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Kinetic treatment of the reaction of *m*-chloroperbenzoic acid and iodide in mixed anionic/non-ionic micelles

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Catalysis and inhibition of the title reaction in mixed micelles of Brij-35 and SDS is described. The kinetics are treated using a combined multiple micellar pseudophase model and transition state pseudoequilibrium constant approach that was previously used for the catalysis and inhibition of the reaction of peracids and iodide in non-ionic and anionic micelles, respectively (D. M. Davies, N. D. Gillitt and P. M. Paradis, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 659). In the present mixed micellar system the following factors are taken into account: (i) the mole ratio of the surfactants in the mixed micelle, which is the relevant quantity for the micellar kinetics and is different from the stoichiometric mole ratio of the surfactants; (ii) non-ideal mixing of the surfactants, which also influences the composition of the mixed micelle; (iii) the ideal behaviour of the apparent molar volume of micellized surfactant in mixed micelles; and (iv) deviations from ideality of the partitioning of reactants and transition state between mixed micelles and the bulk aqueous phase. Logarithms of micellar association constants of the reactants and transition state in the two surfactants have been obtained, together with parameters closely related to the excess Gibbs function associated with the deviations from ideality described by (iv). The relationship between the parameters that describe non-ideal mixing of the surfactants in (ii) and the deviations from ideality in (iv) is discussed.

Reactions in surfactant solutions are usually treated using pseudophase models in which the reactants partition between the bulk aqueous phase and a micellar pseudophase.[1] The sum of the rates of the concurrent reactions in the two phases constitutes the overall rate. We have recently developed a multiple micellar pseudo-phase (MMPP) model of kinetics of bimolecular reactions in aqueous surfactant solutions.[2] Here the reactants partition between water and a number of different micellar pseudophases, where they react with elementary rate constants defined in eqns. (1) and (2).

$$\mathrm{A_w} + \mathrm{B_w} \xrightarrow{k_\mathrm{w}} \text{products} \qquad (1)$$

$$\mathrm{A}_{\mathrm{m},i} + \mathrm{B}_{\mathrm{m},i} \xrightarrow{k_{\mathrm{m},i}} \text{products} \qquad (2)$$

The MMPP model is a generalization of the classical pseudophase model of Berezin and co-workers.[3] The former model recognizes 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 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. The rate law derived from the MMPP model is shown in eqn. (3) where k_obs is the observed

$$k_\mathrm{obs} = \frac{k_\mathrm{w} + (k_\mathrm{mic} - k_\mathrm{w}\bar{V}_\mathrm{mic})([\mathrm{S}] - \mathrm{cmc})}{\{1 + (K^\mathrm{A}_\mathrm{mic} - \bar{V}_\mathrm{mic})([\mathrm{S}] - \mathrm{cmc})\}\{1 + (K^\mathrm{B}_\mathrm{mic} - \bar{V}_\mathrm{mic})([\mathrm{S}] - \mathrm{cmc})\}} \qquad (3)$$

second order rate constant, k_w is the rate constant in the bulk aqueous phase, k_mic is an observed third order rate constant (first order in surfactant concentration), $\bar{V}_\mathrm{mic}$ is the effective molar volume of micellized surfactant, [S] is the total concentration of surfactant and cmc is the critical micelle concentration. The micellar association constants, $K^\mathrm{A}_\mathrm{mic}$ and $K^\mathrm{B}_\mathrm{mic}$, 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 the original paper but suffice it to say that the major problem is that the elementary rate constants defined in eqn. (2) cannot be obtained.[2] 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. (4), where $K^\mathrm{TS}_\mathrm{mic}$ is analogous to $K^\mathrm{A}_\mathrm{mic}$ or $K^\mathrm{B}_\mathrm{mic}$ and represents

$$\frac{k_\mathrm{mic}}{k_\mathrm{w}} = K^\mathrm{TS}_\mathrm{mic} \qquad (4)$$

the stabilization of the transition state by the micelle.[2] Combining eqns. (3) and (4) leads to eqn. (5) which shows how the

