Effects of Alcohol-modified Micelles on Deacylation and Nucleophilic Aromatic Substitution by Azide Ion

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Alcohol-modified micelles and oil–water microemulsions have similar rate effects upon aromatic nucleophilic substitution by N_3^-. Relative values of k_2^m/k_w for aromatic nucleophilic substitution and deacylation show that enhancements of the rate of deacylation can be ascribed wholly to increased reactant concentrations in the micelles, but that there is an additional catalytic effect upon nucleophilic aromatic substitution.

Reactions of azide ion with 1-chloro-2,4-dinitronaphthalene and p-nitrophenyl benzoate in water containing dilute t-pentyl alcohol are accelerated by cationic micelles, but the rate enhancements are lower than in aqueous micelles. At constant $[N_3^-]$, first-order rate constants for reaction of 1-chloro-2,4-dinitronaphthalene go through maxima with increasing concentration of cetyltrimethylammonium chloride or bromide (CTACl or CTABr). Similar behaviour was found with p-nitrophenyl benzoate in CTACl. Rate constants of reaction of the naphthalene substrate in cetyltrimethylammonium azide increase with increasing [surfactant]. Estimated rate constants of deacylation at the micellar surface are slightly lower than in the absence of surfactant, but are higher for reaction of 1-chloro-2,4-dinitronaphthalene.

There are many examples of rate enhancements of bimolecular reactions by micelles which can be explained in terms of a concentration of both reactions in the small volume of the micelles. Second-order rate constants, calculated from reactant concentrations in the micellar pseudophase, are often very similar to or smaller than those in water.[1–4] The treatment is based on the assumption that reaction takes place either in the aqueous or in the micellar pseudophase,[5,6] and it seems to be satisfactory except when an ionic reagent, e.g. OH⁻, is present in high concentration. The abnormally high reaction rates which are then sometimes observed have been ascribed to reaction across the micelle–water interface.[7]

This general model has also been applied to reactions in aqueous solutions of vesicles[8] and in non-micellising hydrophobic ammonium ions,[9] and to some microemulsions and the related alcohol-modified micelles.[10] (We prefer 'alcohol-modified' to 'alcohol-swollen' because moderately hydrophobic alcohols may reduce micellar size). Overall rate enhancements are generally lower in these micelles and oil–water (o/w) microemulsions than in aqueous micelles,[10,11] because the alcohol decreases the binding of ionic reactants[12] and because of the high volume of the droplet pseudophase in microemulsions. The limited evidence suggests that second-order rate constants in the droplets are not very different from those in aqueous micelles.[10]

Aromatic nucleophilic (S_NAr) substitution by azide ion is a striking exception to the generalisation that second-order constants are similar in aqueous micellar pseudophases, because the cationic micellar reaction is faster than predicted.[13] However, the expected behaviour is observed for reactions of azide ion with 2,4-dinitrophenyl benzoate, methyl benzenesulphonate, and the bis-(2,4-dimethoxyphenyl)-(4-methoxyphenyl)methyl cation.[13,14]

These results suggest that some special feature is responsible for the unusually fast S_NAr reaction in micelles, relative to reaction in aqueous or alcoholic solution. Some special feature of micelles could be involved, but it is also possible that azide

ion is unusually unreactive in water or alcohols and reaction is much slower than predicted by the N_+ value for azide.[15]

In the present work we examine reactions of azide ion with 1-chloro-2,4-dinitronaphthalene (CDNN) and p-nitrophenyl benzoate (pNPB) in cationic micelles whose structure is modified by a moderately hydrophobic alcohol. Microemulsions typically contain a hydrocarbon, a surfactant, and a cosurfactant which is generally a moderately hydrophobic alcohol.[10] The cosurfactant is believed to bind at the surface of an oil–water microemulsion droplet, so that the surface of a micelle which contains cosurfactant should be similar to that of a microemulsion droplet. We used t-pentyl alcohol for this purpose because it is sparingly soluble in water and is taken up readily by the micelle or droplet; in addition it is a poor nucleophile and should not intervene chemically. Experiments were made also with t-butyl alcohol. The surfactant used was generally cetyltrimethylammonium chloride (CTACl, $C_{16}H_{33}\overset{+}{N}Me_3Cl^-$) but a few experiments were made with the bromide (CTABr) and the azide (CTAN₃). These experiments were designed to answer two questions: first, is reactivity in oil–water microemulsion droplets similar to that in alcohol-modified micelles, and second, is azide ion unusually reactive in these systems towards aromatic substrates?

