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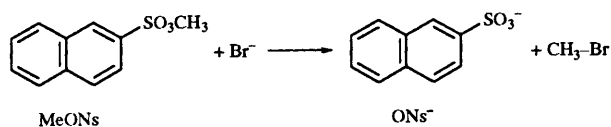
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Addition of the non-ionic surfactant, n-decyl methylsulfoxide (C₁₀SO) to aqueous cetyltrimethylammonium bromide (CTABr) inhibits the micellar-mediated reaction of Br⁻ with bound methyl naphthalene-2-sulfonate (MeONs). The concentration of Br⁻ at the micellar surface is reduced due to an increase in the fractional micellar ionization, α , and in the volume of the micellar pseudophase, which slows the reaction of Br⁻. These concentration effects are partially offset by an increase in the second-order rate constant in the micellar pseudophase on addition of C₁₀SO.

Association colloids, *e.g.*, micelles, microemulsion droplets and vesicles can increase rates of bimolecular reactions by incorporating and concentrating both reactants in the interfacial region at the colloidal surface, which is treated as a reaction region distinct from water, *i.e.*, as a pseudophase.^{1,2} This treatment fits a large amount of data quantitatively in terms of equilibrium transfer of the reactants and second order rate constants in each pseudophase. The overall rate effect depends upon both reactant concentrations at the micelle-water interface and rate constants in that region, and the problem is to separate the contributions of these effects.¹

For reactions in solutions of ionic micelles concentrations of counterions at the micellar surfaces should be related to the fractional micellar coverage, $\beta = 1 - \alpha$, where α is the fractional micellar ionization.¹ Except for very hydrophilic ions α is not very sensitive to total counterion concentrations. The kinetic treatment is simple if the only counterion is the reactive ion, *i.e.*, there is no interionic competition at the micellar surface. In this case, it is easy to calculate the rate constant in the micellar pseudophase.^{1,3}

In this work we consider the S_N2 reaction of Br⁻ with methyl naphthalene-2-sulfonate (MeONs) in micelles of cetyltrimethylammonium bromide (n-C₁₆H₃₃NMe₃Br, CTABr):³



The overall first order rate constant, k_ψ , with respect to MeONs is given by eqn. (1) where k'_w and k'_m are first-order

$$k_\psi = \frac{k'_w + k'_m K_s [\text{CTABr}_M]}{1 + K_s [\text{CTABr}_M]} \quad (1)$$

rate constants in the aqueous and micellar pseudophases respectively, and K_s is the binding constant to micellized CTABr. Subscripts W and M denote aqueous and micellar pseudophases, respectively, and quantities in square brackets are molar concentrations in terms of the total solution volume. If MeONs is fully micellar-bound, and neglecting reaction with H₂O we obtain eqn. (2). In eqn. (2), k'_m , is proportional to the

$$k_\psi = k'_m = \frac{k_M [\text{Br}^-_M]}{[\text{CTABr}_M]} = k_M \beta \quad (2)$$

local concentration of Br⁻ at the interface, and k_M is a second-order rate constant with this concentration written as a mole ratio with the dimensions of reciprocal time, s⁻¹. The second-order rate constant can also be written with the dimensions dm³ mol⁻¹ s⁻¹ by considering the molar volume of the reaction region at the micellar surface.¹

For many bimolecular ionic reactions these rate constants are similar to, or slightly smaller than, those in water. The small contribution of reaction with water can be accounted for by eqn. (3), where k_ψ and k_ψ^c are first-order rate constants with

$$k_\psi^c = k_\psi - k'_{\text{H}_2\text{O}} \quad (3)$$

respect to MeONs, and $k'_{\text{H}_2\text{O}}$ is estimated from reaction in solutions containing weakly non-nucleophilic anions.³ This treatment fits the data reasonably well for reactions of MeONs and Br⁻ or Cl⁻, although in aqueous CTABr (or CTACl) k_ψ increases modestly on addition of Br⁻ (and Cl⁻) because counterion concentrations at micellar surfaces are not strictly constant.^{3,4} The rate increase is much larger for reactions of very hydrophilic ions whose concentrations at the micellar surface increase with their total concentration.⁵ Various models have been developed to fit the increases quantitatively.^{5,6-8}

