Quantitative treatment of micellar effects upon nucleophilic substitution

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Cationic micelles of cetyltrimethylammonium† surfactants [CTA(X), X = Cl, Br, OMs] increase first-order rate constants for the basic hydrolysis of *tert*-butyl perbenzoate and 2-naphthyl benzoate. Dealkylation of both butyl 4-nitrobenzenesulfonate and butyl 4-bromobenzenesulfonate by halide ions in micelles of CTACl, CTABr and CTAOMs, and by azide ion in micelles of cetyltrimethylammonium mesylate (CTAOMs) have been examined. The nucleophilic aromatic substitutions of 2-chloro-3,5-dinitropyridine by OH^- and N_3^- ions in the presence of CTABr, CTACl and CTAOMs micelles have also been examined. The rate enhancements have been treated in terms of concentration of both substrates and nucleophilic anions at the micellar surface. The anionic concentrations depend upon specific and non-specific coulombic interactions, which were calculated by solving the Poisson–Boltzmann equation (PBE). The same parameters were used in fitting data for reactions of N_3^-, Br^- or Cl^- as nucleophiles and for systems with Cl^-, Br^- and OMs^- as inert counter-anions in CTACl, CTABr and CTAOMs, respectively.

Chemical reactivity in ionic colloidal self-assemblies, *e.g.* micelles,[1–5] microemulsion droplets[2] and vesicles,[1] is generally treated in terms of pseudo-phase models with micelles and water regarded as distinct reaction regions. Increased reactant concentrations at the surfaces of the micelles are of major importance. The distribution of substrate between aqueous and micellar pseudophases is generally written in terms of a Michaelis–Menten-type equation.[1–5] For the distribution of ionic reagents coulombic attraction is important, but specific and non-coulombic forces must also be considered because polarizable counter-ions have strong affinities for cationic micelles. For example, Br^- displaces less polarizable hydrophilic anions such as OH^- from the micellar surface.[2,3,5,6] Therefore, ion binding cannot be explained solely in terms of electrostatic potentials of micellar surfaces.

The ion-exchange model is described by eqn. (1) for micellar

$$X_M^- + Y_W^- \rightleftharpoons X_W^- + Y_M^- \qquad (1)$$

binding of a nucleophile, X^-, to a cationic micelle having Y^- as an inert counter-ion: the subscripts M and W denote the micellar and aqueous pseudo-phases, respectively. The ion-exchange constant K_Y^X is given by eqn. (2)[3,5,6] in which

$$K_Y^X = [X_W^-][Y_M^-]/[X_M^-][Y_W^-] \qquad (2)$$

concentrations are written in terms of total solution volume so that if the micellar fractional ionization, α, is assumed to be constant, the concentration of reactive ion of the micellar surface can be calculated.[3,5b,6] This treatment has been used to fit many sets of kinetic data, but it has some limitations.[3,4b–6] A way around these limitations is to write counter-ion binding in terms of a surface potential,[7,8] but this treatment also has limitations.

The aim of the present work is to apply a model that accounts for both coulombic and specific interactions of ions with aqueous ionic micelles for a variety of bimolecular reactions.[9] The Poisson–Boltzmann equation (PBE) has been used to calculate the surface electrical potential of ionic micelles by solving the PBE in spherical symmetry with the inclusion of specific, non-coulombic binding terms.

The treatment applied here depends upon several approximations. (*i*) Micelles are assumed to be smooth uniform spheres.[2,3] (*ii*) Ions are assumed to be point charges.[10] (*iii*) All reactions are assumed to take place in the Stern layer which is assumed to have uniform thickness.[3,5b,6]

In the present work the reactive ions are the hydroxide ion with substrates **1**, **2** and **4**, the azide ion with substrates **3** and **4** and chloride and bromide ions with substrate **3**. The inert ions are chloride and bromide ions with substrate **1**, **2** and **4**, and mesylate ions with all substrates (Scheme 1).

Results

The solution is considered to be made up of electrically uniform cells of radius, R, each containing one micelle with aggregation number, N, and radius, α. The distribution of co- and counter-ions around an ionic micelle is calculated by solving the PBE in spherical symmetry[9] in which R is given by eqn. (3) where

$$\frac{4}{3}\pi R^3 = 1000N/\{N_A([D_T] - \text{cmc})\} \qquad (3)$$

N_A is Avogadro's number, $[D_T]$ is the total surfactant concentration and cmc is the concentration of the monomeric surfacant. The PBE, written in spherical symmetry for a solution containing univalent cations and various charged anions, gives the reduced potential [eqn. (4)] where ψ is

$$\varphi = e\psi/KT \qquad (4)$$

the electrostatic potential and e is the electrostatic charge. The variation of reduced potential with distance r is given by eqn. (5)

$$\frac{1}{r^2}\frac{d(r^2 d\varphi/dr)}{dr} = \frac{-4\pi e^2}{\varepsilon KT}\Sigma_i Z_i n_i^R \exp(-Z_i\varphi) \qquad (5)$$

where ε is the relative permittivity,‡ T is the absolute temperature, K is the Boltzmann constant, Z_i is the ionic valency and n_i^R is the number concentration (ions cm^{-3}) at the