Experimental

Materials.—Cetyltrimethylammonium azide was prepared from cetyltrimethylammonium sulphate and the equivalent amount of barium azide in CO_2-free water; $BaSO_4$ was removed by centrifugation.[13] The surfactant was prepared and used in solution and was tested for the absence of Ba^{2+} and SO_4^{2-}. The other materials were commercial samples or were prepared and purified by standard methods. Reaction solutions were made up in CO_2-free water using t-pentyl alcohol that had been distilled over sodium.

Kinetics.—Reactions were followed spectrophotometrically with ca. 10^{-5}M-substrate at 290 or 380 nm for CDNN and 320 nm for pNPB by using a Gilford or a Beckmann spectrophotometer or a Hewlett-Packard 8450 diode array spectrophotometer. In the absence of surfactant the low

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solubility of NaN_3 limited the range of solvent composition that could be used. All reactions were followed at 25.0 °C; first-order rate constants, k_ψ, are expressed in s^{-1}.

In water, 2,4-dinitrophenyl azide slowly cyclises,[15] with a decrease in absorbance. We see a similar decrease in absorbance after ca. 5 half-lives of the reaction of N_3^- with CDNN,[13] but in surfactant solutions attack of N_3^- is increased relative to cyclisation so that this second reaction can be neglected.

Results

Reactions in the Absence of Surfactant.—The second-order rate constants, k_W, for reaction of pNPB in the absence of surfactant were calculated from first-order rate constants in H_2O, and in the presence of 0.348M-t-pentyl alcohol in 0.1M-solutions of NaN_3 adjusted to pH 9 in the presence of 10^{-2}M-carbonate buffer. In water values of k_ψ in the presence and in the absence of 0.1M-NaN_3 were 8.9 × 10^{-4} and 0.6 × 10^{-4} s^{-1}, respectively, giving k_W = 8.3 × 10^{-3} mol dm^{-3} s^{-1}. In the presence of 0.348M-t-pentyl alcohol the corresponding values of k_ψ were 7 × 10^{-4} and 0.5 × 10^{-4} s^{-1}, giving k_W = 6.9 × 10^{-3} mol dm^{-3} s^{-1}.

The problem is more complicated for reaction of CDNN in the absence of surfactant because of solubility problems and also because of cyclisation of 2,4-dinitronaphthyl azide.[13,15] The importance of cyclisation is minimised by using a high concentration of NaN_3 to speed the initial attack, which is reasonably fast with 1M-NaN_3 in water, giving a second-order rate constant of ca. 10^{-3} mol dm^{-3} s^{-1} based on computer fitting of the first 85% of reaction. However, we could not get reproducible results when we reduced [NaN_3], and it seemed that precipitation was a problem with these slower reactions. Addition of small amounts of MeCN did not improve the results. Our rate constant in 1M-NaN_3 is suspect for experimental reasons, and also because of neglect of salt effects,[13] but we made an independent estimate from the relative reactivities of 1-chloro-2,4-dinitrobenzene and naphthalene with OH^- in water,[16] based on respective second-order rate constants of 6.4 × 10^{-3} and 1.4 × 10^{-4} mol dm^{-3} s^{-1} at 25.0 °C. The second-order rate constant for reaction of aqueous N_3^- with 1-chloro-2,4-dinitrochlorobenzene is 4.6 × 10^{-5} mol dm^{-3} s^{-1} at 25.0 °C,[13] in reasonable agreement with the value of 3.8 × 10^{-5} extrapolated from values at 47.5 and 68.4 °C.[15] Provided that relative reactivities of the two substrates are the same for reactions with OH^- and N_3^-, we estimate a second-order rate constant of ca. 2 × 10^{-3} mol dm^{-3} s^{-1} for reaction of CDNN with N_3^-, and we use this value in the following discussion.

Solubility is less of a problem when 0.334M-t-pentyl alcohol is added; with 0.175M-NaN_3 k_ψ = 1.0 × 10^{-3} s^{-1}, based on the first 80% of reaction, giving a second-order rate constant of ca. 5.7 × 10^{-3} mol dm^{-3} s^{-1} at 25.0 °C.

