S_N2 Reactions of a sulfonate ester in mixed cationic/phosphine oxide micelles

Andrei Blaskó,[a] Clifford A. Bunton,[a] Eduardo A. Toledo,†,[a] Paul M. Holland[b] and Faruk Nome[c]
[a] *Department of Chemistry, University of California, Santa Barbara, California 93106*
[b] *GRC International, PO Box 6770, Santa Barbara, California 93160*
[c] *Departamento de Quimica, Universidade Federal de Santa Catarina, 88049-Florianopolis, SC, Brazil*

Addition of the nonionic surfactant, dodecyl(dimethyl)phosphine oxide ($C_{12}PO$) to aqueous cetyltrimethylammonium bromide (CTABr) inhibits the micellar-mediated reaction of Br^- with fully bound methyl naphthalene-2-sulfonate (MeONs). Reaction in the micellar pseudophase depends on the concentration of Br^- in the interfacial surface region, which is decreased on addition of $C_{12}PO$ by increases in both the fractional micellar ionization, α, and the volume of the micellar pseudophase. The inhibition of the reaction is partially offset by an increase in the second-order rate constant in the micellar pseudophase on addition of $C_{12}PO$ which appears to be related to a solvent-like effect at the micelle–water interface. Interactions of CTABr and $C_{12}PO$ in the mixed micelles were explored by using ^1H and ^{31}P NMR spectroscopy.

Association colloids, such as micelles or microemulsion droplets, can increase rates of bimolecular reactions in aqueous solution by concentrating the reactants in the interfacial region at the colloidal surface.[1–3] As applied to reactions of counter-ions, the concentration of ions at micellar surfaces should be directly related to the fractional micellar coverage, β, given by $1 - \alpha$ where α is the fractional micellar ionization.[1b–e] Values of α are not very sensitive to the total counter-ion concentration, except for very hydrophilic ions.

First order rate constants, k_ψ, with respect to substrate are given by eqn. (1), where k'_W and k'_M are first-order rate

$$k_\psi = \frac{k'_W + k'_M K_s[D_n]}{1 + K_s[D_n]} \qquad (1)$$

constants in the aqueous and micellar pseudophases respectively, K_s, is the binding constant of the substrate to micellized surfactant (detergent) whose concentration, D_n, is that of total surfactant less that of monomer. If the substrate is fully micellar-bound, eqn. (1) simplifies to eqn. (2).

$$k_\psi = k'_M \qquad (2)$$

For bimolecular, non-solvolytic, reactions the first-order rate constant, k'_M, with respect to substrate should be proportional to the concentration of the second (ionic) reagent at the micelle–water interface. This concentration can be expressed in various ways, *e.g.* as a local molar concentration, or as a mole ratio of bound counter-ion to micellar head groups.[1c] In this second case eqn. (2) gives, for reaction of Br^- with fully bound substrate, eqn. (3). The quantities in square brackets are molar

$$k_\psi = k'_M = \frac{k_M[Br^-_M]}{[D_n]} \qquad (3)$$

concentrations written in terms of total solution volume, where the subscript M denotes the micellar pseudophase.

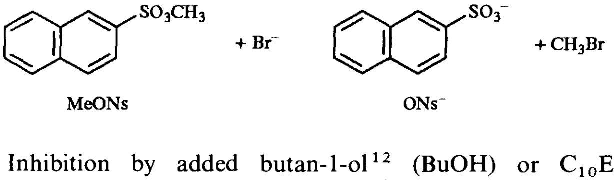
If the surfactant is cetyltrimethylammonium bromide (CTABr) and its concentration is much larger than the critical micelle concentration, cmc (*i.e.* nearly all of the surfactant is micellised), and the substrate is fully bound, the first-order rate constant is given by eqn. (4).[1c,4,5]

$$k_\psi = k_M[Br^-_M]/[CTABr] = k_M\beta \qquad (4)$$

This simple relation fits the rate data reasonably well, although k_ψ typically increases modestly on the addition of Br^-.[5,6] This increase can be explained on the assumption that β, which is directly related to counter-ion concentration, is not strictly constant and increases with the total counter-ion concentration. There is experimental evidence for this increase and it can be fitted by various theoretical treatments.[4–9]

Additions of non-ionic surfactants or hydrophobic non-ionic solutes, *e.g.* butanol or longer-chain alcohols, to cationic micelles, reduces rates of bimolecular, anionic reactions.[2,4,6] The acid hydrolysis of methyl orthobenzoate in solutions of sodium dodecyl sulfate (SDS) is inhibited by butan-1-ol and heptan-1-ol and very strongly by dodecyl(dimethyl)phosphine oxide ($C_{12}H_{25}PMe_2O$, $C_{12}PO$).[10] If the substrate is fully micellar-bound this inhibition could be due to a decrease in the concentration of reactive ion in the interfacial region, or to a decrease in the second-order rate constant.

Organic solutes and non-ionic surfactants decrease fractional micellar coverage, β,[1c,11,12] and they also increase the volume of the micellar pseudophase. These two effects on concentration also explain the decrease in the rate constants for the S_N2 reaction of Br^- with methyl naphthalene-2-sulfonate (MeONs) on addition of a non-ionic surfactant,[4] or hydrophobic alcohol.[12]



Inhibition by added butan-1-ol[12] (BuOH) or $C_{10}E_4$ [$C_{10}H_{21}(OCH_2CH_2)_3OCH_2CH_2OH$][4] was treated quantitatively by estimating β conductimetrically and allowing for the increased volume of the micellar pseudophase by rewriting eqn. (4) as eqn. (5).

$$k_\psi = k_M\beta R \qquad (5)$$

---

† *Present address:* Department of Chemistry, University of Maringa, Maringa, Parana, Brazil.