$$\frac{k_\mathrm{obs}}{k_\mathrm{w}} = \frac{1 + (K^\mathrm{TS}_\mathrm{mic} - \bar{V}_\mathrm{mic})([\mathrm{S}] - \mathrm{cmc})}{\{1 + (K^\mathrm{A}_\mathrm{mic} - \bar{V}_\mathrm{mic})([\mathrm{S}] - \mathrm{cmc})\}\{1 + (K^\mathrm{B}_\mathrm{mic} - \bar{V}_\mathrm{mic})([\mathrm{S}] - \mathrm{cmc})\}} \qquad (5)$$

quotient $k_\mathrm{obs}/k_\mathrm{w}$ relates to the micellar association constants of the transition state and reactants. Thus, eqn. (5) describes the stabilization of the transition state and the reactants by the surfactant micelles relative to their stability in the bulk aqueous phase under the experimental conditions.

The combined MMPP-transition state pseudoequilibrium constant approach described above was previously used to treat the kinetics of the reduction of peracids by iodide in the non-ionic surfactants poly(oxyethylene)(23) dodecyl ether (Brij-35) and Triton X-100, and in sodium dodecyl sulfate (SDS).[2] The present paper describes the effect of mixed anionic–non-ionic micelles of SDS and Brij-35 on the *m*-chloroperbenzoic acid–iodide reaction and demonstrates the usefulness of the MMPP model for the analysis of kinetics in mixed surfactant systems.

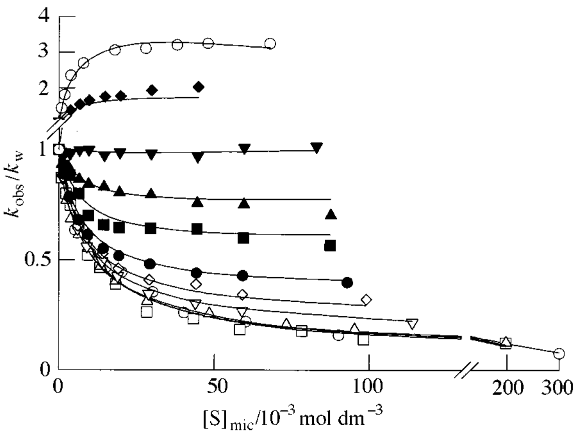

Fig. 1 Kinetics of the *m*-chloroperbenzoic acid–iodide reaction in mixed SDS/Brij-35 micelles at 25 °C in pH 5.5 acetate buffer, ionic strength 0.1 mol dm^{-3}. The curves are calculated from the best-fit parameters in Table 3 using Model 1. Stoichiometric mol fractions of SDS, a_{SDS}, are from the top of the figure: 0, 0.1, 0.2, 0.25, 0.3, 0.4, 0.5 (◇), 0.6 (▽), 0.9 (△), 0.95 (□), and 1 (○).

In the present analysis micellar association constants of reactants and transition state, respectively, are obtained for the two surfactants, together with a parameter, *B* that accounts for the deviations from ideality of the micellar association constants in the mixed micelle. The parameter *B* is used by Treiner to account for deviations from ideal behaviour in the partitioning of solutes between mixed micelles and the bulk aqueous phase.[4] Eqn. (6), which uses notation appropriate to this work, shows

$$\ln K^{X}_{mic} = \chi_{B35}\ln K^{X}_{B35} + \chi_{SDS}\ln K^{X}_{SDS} + \chi_{B35}\chi_{SDS}B^{X} \quad (6)$$

how *B* is used. In eqn. (6) X refers to reactants A or B, or transition state, TS. The mole fraction of each surfactant in the mixed micelle, χ_{SDS} or χ_{B35}, differs from the stoichiometric mole fraction, a_{SDS} or a_{B35}, at low surfactant concentrations.[5]

The peracid–iodide reaction is well characterized in aqueous and mixed-aqueous solvents.[6] The rate limiting step involves nucleophilic attack of iodide on the outer peroxidic oxygen of the peracid, followed by the formation of I_2, which equilibrates with I_3^-. The rate of reaction of the molecular peracid is not influenced by solvent relative permittivity, ionic strength, nor pH, which simplifies the discussion of micellar and other catalytic effects. The rate is, however, enhanced by hydrogen bond donor solvents which stabilize the transition state, and decreased by hydrogen bond acceptor solvents such as 1,4-dioxane, which stabilize the initial state with respect to the transition state.[6] The iodide–peracid reaction has been treated using the transition state pseudoequilibrium constant approach as a probe of the factors that are important in the catalysis of bimolecular reactions by cyclodextrin.[7]

The combined MMPP-transition state pseudoequilibrium constant approach has recently been applied to the reaction of deuteroferrihaem and *m*-chloroperbenzoic acid in SDS micelles and Triton X-100 micelles.[8]

Experimental

Materials and methods were as described previously.[2] All measurements were performed at 25 °C in pH 5.5 sodium acetate–acetic acid buffer, ionic strength 0.1 mol dm^{-3}.