Reaction in Solutions of $CTAN_3$.—Reaction rates in solutions of reactive ion surfactants increase with increasing [surfactant] towards limiting values which correspond to complete micellar incorporation of the substrate and saturation of the micelles by counterions.[13,16a] This behaviour is observed in water with reactive ion surfactants with counterions which are not very hydrophilic, although in some reactions of OH^- rate and equilibrium constants increase steadily on addition of relatively high concentrations of OH^-.[7,16,17]

First-order rate constants for reaction on CDNN with N_3^- solutions containing t-pentyl alcohol increase with increasing [$CTAN_3$] but do not reach limiting values even at high [surfactant] (Figure 1). For the corresponding reaction in aqueous micelles, limiting values of the rate constants are reached at ca. 0.02M-$CTAN_3$,[13] and the limiting value of k_ψ (ca.

1.4 s^{-1}) is larger than the highest value observed in the presence of t-pentyl alcohol (0.26 s^{-1}) (Figure 1).

Addition of NaN_3 speeds reaction, suggesting that the alcohol-modified micelles are not saturated with N_3^-.[16,17] Therefore t-pentyl alcohol appears to be slowing reaction by reducing the binding of both CDNN and N_3^- to the micelles. Rate constants for a given [$CTAN_3$] are very similar in micelles the structure of which is modified by t-pentyl alcohol, and in oil–water microemulsions which contain n-octane (Figure 1). Thus the presence of the oil is not affecting the ability of the colloidal droplets to speed reaction. This behaviour is consistent with reaction occurring at the droplet surface, which should be little affected by oil located in the interior of an o/w microemulsion droplet. There is considerable evidence that polarisable organic solutes bind at water-rich surfaces of aqueous micelles,[18] and the behaviour might be different with very hydrophobic substrates which could enter the oil-rich interior of a microemulsion droplet.

Increasing the concentration of t-pentyl alcohol in an o/w microemulsion with $CTAN_3$ and n-octane sharply inhibits the reaction (Table 1); the rate constant in a microemulsion is very similar to that in a solution containing only surfactant and alcohol.

Reactions in the Presence of Inert Anions.—With 1-chloro-2,4-dinitronaphthalene as substrate and fixed concentrations of NaN_3 and t-pentyl alcohol, rate constants go through maxima with increasing [CTACl] or [CTABr] (Figure 2). Increasing concentration of t-pentyl alcohol slows the reaction. With fixed concentrations of surfactant and NaN_3 both t-butyl and t-pentyl alcohol sharply inhibit reaction, and t-pentyl is much the better inhibitor (Table 2). This difference is consistent with evidence that micellar binding of alcohols increases with increasing hydrophobicity of the alcohol.[19,20] Transfer of alcohol between micelles and the water-rich solvent is much
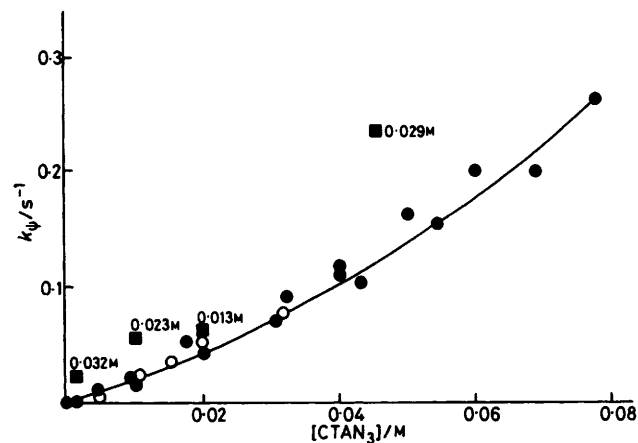

Figure 1. Reaction of $CTAN_3$ with CDNN with 8.49 wt. % t-pentyl alcohol (solid points). The open points refer to reaction in the presence of n-octane ($CTAN_3$:n-octane 2.76:1 w/w). The solid squares refer to reaction with the indicated amount of added NaN_3

Table 1. Effect of t-pentyl alcohol on reaction of CDNN in a microemulsion[a]

t-$C_5H_{11}OH$ (w/w)	2.7	5.5	7.0	8.3
k_ψ/s^{-1}	0.14	0.026	0.014	0.006[b]

[a] At 25.0 °C with 0.0042M-$CTAN_3$ and $CTAN_3$:n-octane 1.37:1 w/w; [b] With $CTAN_3$:n-octane 2.76:1 w/w; k_ψ ca. 0.005 s^{-1} (Figure 1).

faster than the chemical reaction, so that equilibrium is maintained between alcohol in water and micelles.

