

Catalysis and inhibition of the iodide reduction of peracids by surfactants: partitioning of reactants, product and transition state between aqueous and micellar pseudophases

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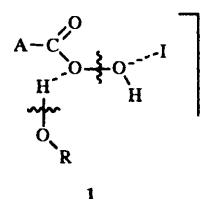
A multiple micellar pseudophase model of kinetics in aqueous surfactant solutions is described. The model has been developed using the transition state pseudoequilibrium constant approach. The advantage of this approach is that no assumptions are made about the nature of the micelle pseudophases. The kinetics of the reduction of pernonanoic and 3-chloroperbenzoic acids by iodide in SDS, Brij-35 and Triton X-100 are reported. The results are used to obtain the micellar association constants of the peracids and also the apparent (virtual) micellar association constants of the transition states. These are compared with the micellar association constants of the parent acids, obtained by pH titration. The association constants are discussed in terms of micellar catalysis and inhibition. Ratios of association constants indicate the relationship between initial, transition and final states.

Reactions in aqueous surfactant solutions are usually treated using the classical pseudophase kinetic model first suggested by Berezin and co-workers.¹ According to this model the reactants partition between the bulk water phase and a micellar pseudophase and the sum of the rates of the concurrent reactions in the two phases constitutes the overall rate. The model yields rate equations that are consistent with the observed kinetics of micellar catalysis and inhibition,^{1,2} and has been extended to cover reactions involving ions and charged micelles.¹⁻⁴ Despite the apparent success of the pseudophase approach, it is unlikely that a model involving a single micellar reaction pseudophase is generally appropriate. Depending on their particular properties amphiphilic micellar-bound reactants show various distributions (that have a maximum more or less close to the micelle-water interface) of concentration with distance from the centre of the micelle.⁵ A rapid change of the local microsolvent properties and hence, provided that the reaction is subject to general medium or specific solvent effects, a rapid change of the local rate constant occurs in this interfacial region and also a rapid change in the concentration of any charged reaction partner. So, in general, the region about the interface should be divided up into an arbitrary number of pseudophases, each with a different mean partition coefficient for the reactant or reactants and each with a different mean rate constant.

This paper describes a multiple micellar pseudophase (MMPP) kinetic model that is a generalisation of the classical pseudophase model. The MMPP model is compatible with the transition state pseudoequilibrium constant approach of Kurz.⁶ The logarithm of the apparent association constant of the transition state and micellar surfactant is used in the present context as a measure of the stabilisation or destabilisation of the transition state by the micelle. This serves as a mechanistic probe of the effect of the micelle on the reaction, independently of any postulated mechanism. We use the MMPP model to treat the effect of anionic and etheric non-ionic surfactants on the reduction of pernonanoic and 3-chloroperbenzoic acids by iodide. The surfactants used are sodium dodecyl sulfate (SDS), poly(oxyethylene)(23) dodecyl ether (Brij-35) and *p*-(1,1,3,3-tetramethylbutyl)phenoxy poly(oxyethylene)(9.5) glycol (Triton X-100).

The reaction between peracids and iodide is well characterised in aqueous and mixed-aqueous solvents. The rate-limiting step involves nucleophilic attack of iodide on the outer

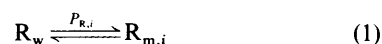
peroxidic oxygen of the peracid, this is followed by the formation of I_2 , which equilibrates with I_3^- .⁷ The rate of reaction of the molecular peracid is not influenced by solvent relative permittivity effects, ionic strength or pH,⁷ which simplifies the discussion of micellar effects. On the other hand, the rate is enhanced by hydrogen bond donor solvents which stabilise the transition state **1** which resembles the parent acid.



Moreover, the rate is decreased by hydrogen bond acceptor solvents such as 1,4-dioxane, a cyclic ether, which is thought to stabilise the initial state with respect to the transition state.⁷ We have recently used the transition state pseudoequilibrium constant approach with the iodide-peracid reaction as a probe of the factors that are important in the catalysis of bimolecular reactions by cyclodextrin.⁸

The multiple micellar pseudophase model

Consider that a micelle comprises n pseudophases consisting of adjacent layers extending from the middle. The partitioning of a reactant, R , between the i th pseudophase and the bulk water phase, eqn. (1), is defined by the partition coefficient, $P_{R,i}$, in



eqn. (2), where the subscripts m,i and w after the square

$$P_{R,i} = \frac{[R]_{m,i}}{[R]_w} \quad (2)$$

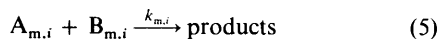
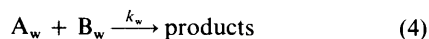
brackets refer to the concentration in the respective phases.

The mass balance is given by eqn. (3) where the total volume

$$[R_T]V_T = [R]_w V_w + \sum_{i=1}^n [R]_{m,i} V_{m,i} \quad (3)$$

is V_T , the volumes of the water and the i th micellar pseudophases are V_w and $V_{m,i}$, respectively and $[R_T]$ is the overall concentration, *i.e.* with respect to the total volume (no subscript after the square brackets), of the total R, *i.e.* that in the water and micellar pseudophases.

For a bimolecular reaction (where A and B are equivalent to R) occurring concurrently in the water phase and each of the n micelle pseudophases as shown in reactions (4) and (5), with



rate constants k_w and $k_{m,i}$, an expression involving the overall reaction rate, v , is given by eqn. (6), provided that the

$$vV_T = k_w[A]_w[B]_wV_w + \sum_{i=1}^n k_{m,i}[A]_{m,i}[B]_{m,i}V_{m,i} \quad (6)$$

equilibration of the reactants between the phases is rapid compared with the rate of reaction.

