Micellar kinetics of acyl transfer from *n*-nonanoyloxybenzenesulfonate and phenyl nonanoate bleach activators to hydrogen peroxide and pernonanoic acid: effect of charge on the surfactant and activator

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The effect of surfactants on the kinetics of the title reactions is analysed using a combined multiple micellar pseudophase model and transition state pseudoequilibrium constant approach which leads to the micellar association constants of the reactants and the apparent (virtual) micellar association constants of the transition states. These association constants reflect the stabilisation of the reactants and transition states, respectively, by the micelle compared with their stability in the bulk aqueous phase. For the reaction of *n*-nonanoyloxybenzenesulfonate with pernonanoate in the presence of sodium dodecyl sulfate (SDS) the apparent micellar association constant of the transition state is larger than the micellar association constant of the activator; this is consistent with micellar catalysis, whilst micellar inhibition occurs with the anion of hydrogen peroxide. The micellar association constant of phenyl nonanoate with SDS is four orders of magnitude greater than that of *n*-nonanoyloxybenzenesulfonate due to the absence of the negatively charged sulfonate group, whilst the apparent micellar association constant of the transition state for its reaction with pernonanoate is more than an order of magnitude less. In the non-ionic surfactant Brij-35, the micellar association constant of *n*-nonanoyloxybenzenesulfonate and the corresponding apparent quantity for the transition state for the reaction with the hydroperoxide anion are, respectively, about one and two orders of magnitude greater than in SDS.

Peroxide bleach activators are used in detergents, biocides, industrial bleaching, effluent treatment and environmental remediation. The function of the activator is to transfer an acyl group to the hydroperoxide anion, HOO^-. In the process the activator undergoes perhydrolysis to form a peracid (acyl hydroperoxide) which is a better oxidant than hydrogen peroxide itself.[1] We have recently reported that acyl transfer from substituted acyloxybenzenesulfonate, $RCOOC_6H_4SO_3^-$, bleach activators to a series of peroxide anion nucleophiles conforms to a Brønsted-type relationship with β_{nuc} 0.42 ± 0.01 and 0.56 ± 0.05 for R = Me and $Me(CH_2)_7$, respectively.[2] These values reflect the rather low selectivity of the rate of reaction to the basicity of the nucleophile, and so peracids react with the activators at comparable rates to those of hydrogen peroxide, particularly at pH values between the pK_a values of the peracid and the hydrogen peroxide, where the fraction of the hydrogen peroxide ionised is low compared with that of the peracid. Hence the initial peracid product of the reaction of the activator and the hydroperoxide anion may accept a second acyl group from another activator molecule.[3]

In detergents the concentration of surfactant as well as the pH has an effect on the relative rates of acyl transfer from activators with hydrophobic acyl substituents, R, to hydroperoxide and peracid anions. The present paper examines the very different effects of sodium dodecyl sulfate (SDS) on the reaction of hydrogen peroxide, on the one hand, and pernonanoic acid, on the other, with sodium *n*-nonanoyloxybenzenesulfonate [SnNOBS, R = $Me(CH_2)_7$]. The kinetics are interpreted in terms of the transition state pseudoequilibrium constant approach[4] using a recently developed multiple micellar pseudophase (MMPP) model[5] which is a generalisation of the classical pseudophase kinetic model.[6] The MMPP model recognises explicitly that sometimes a reactant may associate strongly with one region of the micelle but undergo reaction in an adjacent region where it has lower affinity. This is analogous to non-productive binding in enzyme kinetics. The present paper also examines the apparently much greater inhibition by the non-ionic surfactant poly(oxyethylene)(23) dodecyl ether (Brij-35) than by the anionic surfactant SDS of the reaction between *n*-nonanoyloxybenzenesulfonate and the hydroperoxide anion. This is explained in terms of partitioning, *i.e.* reactant stabilisation, effects despite the greater destabilisation of the transition state by SDS than by Brij-35. In contrast, the greatly reduced reactivity of phenyl nonanoate with pernonanoic acid in SDS micelles compared with *n*-nonanoyloxybenzenesulfonate is explained in terms of transition state destabilisation.