Although t-pentyl alcohol is only sparingly soluble in water, it is solubilised in aqueous cationic surfactants owing, at least in part, to incorporation of the alcohol in the micelles. Dynamic light scattering[21] and fluorescence data[20] show that micelles are present in these solutions, at least up to 10 wt. % t-pentyl alcohol. Small amounts of alcohol (<3 wt. %) appear to

Figure 2. Reaction of N_3^- with CDNN in micelles of CTACl and CTABr with 1.61 × 10^{-3}M-NaN$_3$; solid points in CTACl, open in CTABr; (right-hand scale) ◆, ■, □, ● with 0.884, 0.354, and 0.118M-t-pentyl alcohol. The curves follow predicted data

Table 2. Effect of tertiary alcohols on reaction of CDNN in CTACl[a]

[ROH]		10^2[CTACl]/M			
M	Wt. % ROH	0.46	0.96	1.94	3.20
0.12	1.1	120	139	99.0	60.4
0.21	1.62[b]			(98.8)	
0.31	2.45			(89.4)	
0.35	3.37	55.5	66.4	37.5	25.0
0.41	3.28[b]			(68.0)	
0.51	4.09[b]			(66.3)	
0.59	5.62	16.2			
0.88	8.49	4.1	6.6	4.6	4.2
1.03	8.30[b]			(24.1)	
1.18	11.3			1.6	
1.47	14.3			0.8	1.1

[a] Values of $10^3 k_\psi/s^{-1}$ with 1.61 × 10^{-3}M-NaN$_3$ and t-pentyl alcohol unless specified; values in parentheses are with added t-butyl alcohol; ROH denotes t-butyl or t-pentyl alcohol. [b] t-Butyl alcohol.

decrease micellar fractional charge, but further addition of alcohol shrinks the micelles, and they eventually disappear, i.e. the alcohol 'dissolves' them.[20] This conclusion is consistent with the slow reactions at high alcohol concentrations (Tables 1 and 2).

The rate maxima with increasing surfactant (Figure 2) are similar to those observed with micelles in water, which can be treated quantitatively in terms of the reactions in the Scheme,[5]
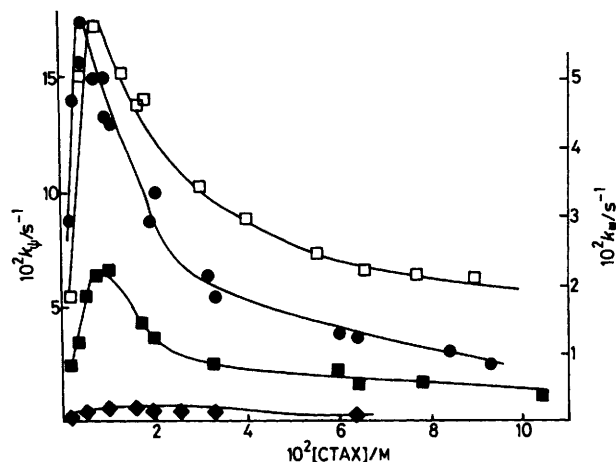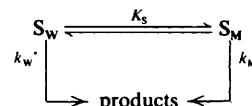
$$S_W \underset{k_W'}{\overset{K_s}{\rightleftharpoons}} S_M$$
$$\downarrow \quad \quad \downarrow k_M'$$
$$\text{products}$$

Scheme.

where S_W and S_M are substrate in bulk solvent and micelles respectively, k_W' and k_M' are the first-order rate constants, and K_s is the binding constant written in terms of micellised surfactant, D_n, i.e. D_{total} less D_{free}.

The first-order rate constants are given by equations (1) and (2), resulting in equation (3). The competition between N_3^- and inert anion, X^-, is written as equation (4).[3,4,22-27] [In

$$k_W' = k_W[N_3^-]_W \tag{1}$$

$$k_M' = k_M[N_3^-]_M/[D_n] \tag{2}$$

$$k_\psi = (k_W[N_3^-]_W + k_M K_s[N_3^-]_M)(1 + K_s[D_n]) \tag{3}$$

$$K_X^{N_3} = [N_3^-]_W[X^-]_M/([N_3^-]_M[X^-]_W) \tag{4}$$

equations (1)—(4) the quantities in square brackets are molarities in terms of total solution volume.]