The volumes of the micellar pseudophases are related to their effective molar volumes, $\bar{V}_{m,i}$, according to eqn. (7) where $[S]$ is the overall concentration of the surfactant, S, and cmc is its critical micelle concentration. The volume of the water phase is given by eqn. (8). Eqns. (7) and (8) assume that the

$$V_{m,i} = \bar{V}_{m,i}([S] - cmc)V_T \quad (7)$$

$$V_w = V_T \left[1 - \sum_{i=1}^n \bar{V}_{m,i}([S] - cmc) \right] \quad (8)$$

concentration of monomer remains constant over the range of $[S]$ under consideration.

From eqns. (2), (3), (6), (7), (8) and the relationship in eqn. (9)

$$k_{\text{obs}} = \frac{v}{[A_T][B_T]} \quad (9)$$

between overall reaction rate, concentration and k_{obs} , the observed second-order rate constant, eqn. (10) is obtained.

$$k_{\text{obs}} = \frac{k_w + \left(\sum_{i=1}^n k_{m,i}P_{A,i}P_{B,i}\bar{V}_{m,i} - k_w \sum_{i=1}^n \bar{V}_{m,i} \right) ([S] - cmc)}{\left\{ 1 + \left[\sum_{i=1}^n (P_{A,i} - 1)\bar{V}_{m,i} \right] ([S] - cmc) \right\} \left\{ 1 + \left[\sum_{i=1}^n (P_{B,i} - 1)\bar{V}_{m,i} \right] ([S] - cmc) \right\}} \quad (10)$$

An alternative expression for eqn. (10) is obtained as follows. The sum of the products of the partition coefficients and the effective molar volumes of the pseudophases is related to the equilibrium constant, K_R , defined in eqns. (11) and (12), by



$$K_R = \frac{[RS]}{[R]([S] - cmc)} \quad (12)$$

applying the mass balance eqns. (13) and (14) together with

$$[RS]V_T = \sum_{i=1}^n [R]_{m,i}V_{m,i} \quad (13)$$

$$[R]V_T = [R]_wV_w \quad (14)$$

eqns. (7) and (8) to obtain eqn. (15). Eqn. (15) shows that the

$$\sum_{i=1}^n P_{R,i}\bar{V}_{m,i} = K_R \left\{ 1 - \sum_{i=1}^n \bar{V}_{m,i}([S] - cmc) \right\} \equiv K_{\text{mic}}^R \quad (15)$$

sum term is approximately equal to the equilibrium constant, k_R , provided that for $i = 1$ to n , $\sum \bar{V}_{m,i}([S] - cmc)$ approaches zero, *i.e.* applying eqn. (8), provided V_w/V_T approaches unity. Defining micellar equilibrium constants, K_{mic}^R , according to eqn. (15) (with R equivalent to A or B), micellar rate constants, k_{mic} , as the observed third-order rate constant (first-order in surfactant concentration) according to eqn. (16), and the

$$k_{\text{mic}} \equiv \sum_{i=1}^n k_{m,i}P_{A,i}P_{B,i}\bar{V}_{m,i} \quad (16)$$

effective molar volume of the micellized surfactant, \bar{V}_{mic} , according to eqn. (17) allows eqn. (10) to be rewritten as eqn. (18).

$$\bar{V}_{\text{mic}} \equiv \sum_{i=1}^n \bar{V}_{m,i} \quad (17)$$

$$k_{\text{obs}} = \frac{k_w + (k_{\text{mic}} - k_w\bar{V}_{\text{mic}})([S] - cmc)}{[1 + (K_{\text{mic}}^A - \bar{V})([S] - cmc)][1 + (K_{\text{mic}}^B - \bar{V})([S] - cmc)]} \quad (18)$$

Eqn. (18) is of the same form as that obtained from the classical single micellar reaction pseudophase model.^{1,2} Since, however, k_{mic} , K_{mic}^A and K_{mic}^B are composite quantities they cannot be used to obtain elementary rate constants for reactions in the micellar pseudophases. Thus it might seem, at first sight, that the interpretation of micellar kinetics is impossible unless a single micellar reaction pseudophase is assumed, even though the kinetics are equally consistent with a multiple micellar pseudophase model.

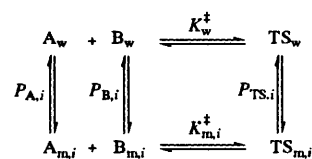
Transition state pseudoequilibrium constants

Fortunately, the assumption of a single micellar reaction pseudophase is not necessary because the MMPP model can be developed in terms of the transition state pseudoequilibrium constant approach, which makes use of thermodynamic cycles.⁶ For the bimolecular reaction occurring concurrently in the water phase and each of the n micelle pseudophases [eqns. (4)

and (5)], the apparent partition coefficient for the transition state, TS, between the i th pseudophase and water, $P_{\text{TS},i}$, is defined in eqn. (19).

$$P_{\text{TS},i} = \frac{[\text{TS}]_{m,i}}{[\text{TS}]_w} \quad (19)$$

Application of transition state theory to the thermodynamic cycle shown in Scheme 1 after multiplication by the appropriate



Scheme 1

$\bar{V}_{m,i}$ leads to the relationship shown in eqn. (20). The numerator of the left hand side of eqn. (20) is k_{mic} , defined in eqn. (16), and

the quantity on the right hand side of eqn. (20) is defined according to eqn. (15) as the transition state pseudo-equilibrium constant, $K_{\text{mic}}^{\text{TS}}$. Hence eqn. (20) can be rewritten as eqn. (21). $K_{\text{mic}}^{\text{TS}}$ reflects the predominant transition state and its variation with the nature of the reactant and surfactant may be used to probe transition-state structure and as a criterion of mechanism.

$$\frac{\sum_{i=1}^n k_{m,i} P_{A,i} P_{B,i} \bar{V}_{m,i}}{k_w} = \sum_{i=1}^n P_{\text{TS},i} \bar{V}_{m,i} \quad (20)$$

$$\frac{k_{\text{mic}}}{k_w} = K_{\text{mic}}^{\text{TS}} \quad (21)$$

Experimental

Materials

SDS, Brij-35 and Triton X-100 were purchased from Aldrich. Molar concentrations of the latter are quoted assuming an average RMM of 626 g. Pernonanoic acid (98%) was provided by Warwick International Ltd and 3-chloroperbenzoic acid (80%) was purchased from Sigma. The peracids contained the parent acid as the only significant impurity. Potassium iodide was the highest grade available from Aldrich, 3-chlorobenzoic acid was obtained from BDH and nonanoic acid from Sigma. Buffer components were AnalaR reagents. Solutions were made up in distilled water. Concentrations of stock peracid solutions were determined by iodometric titration and working solutions obtained by dilution.