Bruice *et al.* have previously reported on the alkaline hydrolysis of *n*-nonanoyloxybenzenesulfonate and the effect of anionic, non-ionic and cationic surfactant micelles on the reaction. They have also described the reactions of related 3-nitro-4-hydroxybenzenesulfonate esters with micelles of surfactants with reactive amino groups.[7]

Experimental

Sodium *n*-nonanoyloxybenzenesulfonate, 97%, phenyl nonanoate, 90% and pernonanoic acid, 90% were provided by Warwick International Group Ltd. The peracid contains the parent acid as the only significant impurity and the major impurities associated with the esters are the respective phenols. Aqueous hydrogen peroxide, 27.5 wt% was purchased from Aldrich. Carbonate buffer components were AnalaR reagents. Solutions were made up in distilled water. Peracid solutions were made up daily by stirring in distilled water for several hours; these were filtered through a sintered glass funnel and standardised by iodometric titration. Working solutions were obtained by dilution. Phenyl nonanoate and SDS were dissolved in AnalaR methanol which was then quickly removed by

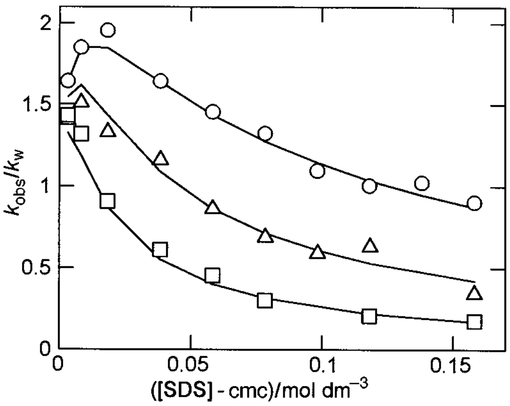

Fig. 1 Effect of SDS on the reaction of pernonanoic acid and *n*-nonanoyloxybenzenesulfonate in carbonate buffer, 25 °C, ionic strength 0.1 mol dm^{-3}; ○, pH 10.5, △, pH 9.98, □, pH 9.5. The lines join the values calculated according to eqn. (11) using the best fit parameters in Table 1.

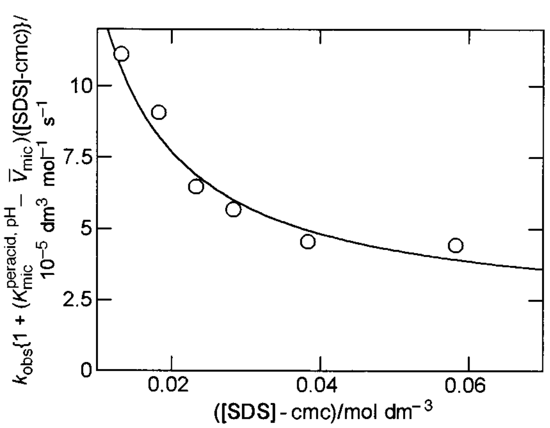

Fig. 2 Effect of SDS on the reaction of pernonanoic acid and phenyl nonanoate in carbonate buffer, 25 °C, ionic strength 0.1 mol dm^{-3}, pH 10.5. Data treated according to eqn. (14) with the micellar association constant term, $(K^{\text{peracid, pH}}_{\text{mic}} - \bar{V}_{\text{mic}})$, 10.4 dm^3 mol^{-1}. The curve represents the equation with the best fit parameters in Table 1.

rotary evaporation and the evaporite dissolved in carbonate buffer to yield a solution 1×10^{-3} mol dm^{-3} in ester and 1.5×10^{-2} mol dm^{-3} in SDS, which was appropriately diluted with SDS in carbonate buffer to obtain working solutions.

Kinetic runs with 5×10^{-6} mol dm^{-3} *n*-nonanoyloxybenzenesulfonate were carried out under pseudo-first order conditions with the peroxide in greater than twenty-fold excess at five or more different concentrations in carbonate buffer, ionic strength 0.1 mol dm^{-3} at 25 °C, monitoring the rise in absorbance due to the release of the oxybenzenesulfonate anion at 254 nm as described previously.[2] The second order rate constant under the experimental conditions, k_{obs}, was calculated as the slope ± standard deviation of a linear regression of the pseudo-first order rate constant (k_ψ) *versus* peroxide concentration. The release of phenol from 5×10^{-6} mol dm^{-3} phenyl nonanoate was followed at 288 nm using 4.6×10^{-4} pernonanoic acid in pH 10.5 carbonate buffer and k_{obs} estimated from the single value of k_ψ.