Addition of non-ionic surfactants or hydrophobic solutes reduces counterionic concentrations at micellar surfaces and therefore rates of bimolecular, counterionic reactions.^{2,3b,9,10} For example, values of α increase (*i.e.* β decreases) significantly under these conditions^{1a,9} and non-ionic solutes or surfactants which enter the micelle also dilute reactants by increasing the volume of the micellar pseudophase. This inhibition is treated by modifying eqn. (3) to eqn. (4),^{3b,9} where R is a mole ratio

$$k_\psi^c = k_M \beta R \quad (4)$$

which, for a solute such as a non-ionic surfactant or hydrophobic alcohol, N_M , is given by eqn. (5).

$$R = \frac{[\text{CTABr}_M]}{[\text{CTABr}_M] + [N_M]} \quad (5)$$

Provided that allowance was made for the distribution of MeONs and butan-1-ol between water and micelles and for a minor contribution of reaction with water, eqns. (4) and (5) fitted the micellar rate data for reaction of Br⁻ with MeONs with a value of k_M that was independent of added butan-1-ol.⁹ The treatment also fitted rate data with mixtures of CTABr and

Table 1 Effect of $C_{10}SO$ on first-order rate constants^a

$[C_{10}SO]/\text{mol dm}^{-3}$	$k_{\psi}^c/10^{-4} \text{ s}^{-1}$
0.0	7.70
0.01	6.24 (5.10)
0.02	5.23 (4.00)
0.025	(3.52)
0.03	5.00 (3.26)
0.04	4.57 (2.88)
0.05	4.42 (2.79)

^a At 25.0 °C with 0.05 mol dm⁻³ CTABr and added $C_{10}SO$, corrected for reaction with water. Values in parentheses are with 0.025 mol dm⁻³ CTABr.

Table 2 First-order rate constants of reaction in constant surfactant^a

$[C_{10}SO]/\text{mol dm}^{-3}$	$k_{\psi}^c/10^{-4} \text{ s}^{-1}$
0.005	6.43
0.0125	5.70 (6.43)
0.015	(6.30)
0.02	4.51
0.025	3.43 (5.65)
0.0275	(5.35)
0.0287	2.80

^a At 25.0 °C with $[CTABr] + [C_{10}SO] = 0.05 \text{ mol dm}^{-3}$, values in parentheses are with 0.05 mol dm⁻³ Br⁻ maintained by addition of NaBr.