Where R is the mole ratio defined as

$$R = \frac{[\mathrm{CTABr}]}{[\mathrm{CTABr}] + [\mathrm{BuOH_M}]} \qquad (6)$$

or

$$R = \frac{[\mathrm{CTABr}]}{[\mathrm{CTABr}] + [\mathrm{C_{10}E_4}]} \qquad (7)$$

with [surfactant] $\gg$ cmc.

Provided that MeONs was fully micellar-bound, values of k_M were very similar in CTABr, in CTABr–BuOH and in CTABr–$C_{10}E_4$.[4,6,12] Therefore incorporation of either BuOH or $C_{10}E_4$ into a CTABr micelle does not significantly affect the properties of the micelle–water interface as a medium for an S_N2 reaction, although the concentration of Br^- at the micellar surface is reduced. These results are in contrast with evidence that rates of S_N2 reactions of anionic nucleophiles in non-micellar systems are sensitive to solvent properties.[13]

In the present study we examine the effect of $C_{12}PO$ on the rate of reaction of Br^- with MeONs in micellized CTABr. Phosphine oxide surfactants have highly polar, aprotic head groups, and so might be expected to behave differently than non-ionic polyethylene oxide surfactants such as $C_{10}E_4$ as kinetic media, based on values of k_M [eqn. (5)].

Experimental

Materials

The preparation and purification of MeONs, CTABr and $CTA(SO_4)_{0.5}$ have been described previously.[4] The sample of $C_{12}PO$ was the single-species surfactant with a purity of 99.89% as determined by gas chromatography.

Fractional micellar ionization *α*

Values of α were estimated from the ratio of slopes of plots of conductance against concentration of mixtures of CTABr and $C_{12}PO$ above and below the cmc at 25 °C.[14]

Critical micelle concentration

The decrease of the cmc on addition of $C_{12}PO$ to CTABr was determined from plots of surface tension against log surfactant concentration by the de Nouy method with a Fisher Tensionmat. There were no minima in these plots.

Kinetics

The reaction of Br^- with 10^{-4} mol dm^{-3} MeONs was followed spectrometrically at 326 nm and 25.0 °C as described.[4] The spontaneous reaction with water was followed in $CTA(SO_4)_{0.5}$ + $C_{12}PO$ with *ca.* 10^{-4} mol dm^{-3} H^+ to suppress any reaction with OH^-. The first-order rate constant, k_{H_2O}/s^{-1}, decreased linearly with the mole fraction of $C_{12}PO$ to total surfactant, x, according to eqn. (8), and we used interpolated values of k_{H_2O}.

$$10^5\, k_{H_2O} = 4.42(1 - 0.71x) \qquad (8)$$

The effect of $C_{12}PO$ on the rate of reaction with water is very similar to that of $C_{10}E_4$. In fitting rate data for the reaction of Br^- we corrected for K_{H_2O} by use of eqn. (9).

$$k_c^{\psi} = k_{\psi} - k_{H_2O} \qquad (9)$$

This correction is of minor importance, except at low R where reaction with Br^- is slowest. For reaction with 0.03 mol dm^{-3} CTABr we assume that the relative effect of $C_{12}PO$ on reaction with water would be as with 0.05 mol dm^{-3} CTABr and modified eqn. (8) to become eqn. (10).

$$10^5\, k_{H_2O} = 3.7(1 - 0.71x) \qquad (10)$$

NMR spectroscopy

^1H and ^{31}P spectra were recorded on a General Electric GN500 spectrometer at 25 °C and chemical shifts were referred to 3-(trimethylsilyl)propane-1-sulfonic acid sodium salt (DSS) and external H_3PO_4, respectively. Spectra were recorded in 16 K and apodized with an exponential function to give line broadening of 0.1 and 1 Hz for ^1H and ^{31}P, respectively. Except where specified ^{31}P spectra were ^1H decoupled.

Results and discussion

Kinetics

Added $C_{12}PO$ inhibits the reaction of Br^- with MeONs in solutions of CTABr (Fig. 1). We used four sets of conditions: (1) $C_{12}PO$ was added to 0.05 mol dm^{-3} CTABr, so that the total [surfactant] increased, but total $[Br^-]$ was held constant (Table 1); (2) constant total surfactant concentration, *i.e.* $[C_{12}PO]$ + [CTABr] = 0.05 mol dm^{-3} with total $[Br^-]$ not constant (Table 2); (3) $[C_{12}PO]$ + [CTABr] = 0.05 mol dm^{-3} with $[Br^-]$ maintained at 0.05 mol dm^{-3} by addition of NaBr (Table 2); and (4) a few experiments were made with 0.03 mol dm^{-3} CTABr and added $C_{12}PO$ (Table 1). For convenience we define R as[4] given in eqn. (11).

$$R = \frac{[\mathrm{CTABr}]}{[\mathrm{CTABr}] + [\mathrm{C_{12}PO}]} \qquad (11)$$

Inhibition by $C_{12}PO$ is less than by $C_{10}E_4$, for example with 0.05 mol dm^{-3} CTABr and 0.05 mol dm^{-3} $C_{12}PO$, $10^4\, k_{\psi}$ = 4.83 s^{-1} as compared with $10^4\, k_{\psi}$ = 3.0 s^{-1} with added 0.05 mol dm^{-3} $C_{10}E_4$ and rate differences are similar over a range of conditions.[4] These qualitative observations indicate that the simple treatment with constant k_M probably does not fit the effects of $C_{12}PO$, although it describes those of both added BuOH and $C_{10}E_4$.[4,6,12] As shown below $C_{10}E_4$ and $C_{12}PO$ have similar effects on β.