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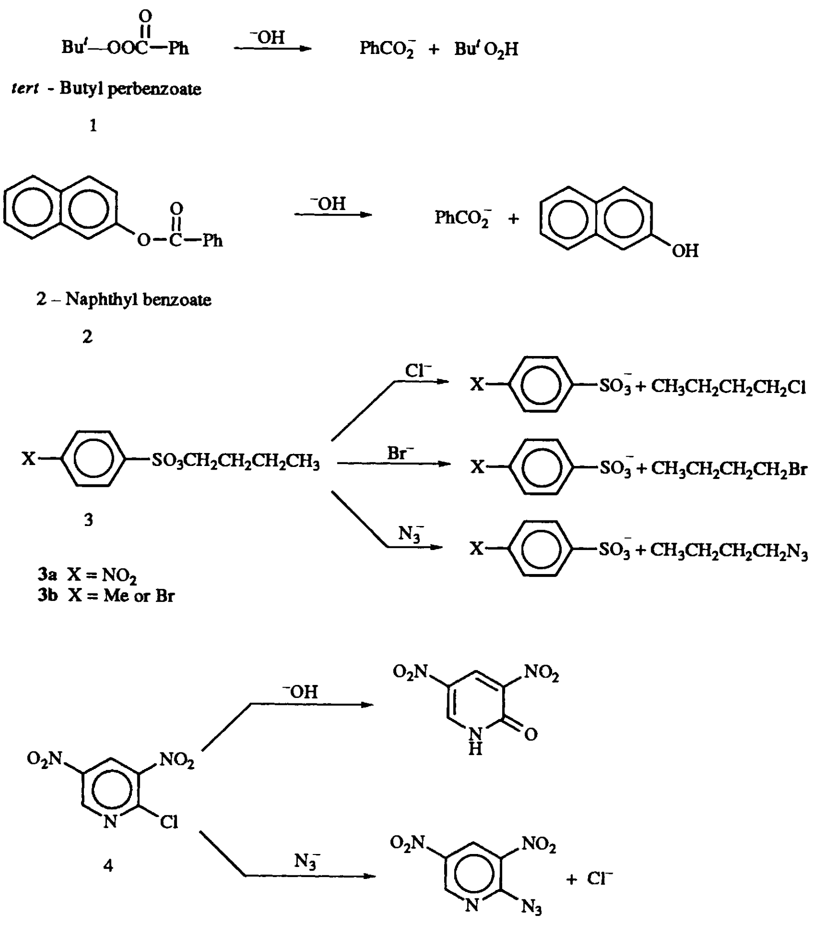
† Cetyl = hexadecyl.

‡ The relative permittivity of water is 78.5 at 25 °C and this value was used throughout.



Scheme 1

cell wall. It is assumed that ions may bind non-coulombically at the micellar surfaces, with partial coverage, *f*, which will reduce the charge density at the micellar surface. The boundary conditions are (*i*) at the cell wall [eqn. (6)] and (*ii*) at the micellar surface [eqn. (7)].

$$\varphi = d\varphi/dr = 0 \text{ at } r = R \qquad (6)$$

$$d\varphi/dr = (1-f)Ne^2/(\varepsilon a^2 KT) \text{ at } r = a \qquad (7)$$

Average concentrations $\bar{n}$ and those at the cell wall are related by

$$n_i^R = \frac{\bar{n}_i V}{\int_a^R \exp(-Z_i\varphi)4\pi r^2 dr} \qquad (8)$$

with

$$V = 4\pi(R^3 - a^3)/3 \qquad (9)$$

Applying charge conservation within the cell gives eqn. (10).

$$V\Sigma\bar{n}_i^- = V\bar{n}^+ + (1-f)N \qquad (10)$$

We assume that *f* is independent of ψ and depends only upon the nature and concentration of counter-ions, and we estimated it using either a Langmuir or a Volmer isotherm [eqn. (11)].[7a]

$$f = \frac{\delta \exp - [-f/(1-f)][X_W^-]}{1 + \delta \exp[-f/(1-f)][X_W^-]} \qquad (11)$$