Results

Plots of the observed pseudo-first order rate constants were directly proportional to the peroxide concentration with negligible intercepts, showing that the contribution of hydrolysis to the overall rate was negligible. Standard deviations of k_{obs} were generally less than 5% of the best fit value (results not shown). The effect of surfactant and, when relevant, pH on the reaction of peroxide and activator is shown in Figs. 1–4. The results are consistent with the reaction scheme shown in eqns. (1)–(6)

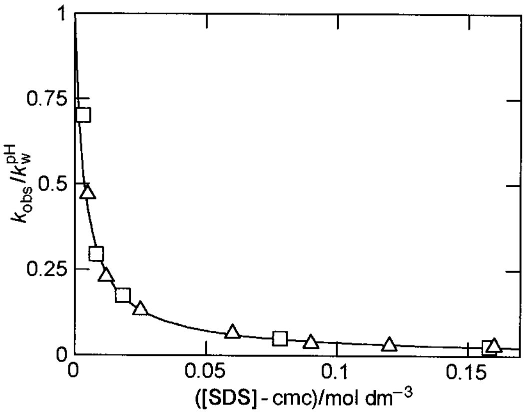

Fig. 3 Effect of SDS on the reaction of hydrogen peroxide and *n*-nonanoyloxybenzenesulfonate in carbonate buffer, 25 °C, ionic strength 0.1 mol dm^{-3}; △, pH 9.87, □, pH 9.5. The curve represents eqn. (16) using the best fit parameters in Table 1.

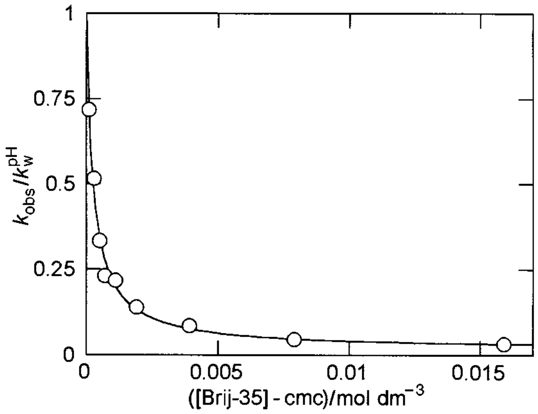

Fig. 4 Effect of Brij-35 on the reaction of hydrogen peroxide and *n*-nonanoyloxybenzenesulfonate in carbonate buffer, 25 °C, ionic strength 0.1 mol dm^{-3}, pH 10.5. The curve represents eqn. (16) using the best fit parameters in Table 1.

$$\text{PH}_w \overset{K_a}{\rightleftharpoons} \text{P}^-_w + \text{H}^+_w \tag{1}$$

$$\text{PH}_w \overset{P_{\text{PH},i}}{\rightleftharpoons} \text{PH}_{m,i} \tag{2}$$

$$\text{P}^-_w \overset{P_{\text{P},i}}{\rightleftharpoons} \text{P}^-_{m,i} \tag{3}$$

$$\text{A}_w \overset{P_{\text{A},i}}{\rightleftharpoons} \text{A}_{m,i} \tag{4}$$

$$\text{P}^-_w + \text{A}_w \xrightarrow{k_w} \text{products} \tag{5}$$

$$\text{P}^-_{m,i} + \text{A}_{m,i} \xrightarrow{k_{m,i}} \text{products} \tag{6}$$

where A is the activator, PH is the peroxide and P$^-$ its anion. Eqn. (1) represents the ionisation of peracid in the bulk water phase and the mixed acid dissociation constant, K_a, is defined in eqn. (7), where $\{\text{H}^+\}_w$ is the hydrogen ion activity measured

$$K_a = \frac{[\text{P}^-]_w\{\text{H}^+\}_w}{[\text{PH}]_w} \tag{7}$$

with the glass electrode. Eqns. (2)–(4) represent the partitioning, with partition coefficients *P*, of the various species between the bulk water phase, w and the *i*th micellar pseudophase, m,*i*, where *i* = 1 to *n*. Eqns. (5) and (6) represent the reaction of peroxide anion and activator in the bulk aqueous phase and *i*th

$$k_{\mathrm{obs}} = \frac{\{k_{\mathrm{w}} + (k_{\mathrm{mic}} - k_{\mathrm{w}}\bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}K_{\mathrm{a}}}{\left\{\begin{array}{l}\{\mathrm{H}^{+}\}_{\mathrm{w}}[1 + (K^{\mathrm{PH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})] \\ +K_{\mathrm{a}}[1 + (K^{\mathrm{P}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})]\end{array}\right\}\{1 + (K^{\mathrm{A}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}} \tag{8}$$

micellar pseudophase with elementary rate constants k_{w} and $k_{\mathrm{m},i}$, respectively.