Kinetics

The reaction of peracid and iodide at 25 °C in phosphate or carbonate buffer, pH 5.6–9.6 and ionic strength 0.1 mol dm⁻³, was followed by measuring the absorbance of the product, triiodide anion, at 415 nm, using a Hi-Tech SF4 stopped-flow spectrophotometer connected to a personal computer fitted with a PCL-812, 12 bit interface card. The initial concentrations of iodide and peracid in mol dm⁻³ were 1.5 × 10⁻³ and ca. 4 × 10⁻⁶, respectively, and the pseudo-first-order rate constant, k_w , was obtained from non-linear regression of the monoexponential change of absorbance with time. The dependence of k_w on pH and surfactant concentrations was analysed using the proportionately weighted non-linear regression routine of a commercial statistics computer programme.

Titrations

Solutions of ca. 1.5 × 10⁻³ mol dm⁻³ 3-chlorobenzoic acid or ca. 1 × 10⁻³ mol dm⁻³ nonanoic acid, unless stated otherwise, containing the required amount of surfactant and 0.1 mol dm⁻³ NaNO₃ were titrated with 0.01 mol dm⁻³ NaOH in a thermostatted vessel at 25 °C using a Metrohm 702 SM Titrino autotitrator. The apparent mixed acid dissociation constant under the experimental conditions, K_a^{app} , was determined as described previously,^{9,10} except that about 20 points on the titration curve were used in the calculation, and the hydrogen ion activity coefficient was assumed to be unity in the application of the electroneutrality principle. The dependence of $\text{p}K_a^{\text{app}}$ on surfactant concentration was analysed using an unweighted non-linear regression routine.

Other methods

Supercritical carbon dioxide chromatography of a 5% (w/v) solution of Triton X-100 was carried out using a Carlo Erba SFC 3000 with flame ionisation detection and a 10 m × 50 μm internal diameter DB-5 column at 90 °C with an increasing linear density ramp. The *cmcs* of the surfactants were obtained under the experimental conditions from the break in the plot of

surface tension, measured using a de Nouy Tensiometer, *versus* the logarithm of the concentration.

Results

Characterisation of micelles

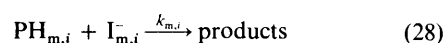
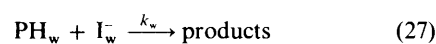
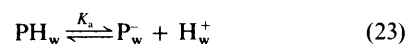
The profile of surface tension *versus* surfactant concentration for the Triton X-100 showed a minimum just before the break point of less than 1 mN m⁻¹, whilst that for SDS was without a minimum. From the break points (results not shown) in 0.01 mol dm⁻³ phosphate buffer, pH 7.4, ionic strength 0.1 mol dm⁻³ (NaNO₃) the *cmcs* of SDS and Triton X-100 were 1.8 × 10⁻³ and 2.0 × 10⁻⁴ mol dm⁻³, respectively. The *cmc* of Brij-35 is assumed to be negligible compared with the concentrations used in the experiments. Fig. 1 is a supercritical carbon dioxide chromatogram of Triton X-100 which clearly shows that the surfactant is polydisperse. The major band pattern corresponds to surfactant molecules with between 1 and 20 oxyethylene units and there is evidence of free poly(oxyethylene) glycols.

Effect of micelles on the kinetics

The observed pseudo-first-order rate constants for the reaction of peracid and iodide, k_w , defined in eqn. (22), vary with

$$k_w \equiv k_{\text{obs}}[\text{I}_T^-] \quad (22)$$

surfactant concentration and pH as shown in Figs. 2–7. Figs. 2 and 3 show the Brij-35 catalysed reactions of pernonanoic and of 3-chloroperbenzoic acid, respectively. Figs. 4 and 5 show the corresponding results for Triton X-100 and Figs. 6 and 7 show the inhibition of the respective reactions by SDS. The results are consistent with the reaction scheme shown in reactions (23)–(28) where PH is the peracid and P⁻ its anion.



The mixed acid dissociation constant, K_a , is defined in eqn. (29), where {H⁺} is the hydrogen ion activity measured with the glass electrode.

$$K_a = \frac{[\text{P}^-]_w \{ \text{H}^+ \}_w}{[\text{PH}]_w} \quad (29)$$

Application of the MMPP model to the reaction scheme shown in reactions (23)–(28), which includes the pH dependent ionisation of the peracid, leads to eqn. (30), where the micellar equilibrium and rate constants are defined according to eqns. (15) and (16), respectively, and the dependence of the pseudo-first-order rate constant on the concentration of iodide [eqn. (22)] is taken into account.