Here X_W^- is the counter-ion in the aqueous part of the cell and δ is the Volmer specificity constant. Eqn. (11) reduces to the Langmuir form $f \rightarrow 0$ and for two specifically binding anions *e.g.* Cl$^-$ and NO$_3^-$ [eqns. (12) and (13)], where δ^L is the appropriate Langmuir constant, which in dilute electrolyte will be half the Volmer constant, δ [eqn. (11)].

$$f = \frac{\delta^L_{Cl}[Cl_W^-] + \delta^L_{NO_3}[NO_{3W}^-]}{1 + \delta^L_{Cl}[Cl_W^-] + \delta^L_{NO_3}[NO_{3W}^-]} \qquad (12)$$

$$f_{Cl}/f_{NO_3} = \delta^L_{Cl}[Cl_W^-]/\delta^L_{NO_3}[NO_{3W}^-] \qquad (13)$$

It has been found that for a mixture of nucleophilic ions and inert halide ions the Volmer isotherm [eqn. (11)] gives the best fit for Br$^-$ solutions, but with Cl$^-$ either of the Volmer and Langmuir isotherms is adequate.[11] Because of the arithmetical simplicity of the Langmuir isotherm we use this form when the solution contains a mixture of specifically binding counter-ions.

Application of the model

It is well known that ionic or polar reagents bind close to micellar surfaces and react in that region.[3] Regardless of the nature or concentration of the reactants, and for the purpose of calculation we assume that the reaction region is a uniform shell of $\Delta = 2.5$ Å thickness.[9] Thus,

$$k_{obs} = \frac{k_W[Y_W^-] + k_2^m K_s([D_T] - \text{cmc})[Y^-]2.5\ \text{Å}}{1 + K_s([D_T] - \text{cnc})} \qquad (14)$$

where k_W and k_2^m are second-order rate constants (dm^3 mol^{-1} s^{-1}) in water and in the micellar shell, respectively, K_s is the substrate binding constant and Y$^-$ is the nucleophile. Eqn. (14) is similar to those of the pseudo-phase model of micellar rate effect,[3] and it involves the same assumptions.[3,12]