Equations (1)—(4) can be combined and allow simulation of the rate–surfactant profiles provided that β (the extent of charge neutralisation of head groups by counterions) is known and is independent of the nature or concentration of counterions. Values of β have been estimated for cationic micelles in water with added t-pentyl alcohol,[12d] and we interpolate β from these data. We also assume that the concentration of monomeric surfactant will be higher in these mixtures than in water. The concentration of free, monomeric surfactant in water is generally taken to be the critical micelle concentration (c.m.c.). However reactions are often speeded with [surfactant] < c.m.c., probably because the reactants associate with surfactant and promote its aggregation so that kinetic estimates of free surfactant are generally lower than the c.m.c. in water.

Fortunately this assumption does not materially affect fitting of the data which are shown in Figure 2 based on the parameters in Table 3. In fitting the data we assume that β and K_s are

Table 3. Rate and equilibrium constants for micellar reactions[a]

Substrate	[t-C$_5$H$_{11}$OH] M	10^3[D$_{free}$] M	β	K_s mol^{-1} dm^3	k_M s^{-1}	k_2^m mol^{-1} dm^3 s^{-1}
CDNN[b]		0.8	0.75	600	2.8	0.4
CDNN	0.118	1.3	0.75	300	2.2	0.3
CDNN	0.354	1.3	0.50	100	2.2	0.3
CDNN[c]	0.354	1.1	0.70	100	1.8	0.26
CDNN	0.884	1.3	0.25	25	0.7	0.1
pNPB[d]		0.5	0.75	1 400	0.014	0.002
pNPB	0.354	1.0	0.50	140	0.008	0.001

[a] At 25.0 °C with CTACl unless specified and $K_{Cl}^{N_3}$ = 1.5 and $K_{Br}^{N_3}$ = 2.1; D_{free} denotes monomeric surfactant. [b] k_W ca. 2 × 10^{-3} mol^{-1} dm^3 s^{-1} in water and 6 × 10^{-3} mol^{-1} dm^3 s^{-1} in the presence of 0.354M-t-pentyl alcohol. [c] In CTABr. [d] k_W = 8 × 10^{-3} mol^{-1} dm^3 s^{-1} in water and 7 × 10^{-3} mol^{-1} dm^3 s^{-1} in the presence of 0.354M-t-pentyl alcohol.

decreased by t-pentyl alcohol, especially at the highest concentration.

The overall reaction is slightly slower in CTABr than in CTACl (Figure 2). These rate differences are also observed with aqueous micelles and are due to the greater affinity of Br^- for the micelle.[22-25] In water, estimated values of $K_X^{N_3}$ are 2 and 1.3 for X = Br or Cl, respectively,[13] and appear to be little affected by addition of t-pentyl alcohol.

For reaction in aqueous CTACl the maximum rate constant is ca. 0.16 s^{-1} at 3 × 10^{-3}M. The rate decrease on addition of t-pentyl alcohol is due to lower reactant binding rather than to differences in k_M (Table 3), although with the highest concentration of t-pentyl alcohol the micelles are probably disrupted.

The rate constants k_M are written with concentration as a molar ratio [equation (2)] which can be defined unambiguously.[26] Rate constants in water or mixed solvents are generally written with concentration as molarity, so that k_W and k_M have different dimensions and cannot be compared directly. Comparison can be made if the molar volume of reaction (V_M) at the micellar surface can be estimated and equation (5) applies.

$$k_2^m = V_M k_M \qquad (5)$$

Estimates of V_M for aqueous micelles range from 0.14 to 0.37 l,[1-4,22,23,26,27] and may be different for alcohol-modified micelles. In our calculations we take $V_M = 0.14$ l.[26]

Nucleophilic attack by anions is often speeded by decreases in the water content of aqueous-organic media;[28] we see this behaviour on addition of a tertiary alcohol to water. Incorporation of t-pentyl alcohol into micelles or microemulsion droplets might assist bimolecular anionic reactions at their surfaces, but the effect, if present, is apparently not large in the present systems. Estimates of k_2^m [equation (5)] depend not only upon the (assumed) value of V_M, but also upon β, which governs the ionic concentration at the droplet surface, and variations of k_2^m (Table 3) may simply be due to changes in the value of V_M on addition of t-pentyl alcohol. Medium effects on second-order rate constants inevitably depend upon concentration units, but the insensitivity of k_2^m to changes in alcohol concentration suggests that the assumptions in the calculations are reasonable.

Also we assume that these values are insensitive to changes in surfactant or electrolyte concentration and although this assumption is satisfactory for aqueous micelles,[3,4] and is probably so for solutions containing only low concentrations of organic solutes, it probably fails when added solute markedly perturbs micellar structures, e.g. at ca. 0.9M-t-pentyl alcohol (Table 3).