There is a minor contribution from the reaction with water

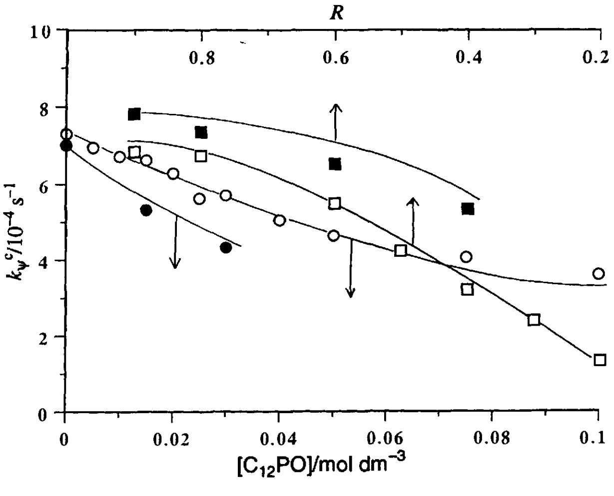


Fig. 1 Reaction in mixed micelles of CTABr + $C_{12}PO$: ○, 0.05 mol dm^{-3}; CTABr + $C_{12}PO$; ●, 0.03 mol dm^{-3}; CTABr + $C_{12}PO$; □, CTABr + $C_{12}PO$ at constant [surfactant] = 0.05 mol dm^{-3}; ■, CTABr + $C_{12}PO$ at constant [surfactant] = 0.05 mol dm^{-3} and 0.05 mol dm^{-3} Br_T^-. The lines are theoretical, from eqns. (9), (10), (13) and (14), respectively.

Table 1 Effect of $C_{12}PO$ on first-order rate constants[a]

$[C_{12}PO]$/mol dm^{-3}	$k_\psi{}^c/10^{-4}$ s^{-1}
0.0	7.30 (7.01)
0.005	6.95
0.01	6.72
0.015	6.62 (5.23)
0.02	6.28
0.025	5.62
0.03	5.70 (4.24)
0.04	5.05
0.05	4.63
0.075	4.05
0.10	3.60

[a] At 25.0 °C with 0.05 mol dm^{-3} CTABr and added $C_{12}PO$, corrected for reaction with water. Values in parentheses are with 0.03 mol dm^{-3} CTABr.

Table 2 First-order rate constants of reaction in constant surfactant concentration[a]

$[C_{12}PO]$/mol dm^{-3}	$k_\psi{}^c/10^{-4}$ s^{-1}
0.005	6.84 (7.82)
0.01	6.74 (7.35)
0.02	5.48 (6.52)
0.025	4.22
0.03	3.20 (5.33)
0.035	2.39
0.04	1.32

[a] At 25.0 °C with [CTABr] + $[C_{12}PO]$ = 0.05 mol dm^{-3}, values in parentheses are with 0.05 mol dm^{-3} Br^- maintained by addition of NaBr.

which is relatively unimportant except at low R, and we correct for it based on reaction in $CTA(SO_4)_{0.5}$ + $C_{12}PO$ (experimental). Values of the first-order rate constant, k_{H_2O}, are similar to those for the reaction in $CTA(SO_4)_{0.5}$ and $C_{10}E_4$.[4] Corrections are based on interpolated values of k_{H_2O} and the corrected first-order rate constant for reaction with Br^-, $k_\psi{}^c = k_\psi - k_{H_2O}$.

Fractional micellar ionization α

Values of α for mixtures of CTABr and $C_{12}PO$ were calculated from the ratio of slopes taken from plots of conductivity against surfactant concentration at concentrations below and above the cmc,[4,12,14] for given values of R [eqn. (11)]. The increase of α on addition of $C_{12}PO$ to CTABr (Table 3) is similar to that observed with $C_{10}E_4$, and plots of $\beta = (1 - \alpha)$ against R are linear for both non-ionic surfactants.[4] Values of β over a range of R were estimated by interpolation or extrapolation.

Critical micelle concentration

Surface tension measurements show that the cmc decreases sharply on the initial addition of $C_{12}PO$ to CTABr, becoming approximately constant with $R < 0.5$ (see Table 4). Analysis of these results using a simple binary non-ideal mixed micelle model[15] shows that the observed cmc behaviour can be well described by using a single dimensionless non-ideality parameter of −1.35 in the pseudophase separation approach. This regular behaviour seen for the CTABr–$C_{12}PO$ mixed system indicates that no unusual effects occur during mixed micelle formation.

Quantitative kinetic treatment

In our experiments with surfactant concentrations ⩾0.05 mol dm^{-3}, we neglect the concentration of monomeric surfactant, based on values of the cmc (Table 4). The binding constant of MeONs in cetyltrimethylammonium mesylate, K_s = 1500 dm^3 mol^{-1}, so in fitting the kinetic data we assume that MeONs is fully micellar-bound,[4] and we neglect the contributions of reactions in the aqueous pseudophase.

Table 3 Fractional micellar ionization, α, from conductivity

$[Cl_{12}PO]$/[CTABr]	R	α
0[a]	1.0	0.25[b]
0.5	0.66	0.41
1.0	0.50	0.49
2.0	0.33	0.60

[a] From conductance. [b] Ref. 13.

Table 4 Critical micelle concentrations[a]

R	cmc/10^{-4} mol dm^{-3}
1.0	9.0
0.67	4.1
0.50	3.4
0.33	3.3
0.0	3.2

[a] From surface tension.