Results

Fig. 1 shows a plot of k_{obs}/k_w *vs.* the concentration of micellar surfactant, $[S]_{mic}$, at various stoichiometric mole fractions of SDS. For single surfactant solutions $[S]_{mic}$ was simply calculated using eqn. (7) where [S] is the total concentration of surfactant

$$[S]_{mic} = [S] - \text{cmc} \quad (7)$$

and the concentration of surfactant monomer, $[S]_{mono}$, above the cmc is assumed to remain constant and equal to cmc. In solutions of two surfactants, S_1 and S_2, the concentrations of the monomers, $[S_1]_{mono}$ and $[S_2]_{mono}$, continue to change above the mixed cmc, cmc_{12}, as the total surfactant concentration changes.[5] Thus, the proportions of each surfactant in the micelles at the cmc are not the same as the stoichiometric mole ratio, although the two quantities will eventually equalize at a higher total surfactant concentration. Clint has treated the mixed micelle as an ideal mixture of its pure components at equilibrium so that the chemical potential of a particular surfactant species is the same in the bulk phase as in the micelle.[5] The extension of this work to systems of non-ideal mixed micelles simply involves the introduction of activity coefficients, f_1 and f_2, for the surfactants in the micelles, leading to eqn. (8)

$$\text{cmc}_{12} = \chi_i f_i \text{cmc}_i / a_i \quad i = 1, 2 \quad (8)$$

and hence eqn. (9), where $\chi \equiv \chi_1$, the mole fraction of S_1 in

$$\chi f_1 \text{cmc}_1 / a = (1 - \chi) f_2 \text{cmc}_2 / (1 - a) \quad (9)$$

the micelle; $(1 - \chi) \equiv \chi_2$, the mole fraction of S_2 in the micelle; cmc_1 and cmc_2 are the cmcs of the pure surfactants; $a \equiv a_1$, the stoichiometric mole fraction of S_1; $(1 - a) \equiv a_2$, the stoichiometric mole fraction of S_2. Rubingh has expressed the micellar activity coefficients as a single interaction parameter, β, according to eqns. (10) and (11).[9] Quantity β multiplied by *RT*

$$f_1 = \exp[\beta(1 - \chi)^2] \quad (10)$$

$$f_2 = \exp(\beta\chi^2) \quad (11)$$

is an excess Gibbs function of mixing that encompasses head group electrostatic repulsion, the effect of counter ions and steric interactions between hydrophilic head groups of non-ionic surfactants.[10,11] Substituting the expressions for the activity coefficients, eqns. (10) and (11), into eqn. (9) enables a particular value of χ, *i.e.* the mole fraction in the micelle at the mixed cmc, to be solved iteratively (ref. 11 provides a simple BASIC program) at the various stoichiometric mole fractions, *a*, used in the experiments, given the measured cmc values of the single surfactants and the interaction parameter, β. Values of cmc for Brij-35 and SDS are, respectively, 2.0×10^{-4} and 1.8×10^{-3} mol dm^{-3} under the present experimental conditions.[2] Values of β of 0, −1.25, −2.5 and −3.5 were used in the data treatment to see which gave the best fit. A value of $\beta = -2.5$ has been calculated from cmc_{12} values of mixtures of Brij-35 and SDS in the absence of added electrolyte.[12] Although electrolyte causes a significant decrease in the cmc of ionic surfactants, it causes only a small decrease in β.[11] Substitution of β and χ into eqns. (10) and (11) gives the values of the activity coefficients. These are used in eqns. (12) and (13) to