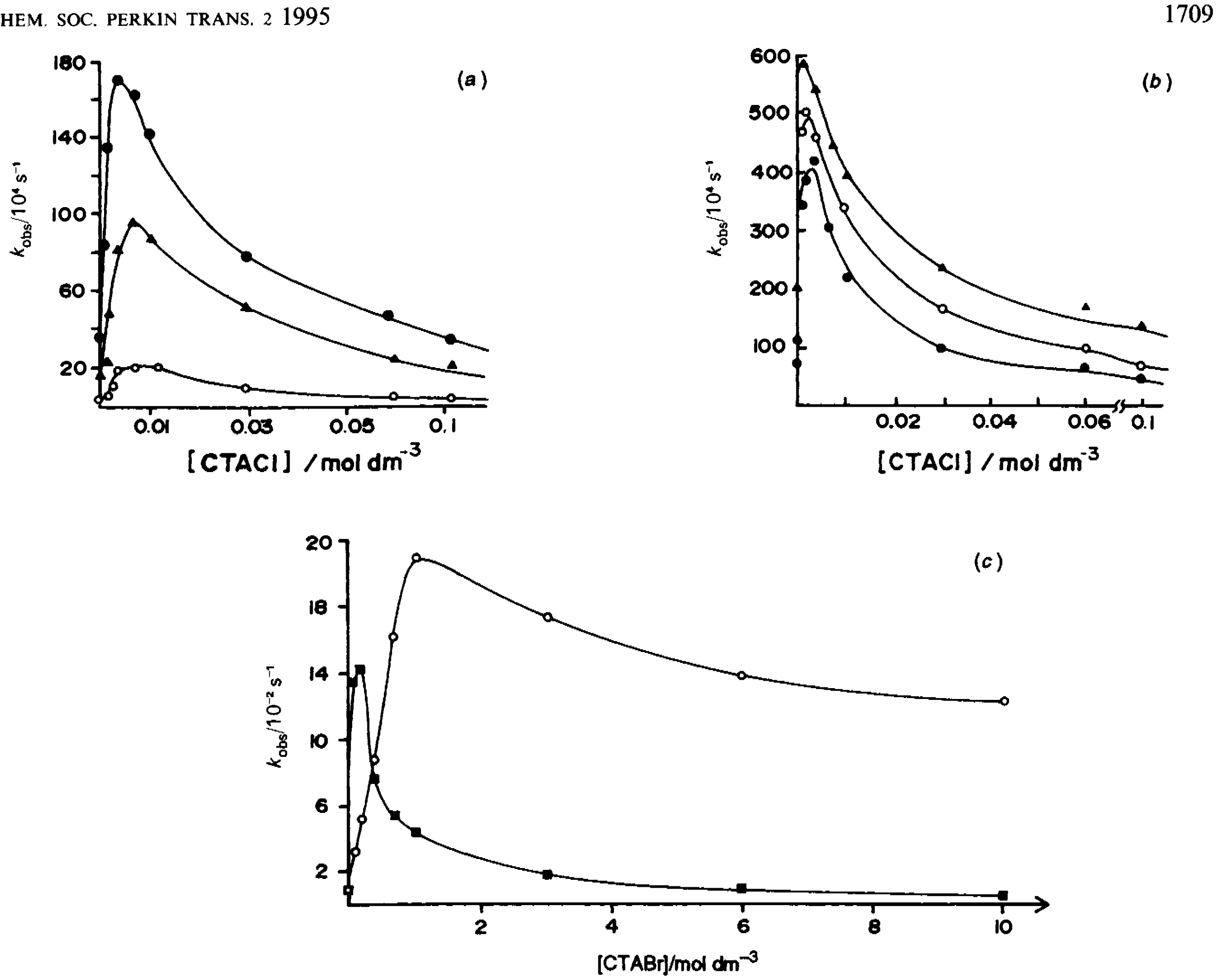


Fig. 1 Predicted variations of k_{obs} with (*a*) [CATCl] for the reaction of *tert*-butyl perbenzoate with (○) 10^{-3} (▲) 5 × 10^{-3} and (●) 10^{-2} mol dm^{-3} NaOH; (*b*) [CATCl] for the reaction of 2-naphthyl benzoate with (●) 10^{-2} (○) 2 × 10^{-2} and (▲) 3 × 10^{-2} mol dm^{-3} NaOH; (*c*) [CATBr] for the reactions of 2-chloro-3,5-dinitropyridine with (■) 10^{-3} and (○) 10^{-4} mol dm^{-3} NaOH

The present model differs from the pseudo-phase model in several aspects. For example, (*i*) it does not assume that fractional ionization α, or ion-exchange parameters are constant[3,5b,6] and (*ii*) the volume of the reactive shell increases with increasing radius, a, whereas it is usually assumed to be constant in the pseudo-phase model.[3,4b,5b,13a]

To fit our data we assume that a is constant and that N is independent of [surfactant], but may increase with added electrolyte. These assumptions are suspect in CTABr because CTABr micelles grow, especially with added Br^-.[13b,14] Micellar growth seems to be much less with CTACl and CTAOMs.[6c,15a] The binding constant K_s is assumed to be independent of surfactant or electrolyte concentration, although electrolytes may 'salt out' the substrate from water into the micelles.[17,18] The substrates discussed here are so hydrophobic that they should be fully micellar bound except in very dilute surfactant.

Discussion

Reactions of hydroxide ion

Reactions of nucleophilic anions such as OH^- with non-ionic substrate are slower in CTABr than in CTACl and Br^- is a better inhibitor than Cl^-: also, both ions displace OH^- from micelles.[5a,17,18] Therefore values of δ [eqn. (11)] should decrease in the sequence $Br^- \geq Cl^- \geq OH^-$, and it is assumed that OH^- does not interact specifically with cationic micelles,[9a] so that $\delta_{OH} = 0$.

We applied this PBE treatment to reactions of OH^- with *tert*-butyl perbenzoate, 2-naphthyl benzoate and 2-chloro-3,5-dinitropyridine. Fig. 1 illustrates the variation of the observed and calculated values of the pseudo-first-order rate constant, k_{obs}, for the reactions of *tert*-butyl perbenzoate and 2-naphthyl benzoate with OH^- in CTACl based on the parameters given in Table 1. Equally good fits were obtained for reactions of OH^- with 2-chloro-3,5-dinitropyridine in CTABr (Table 1). Our values for a and N are similar to the literature values.[8a,15b,19] The fits are only slightly affected by doubling the value of δ. In fitting the data we assume values of cmc lower than those in water,[12] because added electrolytes and hydrophobic solutes reduce the cmc. A problem with the pseudo-phase and the PBE models is that both of them neglect the existence of submicellar aggregates in very dilute surfactant and neither deals with the extent to which a hydrophobic substrate may perturb the aggregation. Thus both models are unsatisfactory with very dilute surfactant. The difference between values of δ for CTACl and CTABr (Table 1) is consistent with the known relative affinities of ions towards cationic micelles.[4b,20]