Application of the MMPP model to the reaction scheme shown in eqns. (1)–(6) leads to eqn. (8), where [S] represents the overall concentration of surfactant and cmc its critical micelle concentration.[5] An equation of the same form with respect to surfactant and hydrogen ion concentration has been derived by Berezin and co-workers for the classical pseudophase model where $n = 1$.[6] In eqn. (8) k_{mic} is an observed third order rate constant (first order in surfactant concentration) and $\bar{V}_{\mathrm{mic}}$ is the effective molar volume of micellised surfactant. The micellar association constants $K^{\mathrm{PH}}_{\mathrm{mic}}$, $K^{\mathrm{P}}_{\mathrm{mic}}$ and $K^{\mathrm{A}}_{\mathrm{mic}}$ are overall quantities whereas k_{mic} relates to the elementary rate constants and the association constants for the specific micellar pseudophases where the reaction takes place. A full discussion of the implications of this is given in ref. 5 but suffice it to say that the major problem is that the elementary rate constants defined in eqn. (6) cannot be obtained.[5] This is not an insurmountable problem for the interpretation of micellar kinetics because the transition state pseudoequilibrium constant approach can be applied to the MMPP model to yield eqn. (9), where $K^{\mathrm{TS}}_{\mathrm{mic}}$ is an apparent or

$$\frac{k_{\mathrm{mic}}}{k_{\mathrm{w}}} = K^{\mathrm{TS}}_{\mathrm{mic}} \tag{9}$$

virtual micellar association constant obtained from a thermodynamic cycle. In all other respects, $K^{\mathrm{TS}}_{\mathrm{mic}}$ is analogous to $K^{\mathrm{PH}}_{\mathrm{mic}}$ *etc.* and represents the stabilization of the transition state by the micelle.[5] Combining eqns. (8) and (9) leads to eqn. (10) which shows how the quotient $k_{\mathrm{obs}}/k_{\mathrm{w}}$ relates to the micellar association constants of the transition state and reactants. Thus eqn. (10) describes the stabilization of the transition state and the reactants by the surfactant micelles relative to their stability in the bulk aqueous phase.

Fig. 1 shows the effect of SDS on the reaction of *n*-nonanoyloxybenzenesulfonate and pernonanoic acid at three different pH values. The K_{a} of pernonanoic acid has been determined from kinetic measurements as $(5.9 \pm 0.5) \times 10^{-9}$ mol dm^{-3} and this is consistent with the results of pH titration.[5,8] Hence under the experimental conditions, pH 9.5–10.5, $K_{\mathrm{a}} \gg \{\mathrm{H}^{+}\}_{\mathrm{w}}$ and eqn. (10) simplifies to eqn. (11). This equation is used to treat the data in Fig. 1 using a cmc for SDS of 1.8×10^{-3} mol dm^{-3} determined under the present experimental conditions.[5] The mean and its standard deviation of the rate constant in water, k_{w}, at the three pHs was 6.4 ± 0.3 dm^{3} mol^{-1} s^{-1}; this compares with a value of 5.3 dm^{3} mol^{-1} s^{-1} for the reaction of the peracetate anion and *n*-nonanoyloxybenzenesulfonate.[2] The best fit values of the micellar association constants minus the effective molar volume of the micellised surfactant are shown in the first row of Table 1 for the reaction of *n*-nonanoyloxybenzenesulfonate and pernonanoic acid. A value of $\bar{V}_{\mathrm{mic}}$ of 0.4 dm^{3} mol^{-1} has been previously estimated for SDS, based on its relative molar mass and density,[5] and this constitutes a negligible correction to the micellar association constant terms.