$$[S_1]_{mono} = \frac{-([S] - \Delta) + \{([S] - \Delta)^2 + 4a[S]\Delta\}^{\frac{1}{2}}}{2\left(\dfrac{f_2\text{cmc}_2}{f_1\text{cmc}_1} - 1\right)} \quad (12)$$

$$\Delta \equiv f_2\text{cmc}_2 - f_1\text{cmc}_1$$

$$[S_2]_{mono} = \left(1 - \frac{[S_1]_{mono}}{f_1\text{cmc}_1}\right) f_2\text{cmc}_2 \quad (13)$$

calculate the concentrations of monomeric surfactants at the total surfactant concentrations and stoichiometric mole fractions used in the experiments. The corresponding total concentration of micellar surfactant and mole fraction of surfactant in the micelle required for the kinetic analysis are given by eqns. (14) and (15).

Table 1 Reduced χ^2 statistics for the best fits of Models 1 and 2, with various β, to the kinetic data

	Model	
β	1	2
0	0.003 92	0.004 45
−1.25	0.003 26	0.003 45
−2.5	0.003 03	0.003 13
−3.5	0.003 19	0.003 22

$$[\mathrm{S}]_{\mathrm{mic}} = [\mathrm{S}] - [\mathrm{S}_1]_{\mathrm{mono}} - [\mathrm{S}_2]_{\mathrm{mono}} \tag{14}$$

$$\chi = (a[\mathrm{S}] - [\mathrm{S}_1]_{\mathrm{mono}})/[\mathrm{S}]_{\mathrm{mic}} \tag{15}$$

The kinetic data in Fig. 1 was analysed as follows. Substitution of eqn. (7) into eqn. (5) and equating A with protonated peracid, PH, and B with iodide, I, gives eqn. (16). Values of

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

$[\mathrm{S}]_{\mathrm{mic}}$ and χ_{SDS} for each [S] and a_{SDS} used in the experiments, and for each chosen value of β, are calculated as described above. The apparent molar volume of micellized surfactant in mixed micelles has recently been reported to show ideal behaviour.[13] Hence $\bar{V}_{\mathrm{mic}}$ is calculated according to eqn. (17) with the effective

$$\bar{V}_{\mathrm{mic}} = \chi_{\mathrm{SDS}}\bar{V}_{\mathrm{SDS}} + \chi_{\mathrm{B35}}\bar{V}_{\mathrm{B35}} \tag{17}$$

molar volume of the pure surfactants, $\bar{V}_{\mathrm{SDS}}$ and $\bar{V}_{\mathrm{B35}}$, 0.4 and 5.0 dm^3 mol^{-1} used previously.[2] The latter value is justified in the light of recent work on Brij-35.[14] Empirical expressions for the micellar association constants, eqns. (18)–(20), are

$$K^{\mathrm{TS}}_{\mathrm{mic}} = \exp(a + b\chi_{\mathrm{SDS}} + c\chi^2_{\mathrm{SDS}}) \tag{18}$$

$$K^{\mathrm{PH}}_{\mathrm{mic}} = \exp(d + e\chi_{\mathrm{SDS}} + f\chi^2_{\mathrm{SDS}}) \tag{19}$$

$$K^{\mathrm{I}}_{\mathrm{mic}} = \exp(g + h\chi_{\mathrm{SDS}} + i\chi^2_{\mathrm{SDS}}) \tag{20}$$

substituted into eqn. (16) to give the nine-parameter kinetic equation that is fitted to the experimental data as Model 1. A second expression in which i is set equal to zero gives the eight parameter Model 2. Proportionately weighted non-linear regression was used for the Model fitting. Table 1 shows that the best fit to the data in Fig. 1 is obtained when a value of $\beta = -2.5$ is used. This gives the lowest reduced χ^2 statistic for both Models. The value −2.5 is in agreement with that calculated from cmc$_{12}$ values of mixtures of Brij-35 and SDS.[12] No further attempt was made to optimize the value of β since the best fit values of the parameters a–i were similar for values of $\beta = -1.25$ and −2.5 for both models (results not shown) and the value of $\beta = -2.5$ was used in all subsequent data treatment. The curves calculated from the best fit values of the parameters according to Model 1 are shown in Fig. 1. Indistinguishable curves were obtained when Model 2 was used.