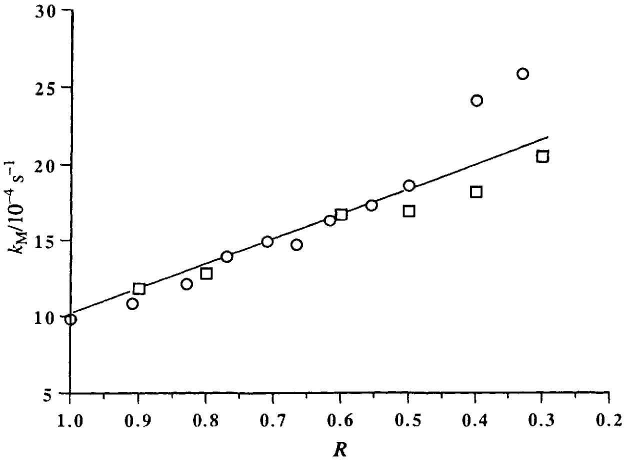


Fig. 2 Effect of added $C_{12}PO$ upon k_M, eqn. (5), symbols as in Fig. 1

At a given mole fraction, R, of CTABr values of k_ψ or $k_\psi{}^c$ are larger than those for reaction in CTABr + $C_{10}E_4$,[4] *i.e.* the simple treatment based on eqn. (5) and constant k_M is inadequate.[4,12] The simplest explanation of this failure is that the second-order rate constant k_M increases on addition of $C_{12}PO$. Values of k_M in mixtures of CTABr and $C_{12}PO$ calculated in terms of R and β [eqn. (5)] increase linearly with $1 - R$, for R in the range 0 to 0.5 with deviations for data for variable [surfactant] at high R (Fig. 2), with a slope of 0.0017 s^{-1}. We modify eqn. (5) to allow for this variation of the second-order rate constant and obtain eqns. (12) and (13) where $k_M{}^\circ$ is

$$k_M = k_M{}^\circ + 0.0017(1 - R) \quad (12)$$

$$k_\psi{}^c = [k_M{}^\circ + 0.0017(1 - R)]\beta R \quad (13)$$

the second-order rate constant for reaction in the micellar-pseudophase of CTABr with concentration of Br^- in the micelles written as a mole ratio with respect to surfactant. The fit to eqn. (12) is reasonably good except at low R where the correction for reaction with water becomes more important (Fig. 2). For reaction in 0.05 mol dm^{-3} CTABr we take $k_M{}^\circ$ = 1.0 × 10^{-3} s^{-1}, as in earlier work,[4,12] and eqn. (10) fits the data reasonably well for reaction in 0.05 mol dm^{-3} CTABr and added $C_{12}PO$, and in mixtures of CTABr and $C_{12}PO$ with 0.05 mol dm^{-3} total surfactant (Fig. 1). We carried out a few experiments with 0.03 mol dm^{-3} CTABr and added $C_{12}PO$

(Fig. 1). Because the substrate should be *ca.* 97% bound in 0.03 mol dm^{-3} CTABr, we corrected the calculated first-order rate constants by 3%, retaining the value of $k_M{}^\circ = 1.0 \times 10^{-3}$ s^{-1}. With interpolated values of β we obtained the fit shown in Fig. 1.

This simple treatment with a variable k_M should in principle also fit rate data for reactions in solutions of [CTABr] + [$C_{12}PO$] = 0.05 mol dm^{-3} and added NaBr, *i.e.* with constant [$Br_T{}^-$]. However, if we take $k_M = 1.0 \times 10^{-3}$ s^{-1}, as for reactions in which the total concentration of Br^- = [CTABr], we underpredict the rate constant in 0.04 mol dm^{-3} CTABr by *ca.* 10% and the discrepancy markedly increases as [CTABr] is decreased.

In experiments without added NaBr the total concentration [$Br_T{}^-$] is either constant, with $C_{12}PO$ added to 0.05 mol dm^{-3} CTABr, or decreases, with [CTABr] + [$C_{12}PO$] = 0.05 mol dm^{-3}, because the Br^- is all derived from CTABr. If [$Br_T{}^-$] is maintained at 0.05 mol dm^{-3} by addition of NaBr and a total surfactant concentration of 0.05 mol dm^{-3} [$Br_M{}^-$] relative to [CTABr] is buffered by Br^- in the aqueous pseudophase.[1b,c] If counter-ions interact strongly with a micelle β is not very sensitive to their total concentration, but as the micelle–counter-ion affinity decreases the sensitivity of β to added counter-ion increases.[1c,e,7] Micelle–ion affinities decrease as the counter-ion becomes more hydrophilic,[1b–e,7,8,12,16] as the bulk of the surfactant head group is increased,[5,17] or on addition of non-ionic solutes,[1b,11,12] but in all cases the sensitivity of β to added counter-ion is qualitatively similar.

This increased sensitivity to added counter-ion can be treated quantitatively by solving the Poisson–Boltzmann equation in the appropriate symmetry[8,9] or in terms of eqn. (14) which has the form of a Langmuir isotherm.[5,7,17]

Eqn. (14), or its equivalent, has been applied to various

$$K'_{Br} = \frac{[Br_M{}^-]}{[Br_W{}^-]([CTABr_M] - [Br_M{}^-])} \qquad (14)$$

surfactants with added counter-ions[5,7,17,18] and K'_{Br} is an indicator of the sensitivity of counter-ion concentrations in the micellar pseudophase to those in water. The relation can be rewritten as eqn. (15),[6] which indicates that a high fractional

$$K'_{Br} = \frac{1 - \alpha}{\alpha^2[CTABr_M]} \qquad (15)$$

ionization, α, corresponds to a low binding parameter K', in qualitative accord with extensive data.[5,6] In the present work with surfactant concentrations $\geqslant$0.05 mol dm^{-3} we are able to neglect the concentration of monomeric surfactant based on the cmc values (Table 4), *i.e.* [$CTABr_M$] = [CTABr].