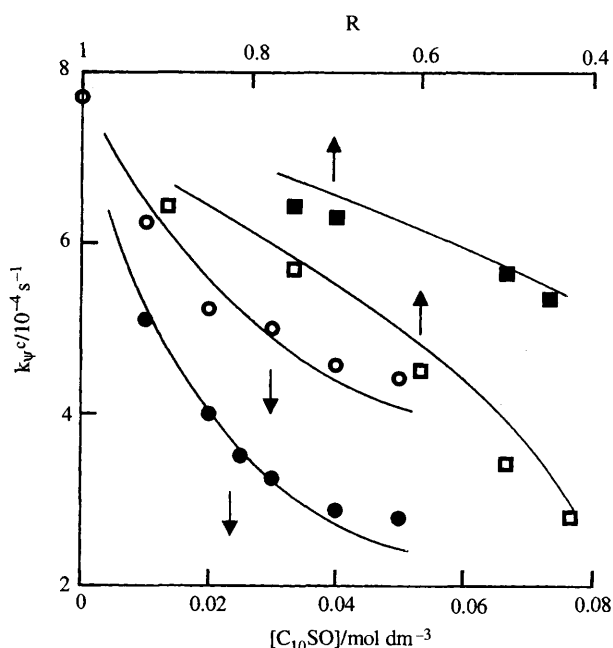


Fig. 1 Corrected first-order rate constants for reaction of Br⁻ with MeONS at 25.0 °C. ○, 0.05 mol dm⁻³ CTABr + $C_{10}SO$; ●, 0.025 mol dm⁻³ CTABr + $C_{10}SO$; □, $[CTABr] + [C_{10}SO] = 0.05 \text{ mol dm}^{-3}$; ■, $[CTABr] + [C_{10}SO] = 0.05 \text{ mol dm}^{-3}$ and $[Br^-_{\text{total}}] = 0.05 \text{ mol dm}^{-3}$. The lines are theoretical.

the non-ionic surfactant $C_{10}E_4$ [$n\text{-C}_{10}\text{H}_{21}(\text{OCH}_2\text{CH}_2)_3\text{O-CH}_2\text{CH}_2\text{OH}$] with constant k_M .^{3b} Therefore, the rate decreases on addition of butan-1-ol or $C_{10}E_4$ to the reaction solution were largely due to a decrease of ionic concentration at the micelle-water interface and not to a change in the second-order rate constant, k_M , in that region.

The situation is different for mixed micelles of CTABr and *n*-dodecyl dimethylphosphine oxide ($C_{12}PO$, $n\text{-C}_{12}\text{H}_{25}\text{PMe}_2\text{O}$).¹¹ The phosphine oxide head group has a strong dipole, so this surfactant could be regarded as either non-ionic or zwitterionic. Addition of $C_{12}PO$ increases α (decreases β) of CTABr and therefore decreases k_{ψ}^c , but less so than predicted by eqns. (4) and (5) with a constant k_M . Analysis

Table 3 Rate effects of salt cations^a

Salt	$R = 0.5$	$R = 0.75$
NaBr	5.64	6.56
LiBr	5.90	6.75
KBr	6.04	6.77
MgBr ₂	5.54	

^a Values of $k_{\psi}^c/10^{-4} \text{ s}^{-1}$ with 0.05 mol dm⁻³ total surfactant and total Br⁻.

of the rate data shows that addition of $C_{12}PO$ increases k_M , i.e., it makes the micelle-water interface a better kinetic medium for an S_N2 reaction of Br⁻, although the non-ionic polyoxyethylene surfactant, $C_{10}E_4$ does not have this effect.^{3b} It appears that the difference in behaviour between $C_{12}PO$ and $C_{10}E_4$ is due to the presence of the dipolar phosphine oxide head group. In this hypothesis other surfactants with dipolar head groups should also behave differently than polyoxyethylene surfactants. We therefore examined the effect of added *n*-decyl methyl sulfoxide ($C_{10}SO$, $n\text{-C}_{10}\text{H}_{21}\text{SMeO}$) on the reaction of Br⁻ with MeONS. Like $C_{12}PO$ this surfactant has a very polar aprotic head group. It has a shorter chain length and a slightly higher critical micelle concentration (cmc) than CTABr, but the two surfactants readily comix with no solubility problems. Rates were followed with sufficient surfactant that MeONS was almost fully micellar-bound,^{3,9,11} and we used values of α to estimate concentrations of Br⁻ at the micellar surface and therefore second-order rate constants in this region.

Results and discussion

Kinetics

Reactions were followed under four sets of conditions similar to those used earlier.^{3b,11} (1) $C_{10}SO$ was added to 0.05 mol dm⁻³ CTABr; (2) $C_{10}SO$ was added to 0.025 mol dm⁻³ CTABr; (3) the total surfactant concentration was constant with $[C_{10}SO] + [CTABr] = 0.05 \text{ mol dm}^{-3}$ and (4) $[C_{10}SO] + [CTABr] = 0.05 \text{ mol dm}^{-3}$ and NaBr was added so that total Br⁻, $[Br^-_{\text{T}}] = 0.05 \text{ mol dm}^{-3}$. Under conditions (1) and (2) $[Br^-_{\text{T}}]$ was constant and total [surfactant] increased, in condition (3) total [surfactant] was constant and $[Br^-_{\text{T}}]$ varied and in condition (4) both total [surfactant] and total $[Br^-_{\text{T}}]$ were constant. Results for the reactions are tabulated and plotted (Tables 1 and 2, and Fig. 1, respectively).