Equating eqns. (18)–(20) with eqn. (6), which accounts for deviations from ideal behaviour of the reactant and transition state micellar association constants, $K^{\mathrm{X}}_{\mathrm{mic}}$, by means of the non-ideality parameter, B^{X}, gives the identities of these parameters in terms of a–i for Models 1 and 2 shown in Table 2. The best-fit values of the logarithms of the micellar association constants and the non-ideality parameters for Model 1 are shown in Table 3. The agreement of ln $K^{\mathrm{XS}}_{\mathrm{SDS}}$ and ln $K^{\mathrm{X}}_{\mathrm{B35}}$ values with previously determined single surfactant association constants[2] is excellent, with the exception of ln $K^{\mathrm{TS}}_{\mathrm{SDS}}$. The present work was carried out in NaOAc–HOAc buffer whilst the previous work was carried out in Na$_2$HPO$_4$–NaH$_2$PO$_4$ in order to vary the pH around the pK_{a} of the peracid.[2] Hence, not only is the inert anion different but the concentration of Na$^+$ required to maintain a constant ionic strength is also different. These differences do not affect k_{w}, the rate constant in the absence of surfactant, but are likely to modulate the interaction of the negatively charged activated complex with the anionic SDS. The value of the micellar association constant of iodide in SDS would be expected to be similarly modulated but the value of ln $K^{\mathrm{I}}_{\mathrm{SDS}}$ is too low to be determined with any degree of precision. It is worthy of note that regression analysis using Model 1 yielded a value of the non-ideality parameter, B^{I}, with reasonably good precision despite the large standard deviation of ln $K^{\mathrm{I}}_{\mathrm{SDS}}$. Because of this, Model 2 was considered. In Model 2, i is set equal to zero; this is not an assumption of ideal behaviour for iodide, but rather that ln $K^{\mathrm{I}}_{\mathrm{SDS}}$ is indeterminably small, and instead there is a slope term S^{I}. The identity of h is S^{I}, the variation, assumed linear, of the micellar association constant of iodide with mole fraction of SDS [see eqn. (20) with $i = 0$] at low values of the mole fraction of SDS. Table 4 shows that all of the best-fit parameters of the transition-state and peracid, and the association constant of iodide in Brij-35, are virtually the same for Model 2 as for Model 1 (Table 3). This demonstrates the robustness of the present approach to modelling kinetics in mixed surfactant systems. The situation is illustrated in Fig. 2 which shows the calculated values of the micellar association constants of the transition-state, peracid and iodide as a function of the mole fraction of SDS in the micelle. The transition-state and peracid values are from Model 1 though Model 2 gives essentially similar values. The filled regions show the standard deviation intervals of ln $K^{\mathrm{I}}_{\mathrm{mic}}$ due to the standard deviation ranges of ln $K^{\mathrm{I}}_{\mathrm{SDS}}$ in Model 1 and S^{I} in Model 2. The best fit values of S^{I} and ln $K^{\mathrm{I}}_{\mathrm{B35}}$ from Model 2 when used to extrapolate to unit mole fraction of SDS, give a lower limit of ln $K^{\mathrm{I}}_{\mathrm{SDS}}$ of −1.0 ± 0.7, which is in the lower range of the same quantity from Model 1.

Table 2 Identity of regression parameters a–i in eqns. (18)–(20) with micellar association constants and non-ideality parameters of transition-state, peracid and iodide defined in eqn. (6)

X	ln $K^{\mathrm{X}}_{\mathrm{B35}}$	ln $K^{\mathrm{X}}_{\mathrm{SDS}}$	B^{X} or $S^{\mathrm{I}\,b}$
TS	a	$a + b + c$	$-c$
PH	d	$d + e + f$	$-f$
I	g	$(g + h + i)^a$	$-i^a$ or h^b

^{a} Model 1. ^{b} Model 2, S^{I} is a slope term.