Berezin and co-workers have derived a comparable equation for the classical pseudophase model, except that the reactive

$$k_{\Psi} = \frac{[k_w + (k_{mic} - k_w \bar{V}_{mic})([S] - cmc)]\{H^+\}_w[I_T^-]}{\left\{ \begin{array}{l} \{H^+\}_w [1 + (K_{mic}^{PH} - \bar{V}_{mic})([S] - cmc)] \\ + K_a [1 + (K_{mic}^P - \bar{V}_{mic})([S] - cmc)] \end{array} \right\} [1 + (K_{mic}^1 - \bar{V}_{mic})([S] - cmc)]} \quad (30)$$

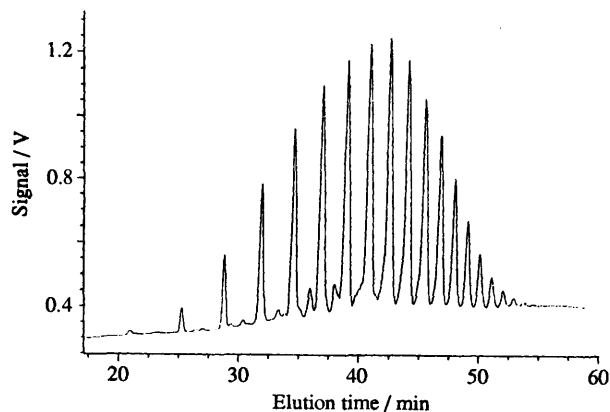


Fig. 1 Supercritical carbon dioxide chromatogram of Triton X-100

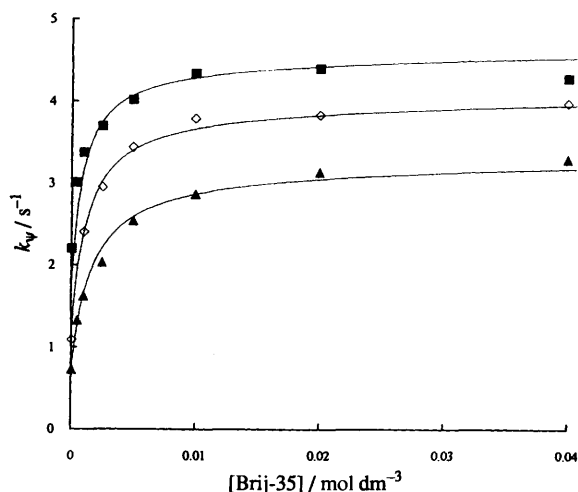


Fig. 2 Brij-35 catalysis of the reaction of pernanonic acid and iodide at 25 °C: pseudo-first-order rate constants with $1.5 \times 10^{-3} \text{ mol dm}^{-3} I_T^-$; ■ pH 5.69, ◇ 7.93, ▲ 8.39

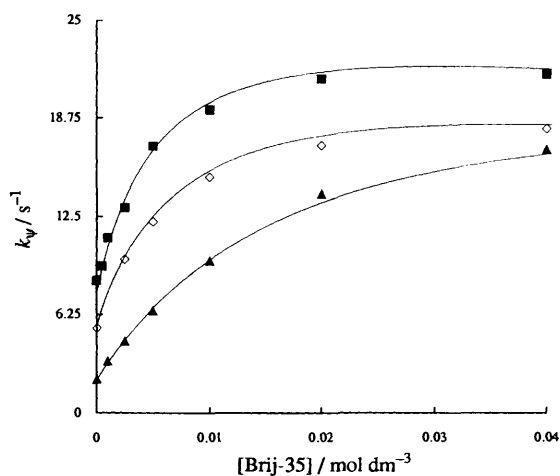


Fig. 3 Brij-35 catalysis of the reaction of 3-chloroperbenzoic acid and iodide at 25 °C: pseudo-first-order rate constants with $1.5 \times 10^{-3} \text{ mol dm}^{-3} I_T^-$; ■ pH 5.69, ◇ 7.09, ▲ 7.93

species was the anionic form of the ionogenic group.¹ The essential feature, however, that distinguishes the MMPP model from the classical pseudophase model is that in the former model the K_{mic} and k_{mic} values are explicitly defined as weighted

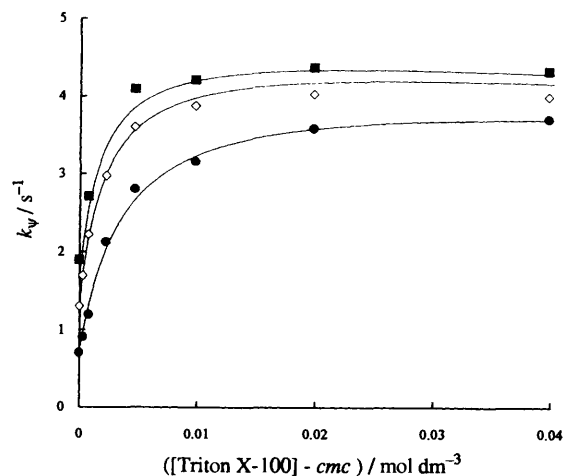


Fig. 4 Triton X-100 catalysis of the reaction of pernanonic acid and iodide at 25 °C: pseudo-first-order rate constants with $1.5 \times 10^{-3} \text{ mol dm}^{-3} I_T^-$; ■ pH 5.95, ◇ 7.68, ▲ 8.22

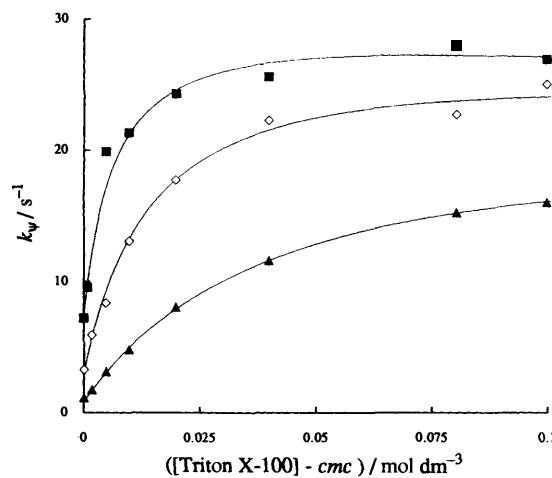


Fig. 5 Triton X-100 catalysis of the reaction of 3-chloroperbenzoic acid and iodide at 25 °C: pseudo-first-order rate constants with $1.5 \times 10^{-3} \text{ mol dm}^{-3} I_T^-$; ■ pH 5.95, ◇ 7.68, ▲ 8.22