Addition of $C_{10}SO$ inhibits reaction under all conditions, as for addition of butan-1-ol, $C_{10}E_4$ or $C_{12}PO$. Inhibition by $C_{10}SO$ is similar to that by $C_{12}PO$, but less than that by $C_{10}E_4$, as shown by comparison of the following values of $10^4 k_{\psi}^c/\text{s}^{-1}$, in 0.05 mol dm⁻³ CTABr on addition of 0.02 and 0.05 mol dm⁻³ (in parentheses) non-ionic surfactant; $C_{10}E_4$, 4.55 (2.85); $C_{12}PO$, 6.28 (4.63); $C_{10}SO$, 5.35 (4.42), and in CTABr alone $10^4 k_{\psi}^c = 7.7 \text{ s}^{-1}$.

The small contribution of reaction of micellar-bound MeONS with water (Experimental) is similar for the non-ionic surfactants, $C_{10}E_4$, $C_{12}PO$ and $C_{10}SO$.^{3b,11} A few experiments were made in 0.05 mol dm⁻³ total surfactant and total Br⁻ but with different salt cations (Table 3). Values of k_{ψ}^c are insensitive to changes in the salt cation.

Fractional micellar ionization, α

Values of α for mixtures of CTABr and $C_{10}SO$ were calculated from the ratio of slopes taken from plots of conductance against [surfactant] above and below the cmc for given values of R [eqn. (5)].¹² Addition of $C_{10}SO$ increases α (Table 4), as for other non-ionic surfactants and non-ionic hydrophobic solutes.^{1,3b,9,11} Plots of α against R are approximately linear, as with $C_{10}E_4$ and $C_{12}PO$.^{3b,11} Values of α at high $[C_{10}SO]$, i.e., low R , are uncertain because slopes of conductance above and

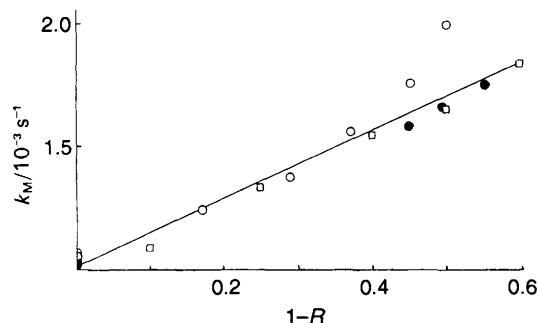
Table 4 Fractional micellar ionization, α , in mixtures of CTABr and C₁₀SO

R	α
1.0	0.25
0.9	0.35
0.8	0.42
0.67	0.45
0.50	0.55
0.33	0.66

Table 5 Critical micelle concentrations of CTABr + C₁₀SO

R	cmc ^a
1.0	0.9
0.91	0.93 ^b
0.80	0.94 ^b
0.67	1.05 ^b
0.50	0.99, 1.05 ^b
0.33	1.00, 1.06 ^b
0.25	1.04
0.11	1.29
0.0	1.92

^a In mmol dm⁻³ from surface tension, unless specified. ^b From conductivity plots.

**Fig. 2** Effect of C₁₀SO upon k_M . Symbols as in Fig. 1.

below the cmc are similar and as the micelle becomes more charged the assumptions involved in the 'method of slopes' become less reliable.

