaction of DNCN in dilute DDDAOH where solubility was a problem and it was necessary to reduce [DNCN] to obtain consistent rate constants. Reactions of DNCB and DNFB were followed at 355 nm and those of DNCN at 390 nm.

Kinetic solutions of the didodecylammonium surfactants were generally made up by serial dilution, but we found no rate differences with solutions which were aged or sonicated. Solutions of DDDAOH were normally used within 10 days, but older solutions did not change the kinetic results.

*Effects on Surface Tension.*—The surface tension of solutions of the surfactants was measured using a du Nouh tensiometer.[31] The behaviour was unusual in that DDDAOH, DDDACl, and DDDABr gave more than one break in plots of surface tension against log [surfactant]. With increasing [surfactant] plots were linear up to a first break point, they were then linear with zero slope to a second break point, they then descended linearly to a third break point, and at higher [surfactant] surface tension was constant. We saw no minima in any of these plots. The surfactant concentrations corresponding to these break points were: for DDDAOH, $2.7 \times 10^{-5}$, $1.66 \times 10^{-4}$, and $1.8 \times 10^{-4}$M; for DDDACl, $5.8 \times 10^{-5}$, $1.2 \times 10^{-4}$, and $2.2 \times 10^{-4}$M; for DDDABr, $4.7 \times 10^{-5}$, $1.22 \times 10^{-4}$, and $3.1 \times 10^{-4}$M.

We have no explanation for this behaviour except to suggest that small aggregates with surface activity were present. Plots of conductivity against concentration were not helpful; with DDAOH the plot curved slightly in the range 3—$6 \times 10^{-4}$M, with DDDACl there was an ill-defined break at *ca.* $1.3 \times 10^{-4}$M, and with DDDABr there was gradual curvature possibly with ill-defiined breaks at $1.2 \times 10^{-4}$ and $3 \times 10^{-4}$M (*cf.* ref. 7*c*).

However, conductivity and other electrochemical measurements depend on ionic materials in solution, whereas surface tension depends on the location of surface active materials at the surface. The presence of submicellar ionic species would be consistent with the different information provided by these various methods (*cf.* refs. 18 and 32). We note also that DDDAOH and related salts which have very hydrophilic counteranions are reported to form vesicles at concentrations as low as $10^{-5}$M,[7b,11] which suggests that concentrations of surface-active monomer should be very low.

## Acknowledgements

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