We use eqn. (15) to estimate changes in K'_{Br} on addition of $C_{12}PO$ to aqueous CTABr based on the values of K'_{Br} = 400 dm^3 mol^{-1} which was used earlier in fitting kinetic data. For a given [CTABr] the change in K'_{Br} is given by eqn. (16) where α_o

$$\Delta K'_{Br} = \frac{(1 - \alpha)\alpha_o{}^2}{(1 - \alpha_o)\alpha^2} \qquad (16)$$

is the value in water which we take as 0.25. Based on values of α for the mixed surfactants (Table 3) we calculate K'_{Br}, dm^3 mol^{-1}, with the various mixtures of CTABr and $C_{12}PO$ with [total surfactant] and [$Br_T{}^-$] = 0.05 mol dm^{-3} with NaBr (Table 2 and Fig. 1) and obtain values of 259, 177, 90 and 47 for 0.045, 0.04, 0.03 and 0.02 mol dm^{-3} CTABr, respectively. We then estimate [$Br_M{}^-$]/[CTABr] for the various mixtures with added NaBr, *i.e.* with 0.05 mol dm^{-3} $Br_T{}^-$ and calculate values of $k_\psi{}^c$ by using eqn. (17), which is equivalent to eqn. (12), and

$$k_\psi{}^c = [k_M{}^\circ + 0.0017(1 - R)]R[Br_M{}^-]/[CTABr] \qquad (17)$$

$k_M{}^\circ = 1.0 \times 10^{-3}$ s^{-1} with 0.05 mol dm^{-3} CTABr. The fit between observed and predicted rate constants is reasonably good (Fig. 1) for experiments with added NaBr considering that we use a constant value of $k_M{}^\circ = 1.0 \times 10^{-3}$ s^{-1}, under all conditions, and assume that the (linear) dependence of k_M upon [$C_{12}PO$] [Fig. 2 and eqn. (12)] is unaffected by changes in total surfactant concentration and addition of NaBr. In quantitative fits of kinetic data in aqueous surfactants, calculated second-order rate constants in the micellar pseudophase often depend to a small extent upon the reaction conditions,[1] and the data with added Br^- would be fitted better with $k_M{}^\circ = 0.95 \times 10^{-3}$ s^{-1}. The fits are insensitive to modest changes in the value of K'_{Br} in water, *e.g.* from 400 to 500 dm^3 mol^{-1}.

The general treatment is that used to explain effects of $C_{10}E_4$ and BuOH upon overall reaction rates and involves similar assumptions.[4,12] Corrections for reaction with water are based on rate data in $CTA(SO_4)_{0.5}$, and these corrections and uncertainties in values of the fractional micellar ionization, α, become more problematic as k_ψ decreases owing to addition of $C_{10}E_4$, $C_{12}PO$ or BuOH. We neglect the concentration of monomeric surfactant because surfactant concentrations are always much higher than the cmc, especially with added NaBr.

Micellar rate constants

For many bimolecular reactions second-order rate constants in the micellar pseudophase are insensitive to concentrations of surfactant and both reactive and inert counter-ions. This generalization applies to S_N2 reactions of Br^- in solutions of CTABr with added BuOH and $C_{10}E_4$,[4] but not with added $C_{12}PO$, where to fit the data we assume that k_M increases on addition of $C_{12}PO$ to CTABr (Fig. 2).

Our comparisons of second-order rate constants, k_M, are based on concentrations in the micellar pseudophase written as mole ratios, *i.e.* as [$Br_M{}^-$]/([CTABr] + [$C_{12}PO$]). Numerical values of second-order rate constants depend upon the choice of concentration units for reactions at colloidal interfaces, just as in homogeneous media, where molarity (mol dm^{-3}) is the accepted measure. Second-order rate constants in micellar pseudophases can be written as molarities which depend directly upon the (assumed) molar volume of the reaction region at the micelle–water interface.[1,8,9] Most methods of estimating molarities at water–micelle interfaces also involve these (assumed) volumes, although trapping in dediazonizations allows estimation of molarities without assumptions regarding molar volumes.[19] We might relate changes in second-order rate constants at surfaces of mixed micelles of CTABr + BuOH, or a non-ionic surfactant, to changes in molar volumes. This hypothesis does not explain the effects of $C_{12}PO$ on k_M, because a dimethylphosphine oxide head group should not be smaller than a trimethylammonium group, so we assume that other factors have to be considered, in particular that the phosphine oxide surfactant exerts a microsolvent kinetic effect which increases the rate constant at the micelle–water interface and is described by eqn. (12).

It is useful to draw analogies between kinetic solvent effects and those of surfaces of association colloids, *e.g.* micelles, microemulsion droplets and vesicles.[1–3] Dipolar aprotic solvents are very effective media for bimolecular reactions of nucleophilic or basic anions because, unlike protic solvents, they do not solvate and deactivate anions.[13] For example, dimethyl sulfoxide and hexamethylphosphoramide [$(Me_2N)_3PO$] are widely used as solvents for bimolecular anionic reactions, either alone, or mixed with water or other protic solvents.[20] Based on this analogy we suggest that the

Table 5 ^1H Chemical shifts in mixtures of CTABr and $C_{12}PO$[a]

	$C_{12}PO$[b]		CTABr			
$[C_{12}PO]$/mol dm^{-3}	PMe_2	ω-CH_3	H1′	H1	H2	ω-CH_3
—			3.197	3.443	1.795	0.890
0.0104	1.561 (1.530)	0.904 (0.897)	3.185	3.428	1.798	0.882
0.0276	1.564 (1.531)	0.896 (0.897)	3.190	3.438	1.800	0.883
0.0653	1.555 (1.533)	0.899 (0.898)	3.170	3.404	1.789	0.883
0.1000	1.551 (1.536)	0.899 (0.902)	3.161	3.393	1.779	

[a] Chemical shifts, ppm, relative to DSS at 25 °C in D_2O. [b] Values in parentheses are in the absence of CTABr, $^2J_{HP}$ = 13 Hz with and without CTABr.

phosphine oxide head group of $C_{12}PO$ increases the nucleophilicity of Br^- at the micellar surface. There is no reason to believe that $C_{12}PO$ interacts directly with Br^- because α decreases on addition of $C_{12}PO$ to CTABr (Table 1), and this behaviour is very similar to that on addition of $C_{10}E_4$,[4] based on plots of α against R for the two systems.