It was not possible to obtain a value of k_{w} for the reaction of pernonanoic acid and phenyl nonanoate because of the insolubility of the latter in water so the following approach was taken. Eqn. (10) can be rewritten as eqn. (12) where $(K^{\mathrm{peracid,\,pH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})$ is the apparent micellar association constant term of the peracid at the pH of the experiment and is given by eqn. (13). It is safe to assume for phenyl nonanoate that $(K^{\mathrm{A}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}}) \gg ([\mathrm{S}] - \mathrm{cmc})^{-1}$ for the concentrations of SDS used in the experiments and so eqn. (12) can be rearranged to eqn. (14). At the pH of the experiment, 10.5, a value of $(K^{\mathrm{peracid,\,pH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})$ of 10.4 dm^{3} mol^{-1} is obtained from eqn. (13) using the association constant terms of pernonanoic acid and its conjugate base given in the first row of Table 1 and the K_{a} of pernonanoic acid, 5.9×10^{-9} mol dm^{-3}, mentioned previously. Fig. 2 shows a plot of the left hand side of eqn. (14) against ([SDS] − cmc). Regression analysis of the data in Fig. 2 according to eqn. (14) leads to the best fit value of the transition state apparent micellar association constant term shown in the second row of Table 1. A best fit value of $(K^{\mathrm{A}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})k_{\mathrm{w}}^{-1}$ of $(8.7 \pm 1.2) \times 10^{5}$ s is also obtained from the regression analysis. The value of k_{w} for the reaction of phenyl nonanoate and pernonanoate is estimated as 3.0 dm^{3} mol^{-1} s^{-1} using the rate constant for the reaction of *n*-nonanoyloxybenzenesulfonate and pernonanoate given in the previous paragraph, the respective pK_{a} values of 4-phenolsulfonate (4-hydroxybenzenesulfonate) and phenol, 8.91 and 9.86,[9] and a recently determined value of β_{lg}, −0.35, for a similar reaction, namely that of substituted phenyl acetates and peracetic acid.[2] This allows the estimation of the micellar association constant term for phenyl nonanoate given in the second row of Table 1.

$$K^{\mathrm{peracid,\,pH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}} = \frac{\{\mathrm{H}^{+}\}_{\mathrm{w}}(K^{\mathrm{PH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}}) + K_{\mathrm{a}}(K^{\mathrm{P}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})}{\{\mathrm{H}^{+}\}_{\mathrm{w}} + K_{\mathrm{a}}} \tag{13}$$

$$k_{\mathrm{obs}}\{1 + (K^{\mathrm{peracid,\,pH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\} = \frac{1 + (K^{\mathrm{TS}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})}{(K^{\mathrm{A}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})k_{\mathrm{w}}^{-1}([\mathrm{S}] - \mathrm{cmc})} \tag{14}$$

Fig. 3 shows the effect of SDS on the reaction of *n*-nonanoyloxybenzenesulfonate and hydrogen peroxide at pH 9.87 and 9.5. The pK_{a} of hydrogen peroxide is 11.6,[10] so under the present experimental conditions the limitation $\{\mathrm{H}^{+}\}_{\mathrm{w}} \gg K_{\mathrm{a}}$ holds. Hence, the reasonable assumption that the micellar

$$\frac{k_{\mathrm{obs}}}{k_{\mathrm{w}}} = \frac{\{1 + (K^{\mathrm{TS}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}K_{\mathrm{a}}}{\left\{\begin{array}{l}\{\mathrm{H}^{+}\}_{\mathrm{w}}[1 + (K^{\mathrm{PH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})] \\ +K_{\mathrm{a}}[1 + (K^{\mathrm{P}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})]\end{array}\right\}\{1 + (K^{\mathrm{A}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}} \tag{10}$$

$$\frac{k_{\mathrm{obs}}}{k_{\mathrm{w}}} = \frac{1 + (K^{\mathrm{TS}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})}{\left\{1 + \left[(K^{\mathrm{P}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}}) + \frac{\{\mathrm{H}^{+}\}_{\mathrm{w}}}{K_{\mathrm{a}}}(K^{\mathrm{PH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})\right]([\mathrm{S}] - \mathrm{cmc})\right\}\{1 + (K^{\mathrm{A}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}} \tag{11}$$

$$\frac{k_{\mathrm{obs}}}{k_{\mathrm{w}}} = \frac{1 + (K^{\mathrm{TS}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})}{\{1 + (K^{\mathrm{peracid,\,pH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}\{1 + (K^{\mathrm{A}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}} \tag{12}$$

Table 1 Best fit micellar association constant terms ± standard deviation for the reaction of peroxides and activators in the presence of surfactants in carbonate buffers, ionic strength 0.1 mol dm^{-3}, 25 °C