Table 3 Model 1 best-fit values ± standard deviation of micellar association constants and non-ideality parameters for transition-state, peracid and iodide with $\beta = -2.5$. Values in parentheses are single surfactant values from ref. 2, where the kinetics were carried out in phosphate buffers

X	ln $K^{\mathrm{X}}_{\mathrm{B35}}$	ln $K^{\mathrm{X}}_{\mathrm{SDS}}$	B^{X}
TS	6.70 ± 0.12 (6.36)	2.5 ± 0.6 (1.0)	−5.4 ± 0.5
PH	5.31 ± 0.19 (5.18)	4.6 ± 0.6 (4.6)	−0.9 ± 0.3
I	2.14 ± 0.22 (2.15)	1.1 ± 2.2 ($\leqslant 0$)^a	−3.9 ± 1.4

^{a} In ref. 2 it was necessary to assume $|(K^{\mathrm{I}}_{\mathrm{SDS}} - \bar{V}_{\mathrm{mic}})|[\mathrm{S}]_{\mathrm{mic}} \ll 1$ in order to prevent over-definition of the model.

Discussion

Only a few quantitative studies of kinetics of reactions in mixed micelles have been carried out. These are considered in terms of pseudophase models.[15–18] Bunton and co-workers have treated the nucleophilic attack of bromide on micelle-bound sulfonate ester in mixed cetyltrimethylammonium bromide/non-ionic micelles using the pseudophase ion exchange model.[15] Addition of non-ionic surfactant to the cationic micelles inhibits the

Table 4 Model 2 best-fit values ± standard deviation of micellar association constants and non-ideality parameters or S^I for transition-state, peracid and iodide with $\beta = -2.5$

X	ln K^X_{B35}	ln K^X_{SDS}	B^X or S^I
TS	6.86 ± 0.12	1.9 ± 0.6	−4.4 ± 0.4
PH	5.59 ± 0.12	4.6 ± 0.5	−1.3 ± 0.2
I	1.76 ± 0.18	NA[a]	−2.8 ± 0.7[b]

[a] Not applicable to Model 2. [b] S^I.

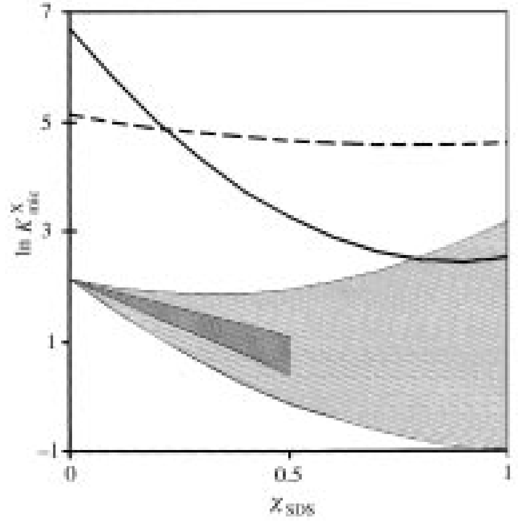

Fig. 2 Calculated values of micellar stability constant of the transition state, filled line, peracid, broken line and iodide, filled regions calculated from the best-fit values of the parameters, except ln K^I_{SDS}, from Model 1 shown in Table 3. The horizontally filled region uses the standard deviation range of ln K^I_{SDS} shown in Table 3 for Model 1. The vertically filled region uses the standard deviation range of the slope term, S^I shown in Table 4 for Model 2.

reaction and an important factor is the reduction of the concentration of Br^- at the micellar surface due to an increase in the fractional micellar ionisation as the charge density at the surface is reduced by the non-ionic surfactant.[15] The hydrolysis of acetals in SDS/sodium decyl hydrogenphosphate mixed micelles was carried out at a high total surfactant concentration where correction for the mole fraction in the micelle is probably unnecessary. A study of the alkaline hydrolysis of chloropentaminecobalt(III) in mixed anionic/non-ionic micelles takes into account the difference in the mole fraction of surfactant in the micelle and the stoichiometric mole fraction.[18] In this study association constants of the cobalt complex are calculated at each mole fraction. This falls short of the present approach where the logarithms of association constants are obtained for the pure surfactants and deviations from ideality in surfactant mixtures are considered using B according to eqn. (6).