Reactions of halide ions

Variations of k_{obs} with [surfactant] or [salt][6,21,22] fit the PBE model reasonably well for reactions of Cl^- or Br^- with butyl 4-bromobenzenesulfonate and butyl 4-nitrobenzenesulfonate in CTACl, CTABr and CTAOMs (Fig. 2 and Table 2). The reaction of alkyl benzenesulfonates with water is inhibited by cationic micelles; thus it should make only a minor contribution under our reaction conditions.[6b,21,22]

Table 1 Parameters that best fit the kinetic results for the reactions of *tert*-butyl perbenzoate, 2-naphthyl benzoate and 2-chloro-3,5-dinitropyridine with hydroxide ion in CTACl

Substrate	[OH$^-$]/ mol dm^{-3}	Cmc/10^{-4} mol dm^{-3}	N	δ	k_w/dm^3 mol^{-1} s^{-1}	k_2^m/dm^3 mol^{-1} s^{-1}	K_s/dm^3 mol^{-1}
tert-Butyl perbenzoate	0.001	10	78	17	0.36	0.016	750
	0.005	8	78	17	0.36	0.016	800
	0.01	6	90	17	0.36	0.016	800
2-Naphthyl benzoate	0.01	6	88	18	0.65	0.018	2100
	0.02	4	90	18	0.65	0.018	2100
	0.03	4	89	18	0.65	0.018	2100
2-Chloro-3,5-dinitropyridine	0.001	10	85	16	0.039	0.0196	600
	0.0001	12	89	17	0.006	0.0252	600

[a] At 25.0 °C with a = 22 Å.