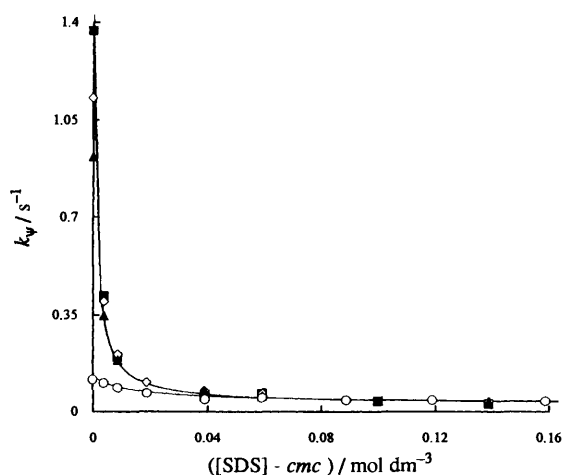


Fig. 6 SDS inhibition of the reaction of pernanonic acid and iodide at 25 °C: pseudo-first-order rate constants with $1.5 \times 10^{-3} \text{ mol dm}^{-3} I_T^-$; ■ pH 7.63, ◇ 7.88, ▲ 8.08, ○ 9.52

averages as shown in eqns. (15) and (16). Thus, as explained in the section describing the MMPP model, it is clear that these values cannot be used to obtain the elementary rate constants,

Table 1 Best-fit micellar rate and association constant terms and their standard deviations, according to eqn. (30), for the reaction of peracids and iodide in the presence of surfactant: buffer ionic strength, 0.1 mol dm⁻³; 25 °C

Surfactant	Peracid	$k_{\text{mic}} - k_w \bar{V}_{\text{mic}} / 10^6 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	$K_{\text{mic}}^{\text{PH}} - \bar{V}_{\text{mic}} / \text{dm}^3 \text{ mol}^{-1}$	$K_{\text{mic}}^{\text{P}} - \bar{V}_{\text{mic}} / \text{dm}^3 \text{ mol}^{-1}$	$K_{\text{mic}}^{\text{TS}} - \bar{V}_{\text{mic}}^a / \text{dm}^3 \text{ mol}^{-1}$
Brij-35	Pernonanoic	3.04 ± 0.46	1010 ± 190	282 ± 85	2510 ± 390
Brij-35	3-Chloroperbenzoic	2.94 ± 0.28	172 ± 35	-9.0 ± 7.6	575 ± 56
TX-100	Pernonanoic	1.68 ± 0.23	518 ± 99	22 ± 28	1390 ± 200
TX-100	3-Chloroperbenzoic	3.15 ± 0.22	152 ± 19	4.1 ± 2.7	620 ± 45
SDS	Pernonanoic	0.0165 ± 0.0026	950 ± 72	0 ^b	13.6 ± 2.2
SDS	3-Chloroperbenzoic	0.0125 ± 0.0036	94 ± 7	0 ^b	2.45 ± 0.71 ^c

^a Obtained using eqn. (21). ^b Assuming that the quantity $[1 + (K_{\text{mic}}^{\text{P}} - \bar{V}_{\text{mic}})([S] - \text{cmc})]$ in eqn. (30) remains close to unity over the range of experimental conditions. ^c $K_{\text{mic}}^{\text{TS}} = 2.85 \pm 0.71 \text{ dm}^3 \text{ mol}^{-1}$, see text.

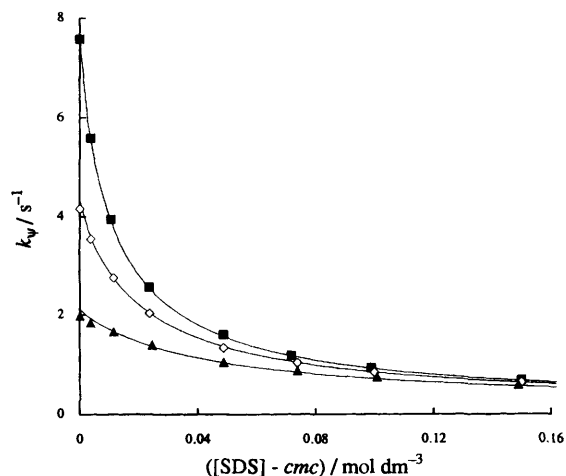


Fig. 7 SDS inhibition of the reaction of 3-chloroperbenzoic acid and iodide at 25 °C: pseudo-first-order rate constants with $1.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ I}_2^-$; ■ pH 5.66, ◇ 7.40, ▲ 7.93

$k_{\text{m},i}$, for the reactions in the micellar pseudophases defined in reaction (28).

The data in Figs. 2–5 for catalysis by the non-ionic surfactants are treated using the full form of eqn. (30). Although the form of this equation is quite complicated-looking it should be borne in mind that both surfactant concentration and hydrogen ion activity are experimental variables. Hence the model is not over-defined and no parameters play similar roles in the function of k_w . This is borne out by the satisfactorily high precision and low correlation of the best-fit parameters, the reasonableness of the fit as shown by the calculated curves in the Figures and by the physical reasonableness of the values of the best fit parameters as discussed further in this paper. For the SDS inhibited reactions, shown in Figs. 6 and 7, a residual reaction of micellar-bound peracid occurs at high concentrations of SDS. Similar results have recently been reported for the SDS inhibited oxidation of organic sulfides by iodate.^{4b} These results are consistent with incomplete exclusion of the reactive anions from the anionic micellar reaction pseudophase. Eqn. (30) is consistent with the experimental results if it is assumed that the micellar association constant with iodide is small, *i.e.* the quantity $[1 + (K_{\text{mic}}^{\text{I}} - \bar{V}_{\text{mic}})([S] - \text{cmc})]$ remains close to unity over the range of experimental conditions. The best-fit values of the rate constant in the bulk water phase, k_w , are $(5.11 \pm 0.11) \times 10^3$ and $(1.21 \pm 0.04) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for 3-chloroperbenzoic and pernonanoic acids, respectively. The best-fit value of K_a for 3-chloroperbenzoic acid, $(3.08 \pm 0.12) \times 10^{-8} \text{ mol dm}^{-3}$, *i.e.* $\text{p}K_a$ 7.49–7.53, is comparable to the $\text{p}K_a$ value 7.53 obtained by pH titration.¹⁰ The K_a , $(5.87 \pm 0.45) \times 10^{-9}$, *i.e.* $\text{p}K_a$ 8.20–8.27, for pernonanoic acid is the first published value to our knowledge, but can be compared with the $\text{p}K_a$ of 8.2 for peracetic acid.¹¹ The best-fit values of the terms involving the micellar rate constants and the equilibrium constants for the association of