The comparability of the results of the data analysis using Models 1 and 2 shows the robustness of the approach. Because of the low affinity of the iodide anion for the negatively charged SDS micelle it is not possible to get a precise estimate of the micellar association constant, K^I_{SDS} using Model 1, see Fig. 2. Nevertheless, using Model 2 it is possible to get a consistent lower limit for this quantity. This leads us to contend that the non-ideality parameter for iodide, B^I, from Model 1 is a valid quantity. Even if this contention is wrong this does not affect the remainder of the results of the analysis. In the course of the analysis we use a value of the effective molar volume of micellized Brij-35 surfactant, $\bar{V}_{B35}$, 5 $dm^3\ mol^{-1}$, to maintain consistency with our previous work in single surfactant systems.[2] Since then, values of the hydrodynamic radius and aggregation number of Brij-35 micelles of 4.4 nm and 40 have been obtained from optical probe studies.[14] A hydrodynamic volume of 5.4 $dm^3\ mol^{-1}$ of micellized surfactant follows, to which our original estimate is sufficiently close. The hydrodynamic volume includes water entrained by the micelle but not water flowing past the outer parts of the polyoxyethylene chain. The effective hydrodynamic volume is considerably larger than the partial molar quantity, 1.18 $dm^3\ mol^{-1}$ determined from density measurements.[19] At present we choose to use the hydrodynamic volume for $\bar{V}_{mic}$. Inspection of eqn. (16) shows that the choice of $\bar{V}_{mic}$ will affect the analysis only if the quantity is significant compared to K_{mic}. This is the case for K^I_{B35}, 8.5 $dm^3\ mol^{-1}$ calculated from the logarithmic quantity in Table 3. Were a value of $\bar{V}_{B35}$, 1.2 $dm^3\ mol^{-1}$, taken instead of 5 $dm^3\ mol^{-1}$ then K^I_{B35} would be 8.5 minus 5 plus 1.2. Because of the ideal behaviour of the effective molar volume of the mixed micelles described by eqn. (17) the choice of $\bar{V}_{B35}$ will have negligable effect on B values.

The interaction parameter for the mixing of two surfactants in micelles, β, was originally considered in terms of the regular solution approximation.[9] It is considered valid to use β as a single parameter to account for all factors contributing to non-ideality, including charge effects in ionic surfactants.[10,11] A negative β value indicates an attractive force between the different types of surfactant in the mixed micelle. Treiner has introduced a parameter B to account for deviations from ideal behaviour in the partitioning of uncharged solutes between mixed micelles and the aqueous bulk phase[4] [see eqn. (6)]. The present work extends the use of B to charged reactant solutes and transition states. In this approach charge effects are implicit in the non-ideality parameter, B, in the same way as they are in β. Treiner has demonstrated the relationship between B and β for neutral solutes shown in eqn. (21). This predicts a value of B

$$B = 0.194 + 0.343\beta \qquad (21)$$

for any neutral solute, such as *m*-chloroperbenzoic acid, of −0.66 in Brij-35/SDS mixtures, where β is −2.5. This prediction is in agreement with the value −0.9 ± 0.3 obtained for the peracid using Model 1. The correlation shown in eqn. (21) can be interpreted as follows. If a solute has a certain affinity for micelles of surfactant 1 and adding surfactant 2 lowers that affinity, then surfactant 2 must be competing for a region of the micelle of surfactant 1 occupied by the solute. So, if surfactant 2 is negatively charged SDS and the solute is negatively charged, there will be an additional repulsive force compared with a neutral solute and B would be expected to be more negative. This is indeed seen for the non-ideality parameters for iodide and the negatively charged transition state shown in Table 3.

The effect of single surfactant micelles of SDS or poly(oxyethylene)-containing Brij-35 on the reaction of peracids and iodide has been discussed previously in terms of the factors stabilizing the reactants and transition states.[2] In the present mixed surfactant system the switch from micellar catalysis to inhibition at a stoichiometric mole fraction of SDS of 0.2 shown in Fig. 1 is reflected in the crossover point of the logarithms of the values of the micellar association constants of the transition state and peracid shown in Fig. 2, calculated from the best-fit parameters. Thus, if the micelles stabilise the transition state more than the peracid then catalysis is observed, otherwise inhibition is observed. The present work suggests that given the micellar association constants of reactants and transition state in single surfactant systems then these quantities can be predicted for the mixed surfactant systems from B which can be estimated using eqn. (21) for neutral species, or from a similar linear Gibbs function relationship for charged species, and a value of β that is easily calculated[11] from a measured mixed cmc.

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