Critical micelle concentration

The cmc increases modestly on addition of C₁₀SO to CTABr with $R > 0.25$ and then it increases more sharply (Table 5). Both surface tension and conductivity results are presented, of which the surface tension results are considered to be the more reliable (due to the small slope changes observed in the conductivity method). Analysis of the surface tension results using a simple binary non-ideal mixed micelle model¹³ shows that the observed cmc behaviour can be well described by using a single dimensionless nonideality parameter of -1.3 in the pseudophase separation approach. This value is very similar to that of -1.35 for the non-ideality parameter determined by us earlier for the CTABr/C₁₂PO mixed system.¹¹ Together with the mixed cmc results, this suggests that no unusual effects are occurring during mixed micelle formation in the CTABr/C₁₀SO system.

Quantitative kinetic treatment

Our initial approach was to attempt to fit values of k_ψ^c to eqns. (4) and (5), with constant k_M , on the assumption that MeONs is almost wholly micellar bound, based on $K_s = 1500 \text{ mol}^{-1} \text{ dm}^3$ in cetyltrimethylammonium mesylate.^{3,9} (This assumption is not strictly correct for reaction in $0.025 \text{ mol dm}^{-3}$ CTABr, but it improves on addition of C₁₀SO, and $< 3\%$ of MeONs is unbound in all conditions.)

The rate data for reaction of Br⁻ with MeONs in CTABr with added butan-1-ol or C₁₀E₄ had been fitted by eqns. (3)–(5) with $k_M \approx 1.0 \times 10^{-3} \text{ s}^{-1}$, as for reaction in aqueous CTABr, *i.e.*, addition of these solutes does not significantly affect second-order rate constants at the micelle–water interface.^{3,9} This simple treatment fails for addition of either C₁₂PO¹¹ or C₁₀SO, based on the values of R and α given in Table 4, and k_M increases smoothly on addition of these surfactants. For experiments with constant total [surfactant] and no NaBr k_M increases linearly with $1 - R$, with $R > 0.5$ and for constant [CTABr] and added C₁₀SO with $R > 0.4$, but there is deviation from linearity at low R (Fig. 2). We neglect the amount of monomeric surfactants in estimating R , which may cause some of the deviations from linearity in Fig. 2. The linear part of the plot (Fig. 2) fits eqn. (6), where $k_M^o = 1.0 \times 10^{-3} \text{ s}^{-1}$

$$\frac{k_M}{k_M^o} = 1 + 1.4(1 - R) \quad (6)$$

in CTABr. The corresponding plot for CTABr + C₁₂PO¹¹ has a slope of 1.7 and $k_M^o = 1.0 \times 10^{-3} \text{ s}^{-1}$.

Based on eqns. (4)–(6) the rate constants for reaction in CTABr plus added C₁₀SO are given by eqn. (7).

$$k_\psi^c = 1.0 \times 10^{-3} [1 + 1.4(1 - R)]\beta R \quad (7)$$

The fit of k_ψ^c to R or to [C₁₀SO] based on eqn. (7) is reasonably good for mixtures of CTABr and C₁₀SO with [C₁₀SO] $< 0.04 \text{ mol dm}^{-3}$ and for 0.05 mol dm^{-3} total surfactant with $R > 0.4$ (Fig. 1). The treatment underpredicts the rate constants at high [C₁₀SO] and variable surfactant for several reasons: (i) the correction for reaction with water is based on experiments with CTA(SO₄)_{0.5} (Experimental) and is relatively more important at high R ; (ii) the method of slopes¹² is least reliable at high α where it tends to overestimate α so that β values are too low and k_ψ^c is therefore underestimated; (iii) we neglect the concentration of monomeric surfactant.

The situation is different when Br⁻ is in excess of CTABr due to addition of NaBr, and conductivity cannot be used to estimate α (or β). In water, for strongly micellar-interacting counterions, *e.g.*, Br⁻, the counterion concentration at the micelle–water interface, as given by β , increases only modestly on addition of the counterion,^{1,3a,10} *e.g.*, the assumption of constant β and constant concentration of Br⁻ at the micellar surface is reasonably satisfactory for CTABr and dilute added Br⁻. However, values of β increase with increasing [counterion] as micelle–ion affinities decrease, *e.g.*, due to addition of a non-ionic solute,^{3b,9} or with very hydrophilic counterions.^{1b,5,8} We may therefore underestimate concentrations of Br⁻ at the micellar surface from values of α determined conductimetrically without added NaBr for mixtures of CTABr and C₁₀SO.