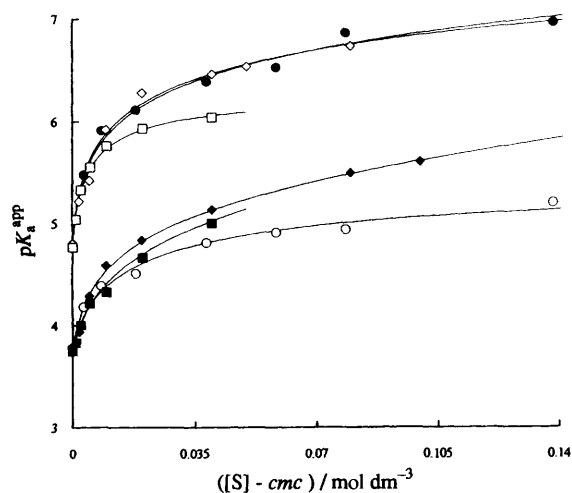
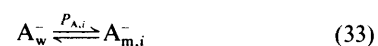
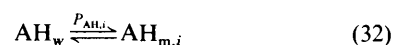
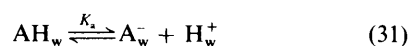


Fig. 8 Effect of surfactants on the apparent $\text{p}K_a$ s of nonanoic and 3-chlorobenzoic acids in $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ at 25 °C: nonanoic acid ● in SDS, ◇ in Triton X-100, and □ in Brij-35; 3-chlorobenzoic acid ○ in SDS, ◆ in Triton X-100 and ■ in Brij-35

the peracids and their anions with the respective micelles are shown in Table 1. The values of $(K_{\text{mic}}^{\text{TS}} - \bar{V}_{\text{mic}})$ in Table 1 are calculated as the quotient of the appropriate values of $(k_{\text{mic}} - k_w \bar{V}_{\text{mic}})$ and k_w according to eqn. (21). The best-fit values of the term $(K_{\text{mic}}^{\text{I}} - \bar{V}_{\text{mic}})$ involving the association constant of iodide and Brij-35 and Triton X-100 are, respectively, 3.6 ± 2.0 and $2.1 \pm 1.4 \text{ dm}^3 \text{ mol}^{-1}$, taking the mean of the values for pernonanoic and 3-chloroperbenzoic acids.

Effect of micelles on the apparent $\text{p}K_a$ values of the parent acids

From preliminary experiments (results not shown) the measured $\text{p}K_a$ of nonanoic acid is independent of its concentration over the range $(0.4\text{--}1.7) \times 10^{-3} \text{ mol dm}^{-3}$. Fig. 8 shows the effects of the concentrations of surfactants on the apparent $\text{p}K_a$ s of nonanoic and 3-chlorobenzoic acids. The results are consistent with the scheme shown in eqns. (31)–(33)



where AH is the parent acid and A^- its anion.

Application of the MMPP model leads to eqn. (34) where

$$\text{p}K_a^{\text{app}} = \text{p}K_a - \log \frac{1 + (K_{\text{mic}}^{\text{P}} - \bar{V}_{\text{mic}})([S] - \text{cmc})}{1 + (K_{\text{mic}}^{\text{PH}} - \bar{V}_{\text{mic}})([S] - \text{cmc})} \quad (34)$$

Table 2 Best-fit micellar association constant terms and their standard deviations according to eqn. (31) from apparent pK_a values of the parent acids in the presence of surfactant and $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ at 25°C

Surfactant	Parent acid	$K_{\text{mic}}^{\text{AH}} - \bar{V}_{\text{mic}} / \text{dm}^3 \text{ mol}^{-1}$	$K_{\text{mic}}^{\text{A}} - \bar{V}_{\text{mic}} / \text{dm}^3 \text{ mol}^{-1}$
Brij-35	Nonanoic	1170 ± 70	37 ± 6
Brij-35	3-Chlorobenzoic	349 ± 45	5.3 ± 5.6
TX-100	Nonanoic	1060 ± 150	-0.7 ± 3.1
TX-100	3-Chlorobenzoic	480 ± 40	-2.9 ± 1.1
SDS	Nonanoic	1190 ± 130	0.7 ± 1.7
SDS	3-Chlorobenzoic	350 ± 50	8.6 ± 3.3

K_a^{app} is defined in eqn. (35) and the use of the subscript T is as in

$$K_a^{\text{app}} = \frac{[\text{P}_T][\text{H}^+]_w}{[\text{PH}_T]} \quad (35)$$

eqn. (3). Berezin and co-workers have derived an equivalent equation for the classical pseudophase model.¹ The data in Fig. 8 were treated using eqn. (34) to yield the best-fit values of the terms involving the equilibrium constants for the association of the parent acids and their anions with the surfactant micelles that are shown in Table 2.