The effect of $C_{12}PO$ upon the rate of reaction of Br^- with MeONs in aqueous CTABr involves several factors, as for mixtures of CTABr with BuOH or $C_{10}E_4$.[4,6,12] Incorporation of the non-ionic surfactants or BuOH into the micelles increases the volume of the micellar pseudophase and the consequent decrease of reactant concentrations in this region slows reaction. It also increases α, which compounds the inhibition, unless $[Br_T^-]$ is constant so that α increases only slightly on addition of $C_{12}PO$. These inhibitory factors are partially offset by the increase in k_M on addition of $C_{12}PO$ and therefore inhibition by $C_{12}PO$ is always lower than by equimolar $C_{10}E_4$.

The major factor in controlling rate enhancements of bimolecular reactions at surfaces of association colloids is concentration of reactants.[1] It is difficult to quantitate concentrations in this region for some ions because of experimental problems, especially for basic anions,[17] and it is difficult to select the appropriate measure of concentration, but some patterns of behaviour emerge. For example, bimolecular reactions of non-ionic reagents are slower at micellar surfaces than in water,[1a] which is consistent with polarities at micellar surfaces being lower than that of water.[1,21] Reactions that involve very hydrophilic transition states, *e.g.* saponifications, are also slower at micellar surfaces than in water,[1b–e,22,23] but S_N2 reactions of moderately hydrophilic anions have similar rate constants in the two media.[5,8b] In all these systems estimated second-order rate constants in the micellar pseudophase depend on the assumed fitting parameters, but these differences in data fitting do not obscure the relations between relative rate constants in micelles and water and the reaction type.[24]

These comparisons between water and micelle–water interfaces as reaction media involve approximations but they are consistent with both physical-organic treatments of solvent effects, and evidence of spontaneous reactions where rate constants are unaffected by uncertainties in transfer equilibria of nucleophiles.[1c,24]

The inhibition of the acid hydrolysis of methyl orthobenzoate in SDS[10] by $C_{12}PO$ is understandable in terms of a decreased hydrogen ion concentration at the micellar surface. These experiments were made in buffered solutions so it is difficult to treat the results quantitatively. However, $C_{12}PO$ is a much better inhibitor than butan-1-ol,[10] whereas we find the opposite behaviour in an S_N2 reaction with Br^-. If, as we assume, $C_{12}PO$ decreases the availability of water at the micellar surface it should inhibit the A1 hydrolysis of methyl orthobenzoate. As discussed later, changes in the ^{31}P and ^1H chemical shifts of the surfactants are consistent with this hypothesis.

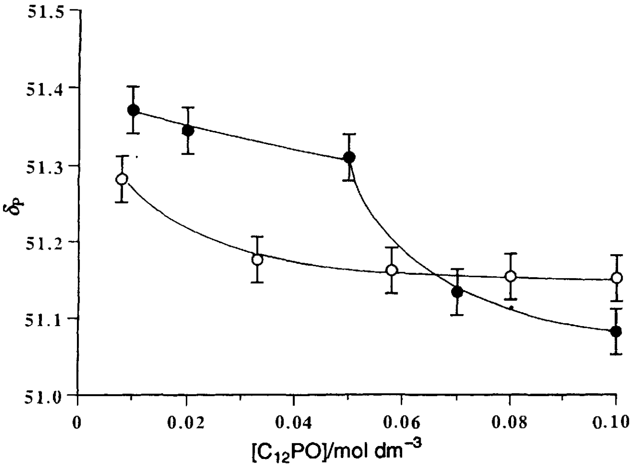


Fig. 3 ^{31}P chemical shifts of $C_{12}PO$ in D_2O at 25 °C relative to external H_3PO_4 with 0.003 ppm error bars: ○, without CTABr; ●, in 0.05 mol dm^{-3} CTABr

NMR spectroscopy

We used ^1H and ^{31}P NMR spectroscopy to obtain evidence on interactions of comicellized CTABr and $C_{12}PO$. Some of the ^1H signals of the surfactants overlap, but we estimated chemical shifts, δ, for H1, H2, NCH_3 (H1′) and ω-CH_3 of CTABr and PCH_3 and ω-CH_3 of $C_{12}PO$. Addition of $C_{12}PO$ to 0.05 mol dm^{-3} CTABr decreases δ of H1′, H1 and H2 (slightly) but has essentially no effect on δ of ω-CH_3 of CTABr (Table 5). Values of δ_H of $C_{12}PO$ are almost unchanged in the range 0.01–0.1 mol dm^{-3} $C_{12}PO$ and no CTABr and comicellization with CTABr has almost no effect on δ_H of ω-CH_3 and slightly decreases that of P–CH_3 while J_{PH} does not change (Table 5).