Reaction of p-*Nitrophenyl Benzoate.*—Values of k_ψ for reaction of p-nitrophenyl benzoate with azide ion in solutions of CTACl go through maxima with increasing [CTACl] (Figure 3). The rate–surfactant profile is similar to that for the reaction with OH$^-$ in aqueous CTABr, which can be fitted to the ion-exchange model [equations (1)—(4)]. In fitting the data for reaction with azide we take the parameters in Table 3. In water the value of K_S is that used earlier to fit kinetic data in CTABr,[29] and values of K_{Cl}^{OH} and β agree with those in the literature;[4] on the basis of comparison of k_W and k_2^m (Table 3) reaction is slightly slower in CTACl micelles than in water.

In water $k_W = 0.24$ mol dm^{-3} s^{-1} for reaction of 2,4-dinitrophenyl benzoate with azide ion at 25.0 °C;[13] this ester is more reactive than pNPB by a factor of 30 in water. For reaction in CTABr micelles, $k_2^m = 0.24$ mol dm^{-3} s^{-1},[13] so that the reactivities of the mono- and the di-nitro derivatives differ by a somewhat larger factor of 120. (Different surfactants were used in reactions of the two esters, but this difference should not materially affect the rate comparisons.)
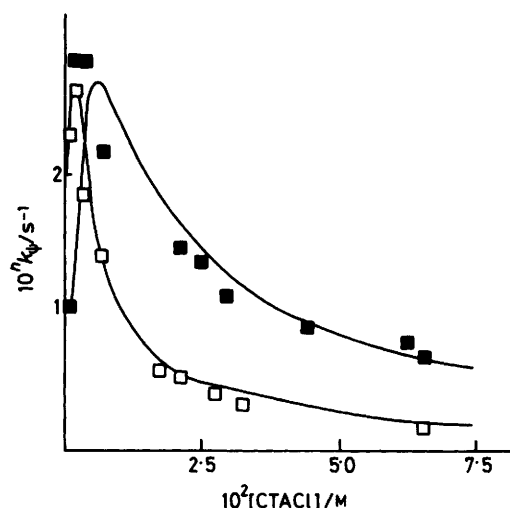

Figure 3. Reaction of N$_3^-$ with pNPB in micelles of CTACl with 1.54 × 10^{-3}M-NaN$_3$; □, ■ in water and with 0.354M-t-pentyl alcohol and n = 3 and 4, respectively

In solutions containing 0.354M-t-pentyl alcohol, the maximum rate constant is lower by a factor of ca. 10 than that in aqueous CTACl (Figure 3). This behaviour is similar to that for reaction of CDNN. The data for solutions of t-pentyl alcohol can be fitted reasonably well to the Scheme and equations (1)—(4) with the parameters in Table 3.

Discussion

Reactions in Alcohol-modified Micelles.—Micellar rate effects in water are generally treated on the assumption that micelles behave as a distinct reaction medium, i.e. as a pseudophase.[1-6] For mixtures of counterions their distribution is described in terms of the ion-exchange model and equations can be developed which fit the experimental data;[3,4,25] alternatively, ion distribution can be estimated by solving the Poisson–Boltzmann equation, generally with allowance for specific interactions.[30]

The pseudophase ion-exchange model or its equivalent for a single ion can also be applied to reactions in microemulsions or alcohol-modified micelles.[10,12d] The differences between the parameters for these systems and for aqueous micelles are qualitatively reasonable, and both kinetic and physical evidence suggests that small amounts of hydrophobic alcohols do not markedly perturb micellar structure,[19-21] although ion binding is reduced. However, further addition of solute, in the present system ca. 0.9M-t-pentyl alcohol, markedly perturbs the micelles and sharply reduces their ability to bind counterions and assist their bimolecular reactions.

In aqueous micelles second-order rate constants, k_2^m, in the micelles are not very different from those in water, k_W, for reactions of azide ion with nitrophenyl benzoates, methyl benzenesulphonate,[13] or the bis-(2,4-dimethoxyphenyl)-(4-methoxyphenyl)methyl cation[14] but k_2^m/k_W is ca. 50 and 200 for reactions of 1-chloro-2,4-dinitro-benzene and -naphthalene, respectively. Our present results for alcohol-modified micelles suggest that, as in water, their effect on the rate of aromatic nucleophilic substitution is larger than predicted from reactant concentration at the micellar surface, but we see no such effect for deacylation.