Discussion

Tee, in a review concerned primarily with the application of the transition state pseudoequilibrium constant approach to cyclodextrin mediated reactions, has also demonstrated its use for micelle mediated reactions.¹² To our knowledge, the present paper is the first to define the approach for a multiple micellar pseudophase (MMPP) model of kinetics in surfactant systems. There are two major advantages of the present treatment compared with the single micellar reaction pseudophase model. First, $K_{\text{mic}}^{\text{TS}}$ reflects the stability conferred on the transition state of the predominant micelle-mediated reaction pathway(s) by its association with the micelle and is thus a fundamental kinetic property independent of any postulated reaction pathways. For example, it is valid in cases where a reactant associates strongly with one region of the micelle but undergoes reaction in an adjacent region where it has lower affinity. This is analogous to non-productive binding in enzyme kinetics. Here the simple pseudophase model gives a derived rate constant that is merely related to the difference in the Gibbs' energy of the transition state in the one region and the reactants in the other region. The second advantage of the use of $K_{\text{mic}}^{\text{TS}}$ is important when considering bimolecular reactions. In the simple pseudophase model the volume of the part of the micelle in which the reaction occurs must be estimated in order to convert the derived rate constant referred to above to one with the same units as k_w in order to compare the two. The choice of a reaction volume is, to a certain extent, equivalent to the postulate of a reaction pathway, which is avoided in the present treatment. In the present treatment the $(K_{\text{mic}} - \bar{V}_{\text{mic}})$ terms obtained in the regression analyses obviously should be corrected for \bar{V}_{mic} . The latter is the total effective molar volume of the surfactant plus any water associated with the micelle. It is, in principle, a measurable quantity and anyway an upper limit can be estimated which in many cases is negligible compared with the quantity to be corrected.

Micellar association constants

The values of K_{mic} for the peracids, the parent acids, and their anions may be calculated by adding \bar{V}_{mic} to the best-fit values of $(K_{\text{mic}} - \bar{V}_{\text{mic}})$ given in Tables 1 and 2. \bar{V}_{mic} is taken as $0.4 \text{ dm}^3 \text{ mol}^{-1}$ for SDS, based on its molecular weight and density.^{1c,4a} The corresponding value for Triton X-100 is $0.5 \text{ dm}^3 \text{ mol}^{-1}$ and

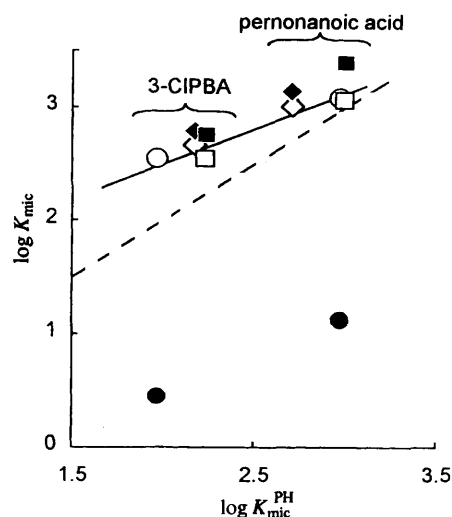


Fig. 9 Gibbs' energy relationships between the logarithms of the micellar association constants of the parent acids, $K_{\text{mic}}^{\text{AH}}$, open symbols; the transition state pseudoequilibrium constants, $K_{\text{mic}}^{\text{TS}}$, closed symbols; and the association constants of the peracids, $K_{\text{mic}}^{\text{PH}}$: SDS, circles; Triton X-100, diamonds; Brij-35, squares

an additional $1.6 \text{ dm}^3 \text{ mol}^{-1}$ is added in order to allow for the water associated with the poly(oxyethylene) mantle.¹³ Assuming a proportionality between Triton X-100 and Brij-35, the corresponding values for the latter are estimated at 1.2 plus $3.8 \text{ dm}^3 \text{ mol}^{-1}$. The correction for the volume of the micelles is satisfying in that it explains the small negative best-fit values for 3-chloroperbenzoate in Brij-35 (Table 1) and nonanoate and 3-chlorobenzoate in Triton X-100 (Table 2). Otherwise the correction is insignificant.

It is generally the case that the nature of the surfactant has considerably less effect than the nature of the associated species on the strength of binding of the latter to micelles.¹⁴ The results in Tables 1 and 2 confirm this. Thus, in each of the surfactants, Brij, SDS and Triton, the highest binding constant is shown by nonanoic acid, followed by pernonanoic acid, 3-chlorobenzoic acid and finally, 3-chloroperbenzoic acid. This order reflects the relative proportions of carbon atoms to oxygen and chlorine atoms in the acids. These results are neatly summarised as a Gibbs' energy relationship between the logarithm of the micellar association constant of the parent acid and that of the peracid, as shown in Fig. 9. Here the line representing the parent acids converges on the dashed line of unit slope and zero intercept that represents the peracids. This demonstrates that the additional oxygen atom of the peracid lowers its affinity for the micelle proportionately less as that affinity increases. The binding constants of the anions of the peracids and parent acids (Tables 1 and 2) are less than the molecular acids. Unfortunately, the former values are too low to be determined with enough precision to allow meaningful comparisons between them, with the exceptions of nonanoate and pernonanoate in Brij-35. Note that the micellar association constant of the pernonanoate anion in Brij-35 is considerably larger than that of the nonanoate. This is in contrast to the affinities of the respective molecular acid forms with Brij-35. The enhanced stability of the peranon in Brij-35 may be related to the lower solvation attributed to α -nucleophiles.¹⁵ Alternatively, it may be due to the different distributions of charge on the nonanoate and pernonanoate anions affecting the interaction with the micelle. We have attributed the similar behaviour regarding the stability constants of α -cyclodextrin complexes of peracid anions and parent acid anions to differences in ion cyclodextrin dipole interactions.⁹ The weak binding of anions with anionic micelles such as SDS is well known. The generally low values of the association constants of iodide and the anions of the acids with the nonionic surfactants

Table 3 Ratios of micellar association constants for peracids, transition states and parent acids