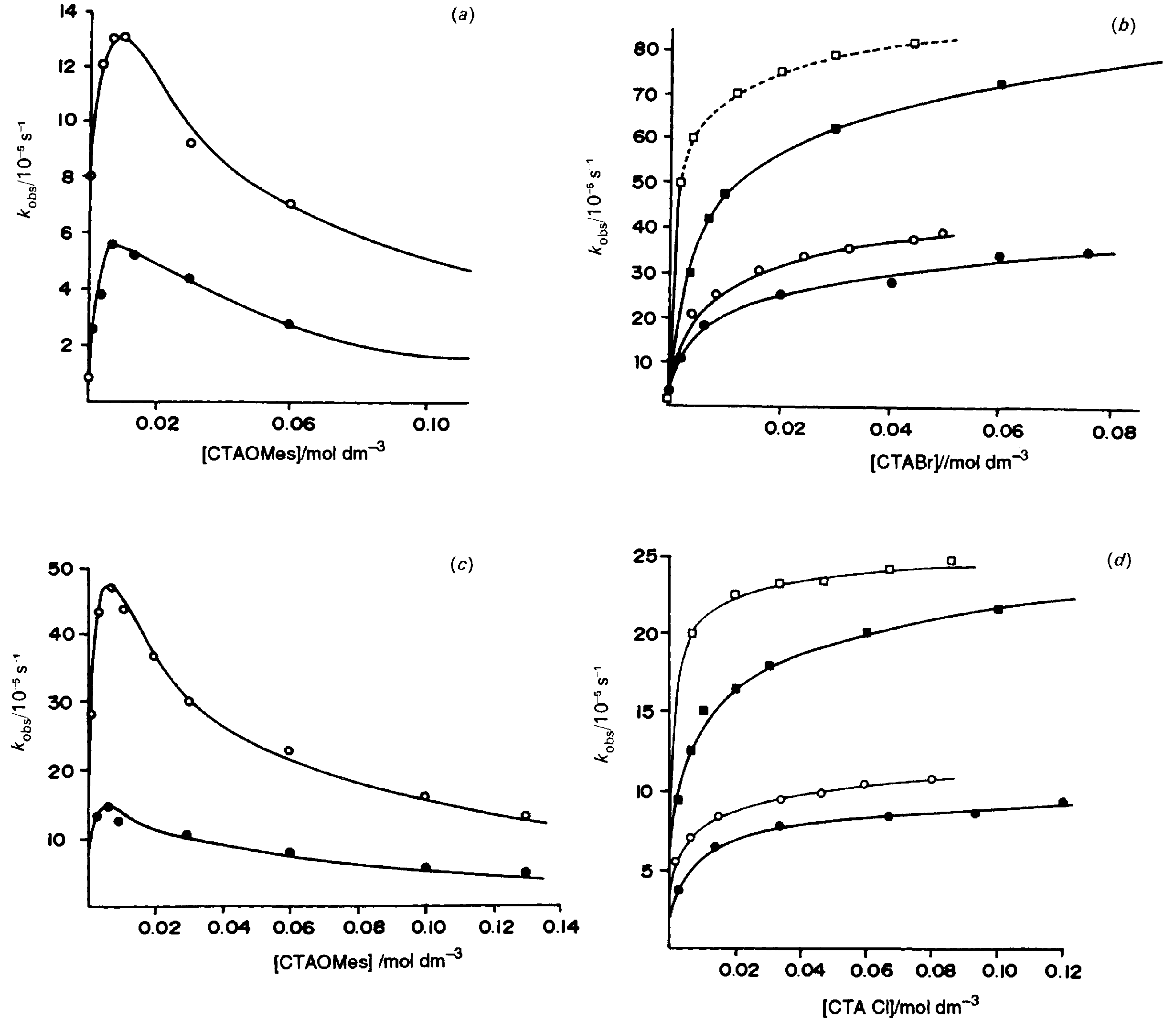


Fig. 2 Predicted variations of k_{obs} with (*a*) [CTAOMes] for the reactions of 0.02 mol dm^{-3} NaCl with **3a** (○) and **3b** (●); (*b*) [CTABr] for the reactions of **3a** (■) and **3b** (●) in CTABr and **3a** with 0.1 mol dm^{-3} NaBr and CTAOBr (□) and **3b** with 0.1 mol dm^{-3} NaBr in CTAOBr (○); (*c*) for the reactions of 0.02 mol dm^{-3} NaBr with **3a** (○) and **3b** (●); (*d*) [CTACl] for the reactions of **3a** (■) and **3b** (●) in CTACl and **3a** with 0.1 mol dm^{-3} NaCl (□) and **3b** with 0.08 mol dm^{-3} NaCl (○) in CTAOBr

However, the observed and predicted rate–[surfactant] profiles for reactions of the halide ions agree reasonably well (Fig. 2) despite changes in micellar structure with changes in concentration of Br$^-$ or Cl$^-$. For reactions in CTAOMs, micellar structure probably alters with changes in relative concentrations of the Br$^-$ ion.

Reactions of azide ion

Theoretical and experimental rate–[surfactant] profiles for the reactions of N$_3^-$ with substituted alkyl benzenesulfonate in CTAOMs and 2-chloro-3,5-dinitropyridine in CTACl and CTABr fit the PBE reasonably well (Fig. 3 and Table 2) assuming that OMs$^-$ does not bind specifically to CTA$^+$

Table 2 Parameters that best fit the kinetic results for the reactions of alkyl arenesulfonate and 2-chloro-3,5-dinitropyridine with halide and azide ions in the presence of cationic micelles

Substrate	Surfactant	Nucleophile	Cmc/10^{-3} mol dm^{-3}	K_s/dm^3 mol^{-1}	$k_2^m/10^{-5}$ dm^3 mol^{-1} s^{-1}	k_2^m/k_w
Butyl 4-methylbenzenesulfonate	CTACl	Cl^-	1.2	120	1.45	0.6
	CTACl + 0.1 mol dm^{-3} NaCl	Cl^-	0.9	130	1.56	0.66
	CTABr	Br^-	0.8	120	5.0	1.6
	CTABr + 0.1 mol dm^{-3} NaBr	Br^-	0.6	120	5.0	1.6
	CTAOMs + 0.02 mol dm^{-3} NaCl	Cl^-	1.1	120	0.88	0.37
	CTAOMs + 0.02 mol dm^{-3} NaBr	Br^-	1.1	120	2.5	0.66
Butyl 4-nitrobenzenesulfonate	CTACl	Cl^-	1.2	120	4.0	0.3
	CTACl + 0.1 mol dm^{-3} NaCl	Br^-	0.9	130	3.9	0.3
	CTABr	Br^-	0.8	120	11.4	0.37
	CTABr + 0.1 mol dm^{-3} NaBr	Cl^-	0.6	120	13.2	0.43
	CTAOMs + 0.02 mol dm^{-3} NaCl	Br^-	1.1	120	2.3	0.66
	CTAOMs + 0.02 mol dm^{-3} NaBr	Br^-	1.1	120	21	0.23
	CTAOMs	N_3^-	1.1	115	34	0.085
	CTAN$_3$	N_3^-	1.1	115	150	0.375
2-Chloro-3,5-dinitropyridine	CTACl	N_3^-	1.2	8.5	550	0.011
	CTABr	N_3^-	0.8	70	550	0.011
	CTAN$_3$	N_3^-	1.1	85	400	0.008

[a] At 25.0 °C with the values of k_w for the reactions of the 4-methyl and 4-nitro derivatives with Br^- and Cl^- ions are 3.7×10^{-5} and 3.3×10^{-5} dm^3 mol^{-1} s^{-1} and 1.26×10^{-4} and 3.0×10^{-3} dm^3 mol^{-1} s^{-1}, respectively. k_w for the reactions of azide ion with the 4-nitro derivative and with 2-chloro-3,5-dinitropyridine are 4×10^{-3} and 0.5 dm^3 mol^{-1} s^{-1}, respectively. [b] The values of a and N which were used are 22 Å and 95 Å and δ Br = 120, δ Cl = 15, δ OMs = 20.