The ^{31}P chemical shift of $C_{12}PO$ (^1H decoupled and relative to external H_3PO_4) decreases slightly (by *ca.* 0.1 ppm) as concentration is increased from 0.01 to 0.1 mol dm^{-3}, but the decrease is larger (by *ca.* 0.3 ppm) in the presence of 0.05 mol dm^{-3} CTABr (Fig. 3). The line shape of the ^{31}P signal, without ^1H decoupling, changes significantly with change of $[C_{12}PO]$ in 0.05 mol dm^{-3} CTABr (Fig. 4). Changes in δ_P are similar with and without ^1H decoupling.

The approximately constant values of δ of ω-CH_3 (Table 5) are understandable because these groups are in the micellar core. Changes in δ_H at, or near, the micellar surface depend largely on interactions with adjacent surfactants, water molecules and Br^-. Incorporation of $C_{12}PO$ into a CTABr micelle brings the phosphine oxide group close to the cationic centre which decreases chemical shifts (Fig. 3 and Table 5) by disfavouring the dipolar canonical form and increasing the d_π–p_π bond order,[25] although the effect decreases as the ratio of phosphine oxide to CTABr is increased. The P=O and Me_3N^+ groups should be close together at the mixed micellar surface and the decreases in δ_H of H1′ and H1 are probably related to

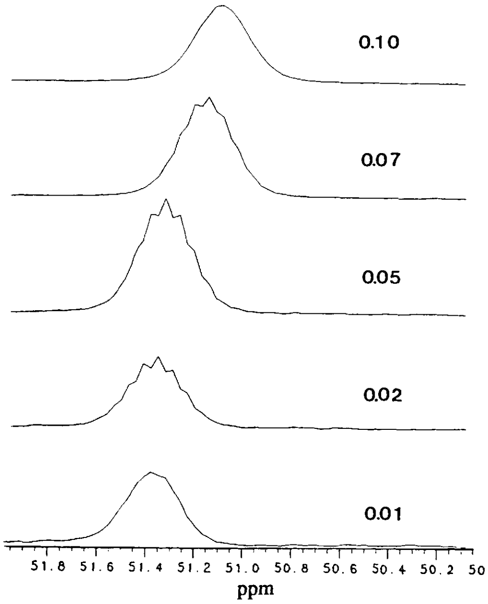


Fig. 4 Changes in the lineshape of the ^{31}P signal (non-decoupled ^{1}H) of $C_{12}PO$ in 0.05 mol dm^{-3} CTABr at the indicated molarities of $C_{12}PO$

efficient hydration of the P=O group which orients the unshared electron pairs of water towards the Me_3N^+ head groups.

The changes in ^{31}P line shape in CTABr (Fig. 4) indicate that the P=O residue can lose some of its mobility on the NMR timescale. With approximately equimolar CTABr and $C_{12}PO$ the disappearance of the fine structure is indicative of slow exchange between interacting molecules. This exchange is slower at high [CTABr] where $C_{12}PO$ molecules are separated and also at high [$C_{12}PO$]. This partial immobilization of the P=O group and of the associated water molecules decreases the local relative permittivity at the micelle–water interface. Strong hydrogen bonding of water to the phosphine oxide will also decrease hydration of Br^- at this interface and both these factors increase the nucleophilicity of Br^- which accounts for the increases in the second-order rate constant, k_M, with increasing $C_{12}PO$ [Fig. 2 and eqn. (13)]. This medium effect partially offsets the inhibition of the micellar-mediated reaction of Br^- with MeONs caused by the addition of non-ionic surfactant to aqueous CTABr.

Conclusions

Increases in rates of bimolecular reactions of ionic reagents by counter-ionic micelles are due largely to concentration of reagents at micelle–water interfaces.[1] This pseudophase model accounts quantitatively for rate enhancements of an S_N2 reaction with Br^- over a range of concentrations of surfactants and added NaBr, as for the reaction in aqueous CTABr and added butan-1-ol or polyoxyethylene surfactants.[4,6,12] Rate constants in the interfacial region are typically similar to those in water,[1] and this generalization applies to alcohol-modified micelles and comicelles with non-ionic polyoxyethylene surfactants, indicating that these added solutes do not perturb the properties of the interfaces as kinetic media, and their kinetic rate inhibitions are due to a decrease in ionic concentration at the interfaces. The situation changes on addition of a phosphine oxide surfactant which makes the interface a better kinetic medium for nucleophilic reactions, just as addition of dipolar aprotic solvents to water speeds these reactions and for the same reasons. This behaviour should be general for reactions mediated by comicelles of ionic surfactants and nonionic surfactants that have dipolar, aprotic, head groups. The kinetic analysis depends upon estimation of reactant concentrations, *e.g.* of Br^-, at the micelle–water interface which is reduced by non-ionic surfactants regardless of their headgroup.

Symbols

D_n	micellized surfactant
K_s	binding constant, dm^3 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^c	corrected overall first-order rate constant; $k_\psi^c = k_\psi + k_{H_2O}$
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
S_W	substrate in the aqueous pseudophase
S_M	substrate in the micellar pseudophase
α	degree of fractional micellar ionization
β	fractional counter-ion binding (neutralization) of micelle, $\beta = 1 - \alpha$
k_ψ	observed first-order rate constant with respect to substrate
k_{H_2O}	first-order rate constant for reaction with water

Acknowledgements

Support by the National Science Foundation (Organic and Macromolecular, and International Programs) is gratefully acknowledged. E. A. T. acknowledges support from CNPq. The authors are grateful to Dr Robert G. Laughlin of Procter & Gamble for supplying us with the $C_{12}PO$ used in this study.