The magnitude of the micellar rate enhancement depends upon an assumed value of V_M [equation (5)] and on the solvent used for estimation of the rate constant in absence of micelles.

For convenience we compare values of $k_2{}^m$ based on $V_M = 0.14$ l and k_w in *water* for both substrates, noting that $k_2{}^m$ depends upon the value of V_M. These uncertainties do not invalidate comparison of rate constants of deacylation and aromatic nucleophilic substitution, relative to those in bulk solvent, provided that comparisons are made for reactions carried out with the same concentration of t-pentyl alcohol (Table 3). For reaction of CDNN, $k_2{}^m/k_w = 320$ and 100 with CTACl in 0.354M- and 0.884M-t-pentyl alcohol, respectively, as compared with *ca.* 200 in aqueous CTACl or CTABr.[13] However for reaction of pNPB, $k_2{}^m/k_w = 0.3$ and 0.17 for CTACl in water and water plus 0.354M-t-pentyl alcohol, respectively. The values of $k_2{}^m/k_w$ depend upon our arbitrary value of V_M, and the (small) effects of t-pentyl alcohol on k_w, but the differences in micellar effects upon nucleophilic aromatic substitution and deacylation are similar to those in aqueous micelles.[13]

There are inherent problems in estimating second-order rate constants at micellar surfaces, and the pseudophase model which we use here has serious weaknesses. However, on the basis of our results it appears that deacylation by azide ion is no faster at a micellar surface than in a solvent of high water content, in sharp contrast to the behaviour of aromatic substrates.

Azide ion, in the absence of micelles, is a very effective nucleophile towards preformed carbocations and in deacylation,[31] but it is much less reactive in aromatic nucleophilic substitution than predicted by its N_+ value.[15] Our values of $k_2{}^m/k_w$ may therefore be a manifestation of its low nucleophilicity towards CDNN in water, as compared with other substrates, but to date S_NAr reactions of azide are a significant exception to the generalisation that second-order rate constants of ionic reactions at micellar surfaces are similar to those in water.

Acknowledgements

References

1 K. Martinek, A. K. Yatsimirski, A. V. Levashov, and I. V. Berezin in 'Micellization, Solubilization and Microemulsions,' ed. K. L. Mittal, Plenum Press, New York, 1977, vol. 2, p. 489.

2 I. M. Cuccovia, E. H. Schröter, P. M. Monteiro, and H. Chaimovich, *J. Org. Chem.*, 1978, **43**, 2248.

3 J. M. Brown in 'Colloid Science,' Specialist Periodical Report, The Chemical Society, London, 1979, vol. 3, p. 253; C. A. Bunton, *Catal. Rev.-Sci.Eng.*, 1979, **20**, 1; J. R. Sudholter, G. B. van der Langkruis, and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 73; J. H. Fendler, 'Membrane Mimetic Chemistry,' Wiley-Interscience, New York, 1981.

4 L. S. Romsted, in 'Surfactants in Solution,' eds. K. L. Mittal and B. Lindman, Plenum Press, New York, 1984, vol. 2, p. 1015.

5 F. M. Menger and C. E. Portnoy, *J. Am. Chem. Soc.*, 1967, **89**, 4698.

6 E. H. Cordes and C. Gitler, *Prog. Bioorg. Chem.*, 1973, **2**, 1.

7 F. Nome, A. F. Rubira, C. Franco, and L. G. Ionescu, *J. Phys. Chem.*, 1982, **86**, 1881.

8 J. H. Fendler and W. Hinze, *J. Am. Chem. Soc.*, 1981, **103**, 5439; I. M. Cuccovia, F. H. Quina, and H. Chaimovich, *Tetrahedron*, 1982, **38**, 917.

9 (a) T. Kunitake, Y. Okahata, and T. Sakamoto, *J. Am. Chem. Soc.*, 1976, **98**, 7799; (b) C. A. Bunton, Y. S. Hong, L. S. Romsted, and C. Quan, *ibid.*, 1981, **103**, 5784, 5788; (c) G. Biresaw, C. A. Bunton, C. Quan, and Z.-Y. Yang, *ibid.*, 1984, **106**, 7178.

10 (a) R. A. Mackay, *Adv. Colloid Interface Sci.*, 1981, **15**, 131; R. A. Mackay and C. Hermansky, *J. Phys. Chem.*, 1981, **85**, 739; (b) R. A. Mackay, *ibid.*, 1982, **86**, 4756; (c) C. A. Bunton and F. de Buzzaccarini, *ibid.*, 1981, **85**, 3139, 3142.