This increase of ion concentration at the micellar surface can be treated by solving the Poisson–Boltzmann equation in the appropriate symmetry,^{6,7} or more simply in terms of eqn. (8),

$$K'_{\text{Br}} = \frac{[\text{Br}^-]_{\text{M}}}{[\text{Br}^-]_{\text{W}}([\text{CTABr}_{\text{M}}] - [\text{Br}^-]_{\text{M}})} \quad (8)$$

which has the form of a Langmuir isotherm,^{1a,5} and is satisfactory over a limited range of counterion concentration¹¹ and is shown for CTABr + Br⁻.

This equation can be written for any anion, X⁻, with the association constant, K'_X . The association constant K'_{Br} (K'_X) is related to the fractional micellar ionization, α , and high values of α correspond to low values of K'_X .^{1b,5} At the simplest level eqn. (8) can be rewritten as eqn. (9)^{9b}.

$$K'_{\text{Br}} = \frac{1 - \alpha}{\alpha^2[\text{CTABr}_{\text{M}}]} \quad \text{or} \quad \frac{\beta}{\alpha^2[\text{CTABr}_{\text{M}}]} \quad (9)$$

Eqn. (9) involves the approximation that $\alpha[\text{CTABr}] \gg \text{cmc}$, which is reasonable for these experiments with added salts where we apply this treatment.^{9b} We use eqn. (9) to relate observed increases in α on addition of C_{10}SO (Table 4) to decreases in K'_{Br} , which allows calculation of changes in $[\text{Br}^-_{\text{M}}]$ on addition of Br^- by using eqns. (8) and (9).

We take $K'_{\text{Br}} = 400 \text{ dm}^3 \text{ mol}^{-1}$ for aqueous CTABr based on earlier kinetic fits^{3a,9b} and estimate the association constant with added C_{10}SO in terms of eqn. (10), where α_0 is the

$$\frac{K'_{\text{Br}}}{K'_{\text{Br}}(\text{H}_2\text{O})} = \frac{(1 - \alpha)\alpha_0^2}{(1 - \alpha_0)\alpha^2} \quad (10)$$

fractional ionization of CTABr in water and values of α in CTABr + C_{10}SO are from data in Table 4. The association constant in water is designated $K'_{\text{Br}}(\text{H}_2\text{O}) = 400 \text{ dm}^3 \text{ mol}^{-1}$ in eqn. (10). This treatment differs slightly from that used earlier,^{2c,9b} but leads to similar estimates of the loss of Br^- from the micelle on addition of a non-ionic solute, based on decreases in K'_{Br} on addition of C_{10}SO .

Values of $[\text{Br}^-_{\text{M}}]$ are estimated in terms of $[\text{CTABr}_{\text{M}}]$ and $[\text{Br}^-_{\text{T}}] = [\text{CTABr}] + [\text{NaBr}]$ and eqn. (8). In our experiments with 0.05 mol dm^{-3} total surfactant we neglect the amount of monomeric surfactant because of the low cmc (Table 5) and decreases in the cmc with added salt.¹