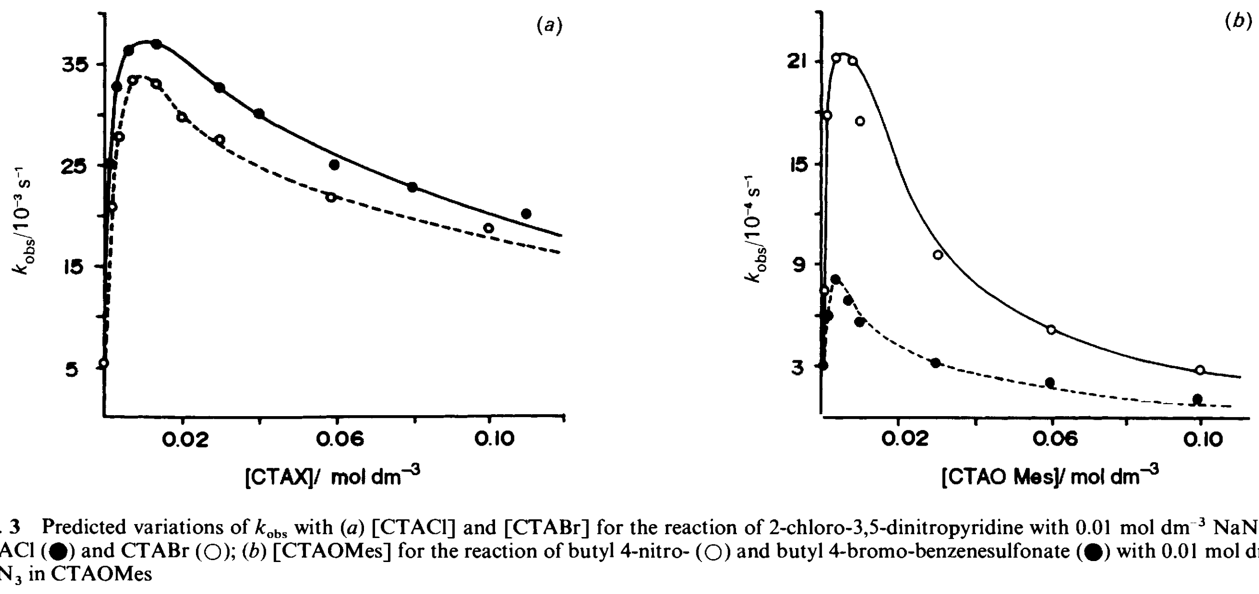


Fig. 3 Predicted variations of k_{obs} with (a) [CTACl] and [CTABr] for the reaction of 2-chloro-3,5-dinitropyridine with 0.01 mol dm^{-3} NaN$_3$ in CTACl (●) and CTABr (○); (b) [CTAOMes] for the reaction of butyl 4-nitro- (○) and butyl 4-bromo-benzenesulfonate (●) with 0.01 mol dm^{-3} NaN$_3$ in CTAOMes

micelles. This assumption is consistent with evidence that Br^- binds more strongly than OMs^- to cationic micelles.[24,25a] However, these data have been fitted using the ion-exchange model [eqn. (2)], for the reaction run in the presence of CTAOMs, CTACl and CTABr.[16]

Rate constants in aqueous and micellar pseudo-phases

Comparison of values of k_2^m and k_W shows that the concentration of reactive ions at the micellar surface (Tables 1 and 2) is a major source of micellar rate enhancements of bimolecular reactions of hydrophilic nucleophiles. This conclusion is supported by evidence based on direct measurements of nucleophile concentrations and by the application of the ion-exchange model. Furthermore, it applies also to bimolecular reactions of hydrophobic reagents where their concentrations at the micellar surface can be measured directly.[3,4]