			Micellar association constant term/dm^3 mol^{-1}			
Activator	Peroxide	Surfactant	$K^{\mathrm{A}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}}$	$K^{\mathrm{P}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}}$	$K^{\mathrm{PH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}}$	$K^{\mathrm{TS}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}}$
SnNOBS	$CH_3(CH_2)_7CO_3^-$	SDS	(2.7 ± 1.2) × 10^2	3.2 ± 1.8	(1.35 ± 0.19) × 10^3	(6.7 ± 2.3) × 10^2
Phenyl nonanoate	$CH_3(CH_2)_7CO_3^-$	SDS	(2.6 ± 0.3) × 10^6 [a]	3.2 [b]	1.35 × 10^3 [b]	17 ± 7
SnNOBS	HOO^-	SDS	(2.7 ± 0.2) × 10^2	0 [c]	0 [c]	0.5 ± 0.8
SnNOBS	HOO^-	Brij-35	(3.9 ± 0.3) × 10^3	0 [c]	0 [c]	66 ± 17

[a] Calculated using an estimated value of k_w, see text. [b] Used in the calculation of $(K^{\mathrm{peracid,\,pH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})$ in eqn. (13). [c] Assuming the quantity $\{1 + (K^{\mathrm{PH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}}) \times ([\mathrm{S}] - \mathrm{cmc})\}$ remains close to unity over the experimental conditions and $(K^{\mathrm{P}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}}) \leqslant (K^{\mathrm{PH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})$.

$$\frac{k_{\mathrm{obs}}}{k_{\mathrm{w}}\dfrac{K_{\mathrm{a}}}{\{\mathrm{H}^+\}_{\mathrm{w}}}} = \frac{1 + (K^{\mathrm{TS}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})}{\{1 + (K^{\mathrm{PH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}\{1 + (K^{\mathrm{A}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}} \tag{15}$$

$$\frac{k_{\mathrm{obs}}}{k^{\mathrm{pH}}_{\mathrm{w}}} = \frac{1 + (K^{\mathrm{TS}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})}{\{1 + (K^{\mathrm{PH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}\{1 + (K^{\mathrm{A}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}} \tag{16}$$

association constant term for the negatively charged SDS micelle with the hydroperoxide anion is less than or equal to that with hydrogen peroxide, *i.e.* $(K^{\mathrm{P}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}}) \leqslant (K^{\mathrm{PH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})$, allows eqn. (10) to be simplified to eqn. (15). The denominator of the left hand side of eqn. (15) is the rate constant in water at the pH of the experiment, $k^{\mathrm{pH}}_{\mathrm{w}}$, under the present experimental conditions. Hence eqn. (15) can be rewritten as eqn. (16). The rate constant in water with respect to the concentration of the hydroperoxide anion, k_{w}, was very close to the value 430 dm^3 mol^{-1} s^{-1} reported previously.[2] Eqn. (16) is consistent with the results shown in Fig. 3 if it is assumed that the micellar association constant with hydrogen peroxide is small, *i.e.* the quantity $\{1 + (K^{\mathrm{PH}}_{\mathrm{mic}} - \bar{V}_{\mathrm{mic}})([\mathrm{S}] - \mathrm{cmc})\}$ remains close to unity over the experimental conditions, then the best fit micellar association constant terms shown in row 3 of Table 1 are obtained. The above assumption is strongly justified by the agreement of the value of the micellar association constant term for *n*-nonanoyloxybenzenesulfonate obtained from its reaction with hydrogen peroxide with that shown in row 1 of Table 1 from the reaction with pernonanoic acid.

Fig. 4 shows the effect of Brij-35 on the reaction of 5 × 10^{-6} mol dm^{-3} *n*-nonanoyloxybenzenesulfonate and hydrogen peroxide. The cmc of the Brij determined from the break in surface tension, measured using a de Nouy tensiometer, *versus* the logarithm of the concentration drops from about 2 × 10^{-4} mol dm^{-3} to 1.0 × 10^{-4} mol dm^{-3} under the experimental conditions upon addition of the working concentration of *n*-nonanoyloxybenzenesulfonate (results not shown). The latter value was used in the treatment of the kinetic data, although the effect of using the former value or neglecting the cmc altogether was insignificant in terms of the results of the regression analysis. The data were treated using eqn. (16), making the same assumptions that were applied to the corresponding runs with SDS and yielded the micellar association constant terms shown in Table 1.