Based on values of α (Table 4) we calculate values of $K'_{\text{Br}}/\text{dm}^3 \text{ mol}^{-1}$, of 110, 93, 54 and 47 in 0.0375, 0.035, 0.027 and 0.025 mol dm^{-3} CTABr, respectively, with $[\text{CTABr}] + [\text{C}_{10}\text{SO}] = 0.05 \text{ mol dm}^{-3}$ and constant $[\text{Br}^-]$. Based on these values of K'_{Br} and eqn. (7) we calculate the values of k_{ψ}^c shown as solid squares in Fig. 1. Predicted values of k_{ψ}^c agree at lower $[\text{CTABr}]$ and are too high in 0.0375 and 0.035 mol dm^{-3} CTABr, but deviations are $< 10\%$ and are understandable in view of the approximations and assumptions of the model. There are random errors in the rate constants (Experimental) and systematic errors due to approximations in the determination of fractional micellar ionization, α , by the method of slopes¹² which are most serious at high $[\text{C}_{10}\text{SO}]$ and low R . For example, the dependence of k_{M} upon R [eqn. (6)] was tested for reactions in the absence of added NaBr (Fig. 2) and the kinetic data with added NaBr would fit better if we use a slightly different slope parameter in eqn (6). In many quantitative fits of micellar rate enhancements calculated values of k_{M} in the micellar pseudophase are not strictly constant but depend to some extent on the experimental conditions of the reaction.¹ However, our very simple model fits the kinetic data within experimental errors in k_{ψ} and α and uncertainties in the concentrations of monomeric surfactant provided that C_{10}SO or (C_{12}PO) is not in large excess over CTABr. Changes in the salt cation have minor effects on reaction rates (Table 3).

Micelles as reaction media

We calculate second-order rate constants in the micellar pseudophase in terms of $k_{\text{M}}/\text{s}^{-1}$, where the concentration of Br^- is written as $[\text{Br}^-_{\text{M}}]/([\text{CTABr}] + [\text{C}_{10}\text{SO}])$. These units of concentration are defined unambiguously,^{1,3,5} but cannot be compared directly with second-order rate constants in water written as $k_{\text{W}}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, with concentration as molarity. This measure of concentration is convenient, but its significance is not obvious when solvent compositions are changed. Mole ratios can be converted into molarities at micelle-water interfaces in terms of an assumed molar volume, V_{M} , of this region.¹ The second-order rate constants, $k_2^{\text{m}} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, written with concentration as a local molarity, are then given by eqn. (11).

$$k_2^{\text{m}} = k_{\text{M}}V_{\text{M}} \quad (11)$$

A range of values from 0.14 to 0.37 $\text{dm}^3 \text{ mol}^{-1}$ has been applied to the reactive regions of aqueous micelles¹ and second-

order rate constants in micellar and aqueous pseudophases, k_2^{m} and k_{W} , have been compared in terms of selected values of V_{M} . Therefore, differences in values of $k_2^{\text{m}}/k_{\text{W}}$ for various reactions may be due simply to differences in V_{M} . However, concentrations of Br^- estimated by trapping in dediazonizations experiments are similar to those estimated in terms of the size of the reaction region at the micellar surface, equivalent to V_{M} ,^{6d} although the trapping method involves no assumptions regarding V_{M} .¹⁰ We therefore believe that assumed values of V_{M} are not badly wrong, although they are probably not strictly constant over a range of conditions. Within the uncertainties in the treatment $k_2^{\text{m}} \approx k_{\text{W}}$ for reaction of Br^- with MeONs in aqueous micelles of CTABr.^{6a,b,d}

Calculated second-order rate constants of reaction, k_{M} , are very similar for reaction of Br^- with MeONs in CTABr micelles in water,³ in water and butan-1-ol⁹ and in mixed micelles of CTABr and C_{10}E_4 ,^{3b} indicating that it is reasonable to analyse rate data in terms of the mole ratio of bound Br^- to total surfactant or surfactant + bound butan-1-ol or C_{10}E_4 , *i.e.*, in terms of local concentrations at the micellar surface. It seems, therefore, that differences in the behaviour of C_{10}SO or the phosphine oxide, C_{12}PO ,¹¹ relative to the other nonpolar solutes, *e.g.*, butan-1-ol and C_{10}E_4 , are due not to differences in estimated concentrations of bound Br^- , but to differences in its nucleophilicity at micellar surfaces. On this hypothesis both C_{10}SO and C_{12}PO are increasing the nucleophilicity of Br^- at the micellar surface, just as the nucleophilicities of anions in dipolar organic solvents, *e.g.*, dimethyl sulfoxide or hexamethyl phosphoramide $(\text{Me}_2\text{N})_3\text{PO}$, are higher than those in protic solvents, *e.g.*, H_2O or primary alcohols.¹⁴