Surfactant	$K_{\text{mic}}^{\text{PH}}$ (Pernonanoic)	$K_{\text{mic}}^{\text{TS}}$ (Pernonanoic)	$K_{\text{mic}}^{\text{AH}}$ (Nonanoic)
	$K_{\text{mic}}^{\text{PH}}$ (3-CIPBA)	$K_{\text{mic}}^{\text{TS}}$ (3-CIPBA)	$K_{\text{mic}}^{\text{AH}}$ (3-CIBA)
Brij-35	5.9 ± 1.6	4.4 ± 0.8	3.4 ± 0.5
Triton X-100	3.4 ± 0.8	2.2 ± 0.4	2.2 ± 0.4
SDS	10.1 ± 1.0	4.8 ± 1.6	3.4 ± 0.6

are also expected on the grounds of the lower relative permittivity of the mantle region of the micelle¹⁶ and the double layer potential of the inner core.¹⁷ It has recently been reported that 4-nitrobenzoate associates very weakly with Triton X-100 but the molecular acid binds quite strongly.¹⁸ Micellar association constants of a series of 3- and 4-substituted benzoic acids with SDS in the absence of added electrolyte have been measured using a similar method to that used here.¹⁹ The association constant reported for 3-chlorobenzoic acid was *ca.* 30% of our value. This is a reasonable agreement considering the different conditions.

Transition state pseudoequilibrium constants

The terms involving the transition state pseudoequilibrium constants for association with the micelles, shown in Table 1, are calculated using eqn. (21). Only the term for the reaction of 3-chloroperbenzoic acid in SDS needs to be corrected for $\bar{V}_{\text{mic}}^{\text{mic}}$ as described in the previous section. This gives a value of $K_{\text{mic}}^{\text{TS}}$ of $2.85 \pm 0.71 \text{ dm}^3 \text{ mol}^{-1}$. The correction has no effect on our final conclusions. The Gibbs' energy relationship between the logarithms of the transition state pseudoequilibrium constants and the micellar association constants of the peracids is shown in Fig. 9. The data for the peracid iodide reaction in the non-ionic micelles lies above the dashed line of unit slope and zero intercept that represents the identity line for the association constants of the peracids. Thus the transition state is stabilised by the non-ionic micelles more than the peracid initial state. This represents micellar catalysis. If, as seems reasonable, the reaction occurs in the poly(oxyethylene) mantle then it is surprising that micellar catalysis is observed at all when the etheric nature of the mantle is considered. Etheric hydrogen bond acceptor solvents such as 1,4-dioxane inhibit the reaction by stabilising the peracid initial state with respect to the transition state.⁷ However, we have shown by supercritical carbon dioxide chromatography that the Triton X-100 is polydisperse, as is certainly the case for the Brij-35, and so there is a considerable proportion of surfactant molecules with less than the average poly(oxyethylene) chain length. For these molecules the terminal OH end of the surfactant is located in the mantle region of the micelle. These terminal OH groups may serve as hydrogen bond donors which stabilise the transition state **1**. Moreover, there is a considerable amount of water associated with the mantle.¹³ This associated water can act as a hydrogen bond donor to the transition state and also, as shown by Monte Carlo simulations,²⁰ to the etheric oxygens of the poly(oxyethylene) mantle. Thus the water not only stabilises the transition state **1** directly but also opposes the stabilising effect of the etheric mantle on the peracid reactant initial state.

In contrast to the non-ionic micelles, the transition state pseudoequilibrium constant for the reaction in the anionic SDS micelles lies some way below the association constants of the peracids, Fig. 9. This represents micellar inhibition, from the point of view of the peracid. This is due to the participation of the iodide anion in the transition state, which is not favoured in the negatively charged micelle. Besides this simple partitioning effect, SDS may also inhibit the reaction by destabilising the transition state **1** for the following reason. From a detailed consideration of the factors that influence the distribution of well over a hundred solutes between water and SDS micelles, Abraham *et al.* conclude that the region of the micelle where the

solutes tend to associate has less (although still considerable) hydrogen bond acidity than bulk water.²¹ On the other hand, these workers suggest that this region of the micelle has a similar hydrogen bond basicity to water. So it seems unlikely that in the micelle the peracid is stabilised with respect to the transition state to a significantly different degree than in water.

It is interesting that in the non-ionic surfactants the values of the transition state pseudoequilibrium constants, $K_{\text{mic}}^{\text{TS}}$, are quite similar to the association constants of the parent acids, $K_{\text{mic}}^{\text{AH}}$ (compare the values in Tables 1 and 2 and see Fig. 9). We observed the same result for the cyclodextrin mediated reaction of substituted perbenzoic acids and iodide for those cases where the peracid was thought to be included in the cyclodextrin cavity in the transition state.⁸ This result was discussed in terms of the similarity of the transition state **1** and the parent acid product of the reaction.⁸ In the present case the similar stabilisation by the micelle of the transition state and the parent acid may be fortuitous since the association of the other products of the reaction with the micelle should be taken into account. This is not possible since the HOI produced is unstable under the reaction conditions. It is possible, though, to compare the two different peracids in order to factor out, to a first approximation, the contributions of the common reactants and products to the Gibbs' energy changes. Table 3 is a comparison of the ratios of the association constants of the peracids, the transition states and the parent acids in each of the surfactant systems. The ratios for the peracids and the parent acids are almost certainly different in all three surfactants. Hence the relative stabilities conferred on the peracids in the initial states by the micelles are different to the relative stabilities conferred by the micelles on the parent acids in the final states. It is gratifying to see that the relative stabilities conferred by the micelles on the transition states lie between those of the initial and final states. This is because we would expect the properties of the transition state to lie between those of the initial and final states. Moreover, within the limits of the errors of the derived quantities, the relative stabilities conferred on the transition states resemble those conferred on the products more than the reactants. This is in accord with the product-like nature of the transition state.⁷ It is disappointing that, even though their precisions are good, the differences in the ratios shown in Table 3 are so small compared with their precisions. This limits the interpretation of the results. In principle, the differences in the ratios provide an indication of the effect of the various surfactants on the position of the transition state on the reaction coordinate. We hope to find a system involving peroxide reactions in which this aspect can be explored further.

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