Our values of k_2^m predicted by the PBE model are similar to those predicted by the ion-exchange model or estimated from reactions in reactive counter-ion micelles i.e. in the absence of inert counter-ions[4,6,21] (Tables 1 and 2). The ion-exchange model [eqn. (2)] provides a simple and convenient method of treating ionic reactions in micelles despite its empirical nature. However, k_2^m is usually calculated by eqn. (15) where V_M is

$$k_2^m = V_M k_M \qquad (15)$$

the molar volume of the reactive region at the micelle surface, ranges from 0.14 to 0.35 dm^3 [3,4b,21a] and k_M is the second-order rate constant expressed in reciprocal seconds (the concentration is written as a mole ratio). To treat the problem by solving PBE, we assume that the reaction took place in a region surrounding the micelles 2.5 Å thick, and that the substrate is distributed uniformly in this region. The volume of this reactive shell depends upon the micellar radius, *a*, rather than upon the total amount of micellized surfactant, as in the ion-exchange model.[3,4,16–18] All these assumptions have their limitations because the thickness of the reaction region or V_M may depend on the nature of the reaction and because many organic substrates are larger than the 2.5 Å which we assumed to be the thickness of the reaction region.[3,13a] Values of k_2^m/k_W for a given reaction do not depend markedly upon the nature or concentration of the inert counter ion or upon limited changes in the concentration of ionic reagent.

However in hydroxylic solvent, Br^- is a better nucleophile than Cl^- because hydrogen bonding reduces the nucleophilicity of anions and the effect is greatest with small hydrophilic anions of high charge density.[24,25] The values of k_2^m/k_W for the reaction of substituted alkyl benzenesulfonate do not depend upon the hydrophobicity or arenesulfonate, but appear to depend upon the hydrophilicity or polarizability of the nucleophile *i.e.* they follow the sequence $N_3^- \geq Br^- \geq Cl^-$.

Water is more polar than micellar surfaces.[20] Thus values of k_2^m/k_W for different anionic nucleophiles, should be affected by the polarity of the micellar surface and these values (Table 2) are not related in any obvious way to estimated polarities of micellar surfaces.[25b] However bulk solvent parameters may not be applicable to submicroscopic micellar surfaces.

The different relative values of k_2^m/k_W (Table 2), may simply reflect the fact that the micellar surface does not provide a uniform reaction medium so that hydrophilic anions such as OH^- may be located more in the aqueous region of the micellar surface than Br^- and therefore be further from the micellar bound substrate. Micellar surfaces are water-rich,[25c] therefore the head groups and associated ions are believed to be fully hydrated [3] and any beneficial effects of dehydration should be most important for hydrophilic anions such as OH^-, which is most strongly deactivated by protic solvents.

Comparison of PBE with the ion-exchange model

The ion-exchange model is essentially an empirical description of interionic competition for an ionic micelle, but it gives values of k_2^m which are similar to those calculated by solving the PBE with inclusion of a specific adsorption term for the halide ion. The agreement between these two models depends upon the choice of the volume element of the reaction or the thickness of the reactive shell. Most workers have assumed that the volume element of the reaction is independent of the nature of the reactant, just as we assume that the reaction occurs in a 2.5 Å shell.§,[9a,26a] However doubts have been expressed about this assumption [13a] and variations of k_2^m/k_W (Table 2) may simply be due to dependence of the volume element of the reaction upon the reactants. But the simplicity of the ion-exchange model makes it a convenient way to rationalize rate–surfactant profiles.

The major difference between PBE and the ion-exchange model is that the PBE model describes interionic competition as a combination of coulombic and specific interactions so that a simple equilibrium equation, such as eqn. (1), should be useful only over a limited concentration range. There is some kinetic and other evidence showing that ion-exchange parameters may depend upon the method of estimation and ionic concentration.[4b,20,23] Thus recent experiments show the failure of the ion-exchange model at high $[H_3O^+]$ or $[OH^-]$.[26,27]

Experimental

Materials

The preparation and purification of reagent, substrate and surfactant followed standard methods.[16,23,28] Reactions were followed spectroscopically in distilled, deionized, CO_2-free water using a Perkin-Elmer model 330 UV–VIS spectrophotometer. 2-Chloro-3,5-dinitropyridine was reagent grade from Aldrich.

Kinetics

Rate measurements of alkaline hydrolysis of *tert*-butyl perbenzoate, 2-naphthyl benzoate and nucleophilic substitutions by halide and azide ions have been described.[6c,16,21,22,28a] The reaction of hydroxide ion with 2-chloro-3,5-dinitropyridine was followed spectrophotometrically at 426 nm with 10^{-3} mol dm^{-3} NaOH and 10^{-5} mol dm^{-3} substrate at 25.0 °C. For reactions with Cl^- or Br^-, 10^{-3} mol dm^{-3} HCl or HBr was added to suppress the reaction with OH^-.

Acknowledgements

This research (Chem/1412/14) was supported by the Research Center College of Science, King Saud University, Riyadh, Saudi Arabia.

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§ Changing the shell thickness between 2.5–3 Å does not affect the quality of the fits, but it modestly increases k_2^m.

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Paper 4/06406B
Received 19*th November* 1994
Accepted 5*th April* 1995