Addition of C_{10}SO (or C_{12}PO) to aqueous CTABr affects the overall rate of the micellar reaction of Br^- with MeONs in two opposing ways. (i) It decreases the amount of Br^- at the micellar surface, as shown by the increase in α . (ii) It increases the nucleophilicity of Br^- at the micellar surface, as in non-micellar systems.¹⁴ In the microsolvent reaction region at micellar surfaces, a sulfoxide, *e.g.*, C_{10}SO , or a phosphine oxide, *e.g.*, C_{12}PO ,¹¹ accepts hydrogen bonds of water at the surface, *i.e.*, it competes with Br^- as a hydrogen bond acceptor. Primary alcohols, *e.g.*, butan-1-ol, or polyoxyethylated surfactants, *e.g.*, C_{10}E_4 , are both hydrogen bond donors and acceptors, and therefore are less effective than C_{10}SO or C_{12}PO in increasing the nucleophilicity of Br^- at micellar surfaces. This consideration of the balance between hydrogen bond donation and acceptance has been invoked in considerations of kinetic solvent effects upon ionic reactions in solution,¹⁵ and it can be extended to the behavior of the micelle-water interface as a reaction medium.

Experimental

Materials

The reagents and ionic surfactants were samples used in earlier work^{3,9} and the C_{10}SO was the single-species surfactant.

Fractional micellar ionization, α

Values of α (Table 4) were estimated from the ratio of slopes of plots of conductance against concentration of mixtures of CTABr and C_{10}SO above and below the cmc at 25 °C.¹²

Critical micelle concentration

The effect on the cmc of CTABr on addition of C_{10}SO was monitored from plots of surface tension against log [surfactant] by the du Nouy method with a Fisher Tensionmat. There were no minima in these plots. Values were also estimated from conductance plots (Table 5).

Kinetics

The reaction of Br^- with $10^{-4} \text{ mol dm}^{-3}$ MeONs was followed spectrophotometrically at 326 nm and 25.0 °C as described.^{3,9}

There is a minor contribution of reaction with water and we made a correction based on values of $10^4 k_{\text{H}_2\text{O}}$ of 0.13 and 0.43 s^{-1} in 0.05 mol dm^{-3} CTA(SO₄)_{0.5} with and without added 0.05 mol dm^{-3} C₁₀SO on the assumption that, as with other non-ionic solutes and surfactants, $k_{\text{H}_2\text{O}}$ decreases approximately linearly with [C₁₀SO]. In this and earlier work on this reaction first-order rate constants were reproducible to within $\pm 5\%$.

Symbols

K_s	binding constant/ $\text{dm}^3 \text{ mol}^{-1}$ of substrate based on concentration of micellized surfactant
k'_{W}	first-order rate constant/ s^{-1} with respect to substrate in the aqueous pseudophase
k'_{M}	first-order rate constant/ s^{-1} with respect to substrate in the micellar pseudophase
k_{ψ}	observed first-order rate constant with respect to substrate
$k_{\text{H}_2\text{O}}$	first-order rate constant for reaction with water
k_{ψ}^{c}	corrected overall first-order rate constant; $k_{\psi}^{\text{c}} = k_{\psi} - k_{\text{H}_2\text{O}}$
k_{M}	second-order rate constant/ s^{-1} in the micellar pseudophase, with concentration as a mole ratio
R	ratio of CTABr to total surfactant
α	degree of fractional micellar ionization
β	fractional counterion binding (neutralization) of micelle, $\beta = 1 - \alpha$

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