Discussion

Hydroperoxides are oxidants and the anions are α-nucleophiles and, in addition to bleaching and bleach activation involving acyl transfer,[1,2,11] they are important in the degradation of toxic organophosphorus and sulfur pesticides and chemical weapons.[12] These degradation processes occur *via* oxidative and nucleophile-catalysed hydrolytic pathways and, in common with similar processes involving hypochlorite, are often carried out in surfactant systems.[12,13] A number of studies of the kinetics of micellar catalysis and inhibition of hydroperoxide reactions are considered in terms of pseudophase models.[5,14–16] The present MMPP model is a generalisation of the classical pseudophase model of Berezin and co-workers.[6] The MMPP model leads to the same formal dependence of rate on surfactant concentration as the classical model but the significance of the kinetic parameters is different. In particular the MMPP model shows that k_{mic} in eqn. (8) is a composite quantity and that the elementary bimolecular rate constants defined in eqn. (6) cannot be obtained.[5] This is not, however, an insurmountable problem for the interpretation of micellar kinetics because the transition state pseudoequilibrium constant approach of Kurz[4] can be applied to the MMPP model.[5] This approach yields eqn. (10) which contains an apparent or virtual micellar association constant for the transition state as a result of the application of a thermodynamic cycle. No transfer of the transition state between micelles and the bulk aqueous phase is inferred. The apparent micellar association constant of the transition state is a fundamental kinetic property independent of any postulated reaction pathway or any choice of micellar reaction volume. The latter quantity is, however, required for the comparison of rate constants of biomolecular reactions in the micellar and aqueous phases if the transition state pseudoequilibrium constant approach is not applied.[6] In contrast, $\bar{V}_{\mathrm{mic}}$, the effective molar volume of the micellar surfactant in eqn. (10), represents a small correction to the micellar association constant terms. Thus the advantage of the present approach to the interpretation of the kinetic data is in the comparison of the apparent micellar association constant of the transition state and the actual micellar association constant of the reactants. This provides a comparison of the stabilisation of the transition state and the reactants by the surfactant micelles relative to their stability in the bulk aqueous phase.[5]

The effect of SDS on the reaction of pernonanoic acid and *n*-nonanoyloxybenzenesulfonate is shown in Fig. 1. It is necessary to carry out the reaction at more than one pH in order to distinguish between the micellar association constants of the activator and the peracid in the regression analysis. This can be done because the latter is pH-dependent whilst the former is not. The effect of increasing surfactant concentration is to firstly cause an increase in the observed rate constant above that in the absence of surfactant, then, with a further increase in surfactant the rate constant drops. This is typical of systems that are overall second order with respect to reactant concentrations and where both reactants associate strongly with the micelle. The initial increase is at least partly due to the concentration of reactants in the micelle and the subsequent fall off in the observed rate constant is due to the dilution of the two reactants since they are both partitioned predominantly into the micelle. The maximal rate acceleration by SDS is relatively small since the reactive form of the peracid is the anion whereas the unchanged molecular form of the peracid has a much higher affinity for the negatively charged micelle. The reaction shown in eqns. (1)–(6) together with the micellar association constant terms in row 1 of Table 1 describe the system fully. The micellar association constant terms contain the quantity $\bar{V}_{\mathrm{mic}}$ which for SDS is estimated at 0.4 dm^3 mol^{-1} and so is negligible for the present reaction.[5] The value of $K_{\mathrm{mic}}^{\mathrm{PH}} - \bar{V}_{\mathrm{mic}}$ for pernonanoic acid in SDS in the present work is in satisfactory agreement with the value, 950 ± 70 dm^3 mol^{-1}, obtained for the iodide reduction of pernonanoic acid in SDS.[5] The order of micellar association constants for the SDS–pernonanoic acid–*n*-nonanoyloxybenzenesulfonate system is as follows. The unchanged pernonanoic acid has the highest affinity for the SDS micelle; this species does not take part in the reaction. Next comes the transition state, then the *n*-nonanoyloxybenzenesulfonate, then the pernonanoate anion. The low micellar association constant of the latter is consistent with the charged outer peroxidic oxygen being in a region of the micelle much closer to the charged sulfate headgroups than the region occupied by the sulfonate on the activator. This is very different to the SDS–pernonanoic acid–phenyl nonanoate system discussed in the next paragraph, where the activator lacks a negatively charged 4-sulfonate substituent.