References

1 (*a*) K. Martinek, A. K. Yatsimirski, A. V. Levashov and I. Berezin, in *Surfactants in Solution*; ed. K. L. Mittal, Plenum Press, New York, NY, 1977, vol. 2, p. 489; (*b*) L. S. Romsted, in *Surfactants in Solution*; eds. K. L. Mittal and B. Lindman, Plenum Press, New York, NY, 1984, vol. 2, p. 1015; (*c*) C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, 1986, **22**, 213; (*d*) C. A. Bunton, in *Cationic Surfactants: Physical Chemistry*, eds. D. N. Rubingh and P. M. Holland, Surfactant Science Series 37, Marcel Dekker, New York, NY, 1990, p. 323; (*e*) C. A. Bunton, F. Nome, F. H. Quina and L. S. Romsted, *Acc. Chem. Res.*, 1991, **24**, 357.

2 R. A. Mackay, *Adv. Colloid Interface Sci.*, 1981, **15**, 131.

3 M. K. Kawamuro, H. Chaimovich, E. B. Abuin, E. A. Lissi and I. M. Cuccovia, *J. Phys. Chem.*, 1991, **95**, 1458.

4 C. A. Bunton, S. Wright, P. M. Holland and F. Nome, *Langmuir*, 1993, **9**, 117.

5 R. Bacaloglu, C. A. Bunton and F. Ortega, *J. Phys. Chem.*, 1989, **93**, 1497.

6 C. R. A. Bertoncini, M. de F. S. Neves, F. Nome and C. A. Bunton, *Langmuir*, 1993, **9**, 1274.

7 C. A. Bunton, L.-H. Gan, J. R. Moffatt, L. S. Romsted and G. Savelli, *J. Phys. Chem.* 1981, **85**, 4118.

8 (*a*) C. A. Bunton and J. R. Moffatt, *J. Phys. Chem.*, 1986, **90**, 538; (*b*) C. A. Bunton and J. R. Moffatt, *J. Phys. Chem.*, 1988, **92**, 2896.

9 (a) E. Rodenas, C. Dolcet and M. Valiente, *J. Phys. Chem.*, 1990, **94**, 1472; (*b*) C. Dolcet and E. Rodenas, *Colloids Surfaces*, 1993, **75**, 39.

10 R. B. Dunlap and E. H. Cordes, *J. Phys. Chem.*, 1969, **73**, 361.

11 (*a*) J. W. Larsen and L. B. Tepley, *J. Colloid Interface Sci.*, 1974, **49**, 113; (*b*) R. A. Mackay, *J. Phys. Chem.*, 1982, **86**, 4756; (*c*) C. A. Bunton and F. de Buzzaccarini, *J. Phys. Chem.*, 1982, **93**, 1497.

12 C. R. A. Bertoncini, F. Nome, G. Cerichelli and C. A. Bunton, *J. Phys. Chem.*, 1990, **94**, 5875.

13 (*a*) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, New York, 2nd edn., 1969, ch. 7; (*b*) T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, New York, 3rd edn., 1987, ch. 4.

14 (*a*) R. Zana, *J. Colloid Interface Sci.* 1980, **78**, 330; (*b*) P. Lianos and R. Zana, *J. Colloid Interface Sci.*, 1982, **88**, 594.

15 P. M. Holland, in *Mixed Surfactant Systems*, eds. P. M. Holland and

D. N. Rubingh, ACS Symposium Series Vol. 501, American Chemical Society, Washington DC, 1992, p. 31.

16 M. de F. S. Neves, D. Zanette, F. Quina, M. T. Moretti and F. Nome, *J. Phys. Chem.*, 1989, **93**, 1502.

17 R. Bacaloglu, C. A. Bunton, G. Cerichelli and F. Ortega, *J. Phys. Chem.*, 1990, **94**, 5068.

18 (*a*) R. Germani, P. Ponti, G. Savelli, N. Spreti, C. A. Bunton and J. R. Moffatt, *J. Chem. Soc., Perkin Trans. 2*, 1989, 401; (*b*) E. Rodenas and S. Vera, *J. Phys. Chem.*, 1985, **89**, 513.

19 (*a*) A. Chaudhuri and L. S. Romsted, *J. Am. Chem. Soc.*, 1991, **113**, 5052; (*b*) A. Chaudhuri, J. A. Laughlin, L. S. Romsted and J. Yao, *J. Am. Chem. Soc.*, 1993, **115**, 8351; (*c*) A. Chaudhuri, L. S. Romsted and J. Yao, *J. Am. Chem. Soc.*, 1993, **115**, 8362.

20 (*a*) J. March, *Advanced Organic Chemistry*, Wiley-Interscience, New York, 3rd edn., 1985, p. 316; (*b*) E. Buncel and H. Wilson, *Adv. Phys. Org. Chem.*, 1974, **14**, 133; (*c*) C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH New York, 2nd edn., 1988, ch. 5.

21 (*a*) K. A. Zachariasse, N. V. Phuc and B. Kozankiewicz, *J. Phys. Chem.*, 1981, **85**, 2676; (*b*) C. Ramachandran, R. A. Pyter and P. Mukerjee, *J. Phys. Chem.*, 1982, **86**, 3198.

22 V. R. Correia, I. M. Cuccovia and H. Chaimovich, *J. Phys. Org. Chem.*, 1991, **4**, 13.

23 A. Bartoletti, S. Bartolini, R. Germani, G. Savelli, G. Cerichelli and C. A. Bunton, *J. Chem. Soc., Perkin Trans. 2*, 1994, 723.

24 C. A. Bunton, in *Nucleophilicity*, eds., J. M. Harris and S. P. McManus, Adv. Chem. Ser. 215, American Chemical Society, Washington DC, 1987, ch. 29.

25 D. G. Gorenstein, in *Phosphorus 31 NMR*, ed. D. G. Gorenstein, Academic Press, New York, 1984, ch. 1.

Paper 5/00539F
Received 30*th January* 1995
Accepted 17*th July* 1995