11 M. J. Blandamer, J. Burgess, and B. Clark, *J. Chem. Soc., Chem. Commun.*, 1983, 659; M. J. Blandamer, B. Clark, J. Burgess, and J. W. M. Scott, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1651; P. D. I. Fletcher and B. H. Robinson, *ibid.*, p. 2417.

12 (a) J. W. Larsen and L. B. Tepley, *J. Colloid. Interface Sci.*, 1974, **49**, 113; (b) R. Zana, *ibid.*, 1980, **78**, 330; (c) P. Lianos and R. Zana, *ibid.*, 1981, **84**, 100; (d) C. A. Bunton and F. de Buzzaccarini, *J. Phys. Chem.*, 1982, **86**, 5010.

13 C. A. Bunton, J. R. Moffatt, and E. Rodenas, *J. Am. Chem. Soc.*, 1982, **104**, 2653.

14 C. A. Bunton and A. Cuenca, *Can. J. Chem.*, 1986, **64**, 1179.

15 C. D. Ritchie and M. Sawada, *J. Am. Chem. Soc.*, 1977, **99**, 3754.

16 (a) C. A. Bunton, L. S. Romsted, and G. Savelli, *J. Am. Chem. Soc.*, 1979, **101**, 1253; (b) C. A. Bunton, L.-H. Gan, J. R. Moffatt, L. S. Romsted, and G. Savelli, *J. Phys. Chem.*, 1981, **85**, 4118.

17 L.-H. Gan, *Can. J. Chem.*, 1985, **63**, 598.

18 F. M. Menger, *Acc. Chem. Res.*, 1979, **12**, 111; D. G. Whitten, J. B. S. Bonilha, K. S. Schanze, and J. R. Winkle, ref. 4, p. 585.

19 D. Hall, P. Jobling, J. E. Rassing, and E. Wyn-Jones, *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**, 1582; A. M. Bellocq, J. B. Baais, B. Clin, P. Lalanne, and B. Lemanceau, *J. Colloid Interface Sci.*, 1979, **70**, 524; L. G. Ionescu, L. S. Romanesco, and F. Nome, ref. 4, p. 789.

20 R. Zana, S. Yiv. C. Strazielle, and P. Lianos, *J. Colloid Interface Sci.*, 1981, **80**, 208.

21 V. Athanassakis, D. C. McKenzie, C. A. Bunton, and D. F. Nicoli, 'Surfactants in Solution,' ed. K. L. Mittal, Plenum Press, New York, in the press.

22 L. S. Romsted, ref. 1, p. 509.

23 F. Quina and H. Chaimovich, *J. Phys. Chem.*, 1979, **83**, 1844.

24 E. B. Abuin, E. Lissi, P. S. Araujo, R. M. V. Aleixo, H. Chaimovich, N. Bianchi, L. Miola, and F. H. Quina, *J. Colloid Interface Sci.*, 1983, **96**, 293; E. Abuin, E. Lissi, N. Bianchi, L. Miola, and F. H. Quina, *J. Phys. Chem.*, 1983, **87**, 5166.

25 H. Chaimovich, J. B. S. Bonilha, M. J. Politi, and F. H. Quina, *J. Phys. Chem.*, 1979, **83**, 1851; D. Bartet, C. Gamboa, and L. Sepúlveda, *ibid.*, 1980, **84**, 272.

26 C. A. Bunton, N. Carrasco, S. K. Huang, C. H. Paik, and L. S. Romsted, *J. Am. Chem. Soc.*, 1978, **100**, 5420.

27 M. Almgren and R. Rydholm, *J. Phys. Chem.*, 1979, **83**, 360; E. Rodenas and S. Vera, *ibid.*, 1985, **89**, 513; N. Funasaki and A. Murata, *Chem. Pharm. Bull.*, 1980, **28**, 805; T. J. Broxton and D. B. Sango, *Aust. J. Chem.*, 1983, **36**, 711; J. R. Hicks and V. C. Reinsborough, *ibid.*, 1982, **35**, 15.

28 A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

29 G. Biresaw, C. A. Bunton, C. Quan, and Z.-Y. Yang, *J. Am. Chem. Soc.*, 1984, **106**, 7178.

30 C. A. Bunton and J. R. Moffatt, *J. Phys. Chem.*, 1985, **89**, 4166; 1986, **90**, 538.

31 C. D. Ritchie, *Pure Appl. Chem.*, 1978, **50**, 1281.