The observed rate constants for the reaction of pernonanoic acid with phenyl nonanoate in the presence of SDS are very much less than those for reaction with *n*-nonanoyloxybenzenesulfonate. This indicates that the relative stability of the transition state with respect to the reactant is much less in the former than in the latter reaction. In the data treatment according to eqn. (14) shown in Fig. 2, the micellar association constant term for the pernonanoic acid is taken from the pernonanoic acid–*n*-nonanoyloxybenzenesulfonate study. This is justified because the micellar association constants of reactants or related species are overall quantities. This point has been discussed in a study of the effect of micelles on the reaction of *m*-chloroperbenzoic acid and an iron(III)–porphyrin complex.[14] Inspection of eqn. (14) shows that an estimate of the rate constant in the absence of surfactant is required to obtain the micellar association constant for phenyl nonanoate. Table 1 shows that, as expected, the micellar association constant of phenyl nonanoate with SDS is much larger than that of *n*-nonanoyloxybenzenesulfonate because of its lack of a negative charge. The apparent association constant for the transition state of the reaction of pernonanoic acid and phenyl nonanoate is, however, much lower than that with *n*-nonanoyloxybenzenesulfonate. This is consistent with the carbonyl carbon of the unchanged activator being less accessible to the outer peroxidic oxygen anion of the pernonanoate in the SDS micelle and can be interpreted as the activator lying deeper in the micelle whilst the pernonanoate anion lies further out. Bruice has discussed orientational effects in similar terms for the reaction of hydrophobic 3-nitro-4-hydroxybenzenesulfonate esters with micelles of surfactants with reactive amino groups.[7]

The effect of SDS on the reaction of hydrogen peroxide and *n*-nonanoyloxybenzenesulfonate is shown in Fig. 3. Here the steep drop in observed rate constant with increasing surfactant concentration is consistent with partitioning of the *n*-nonanoyloxybenzenesulfonate into the micelle whilst the hydroperoxide anion remains in the bulk aqueous phase. In order to treat the kinetics according to eqn. (16) it was necessary to assume that the overall micellar association constant for hydrogen peroxide was small. This was justified by the agreement of the micellar association constant for *n*-nonanoyloxybenzenesulfonate obtained in this reaction and in that with pernonanoic acid. The value of the apparent micellar association constant for the transition state is marginally greater than zero when the value of $\bar{V}_{\mathrm{mic}}$, 0.4 dm^3 mol^{-1}, is taken into account. A positive value of $K_{\mathrm{mic}}^{\mathrm{TS}}$ is indicative of a residual reaction of micellar bound activator with the hydroperoxide anion at high concentrations of SDS. This is consistent with incomplete exclusion of the reactive anion from the anionic micellar reaction pseudophase and has been observed for the reaction of other anions with organic substrates in SDS.[5,17] Chemical trapping experiments indicate that interfacial co-ion concentrations associated with SDS micelles are about 10% of the bulk concentration.[18]

Fig. 4 shows the effect of Brij-35 on the reaction of the hydroperoxide anion and *n*-nonanoyloxybenzenesulfonate. It seems surprising at first sight that this non-ionic surfactant apparently inhibits the reaction at much lower concentrations than does SDS (note the different concentration scales in Figs. 3 and 4). The data are treated according to eqn. (16) and the resulting micellar association constants (the correction for $\bar{V}_{\mathrm{mic}}$ for Brij-35 is about 5 dm^3 mol^{-1})[5,15] are compared in Table 1 with those for the same reaction in SDS. This comparison explains the apparently greater inhibition by Brij-35. The much larger micellar association constant of the negatively charged activator in the non-ionic micelles means that it partitions more effectively out of the bulk aqueous phase whilst the hydroperoxide anion would be expected to have a low micellar association constant because of the low relative permittivity of the mantle region of the micelle as discussed for the iodide–peracid reaction.[5] The transition state micellar association constant for the reaction in Brij-35, nevertheless, is significantly larger than that in SDS. This is consistent with a more favourable approach of the hydroperoxide anion to Brij compared with SDS. A possible complicating factor in the Brij-35–*n*-nonanoyloxybenzenesulfonate system is that the activator confers a negative charge on the micelle with which it associates and changes the affinity of the micelle for other charged reactants and the transition state. We have recently carried out extensive studies on mixed anionic–non-ionic surfactant micelles using the MMPP transition state stability model which suggest that the influence of the generally very low ratios of charged activator to non-ionic surfactant used in the present work should not have a very significant effect.[15]

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