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ANOMALOUS SALT EFFECTS ON A MICELLAR-MEDIATED REACTION OF BROMIDE ION

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Reaction of bromide ion with α-picryl-*p*-bromoacetophenone (1) is speeded by aqueous cationic micelles of cetyltrimethylammonium bromide (CTABr; $C_{16}H_{33}NMe_3Br$) and dodecyltrimethylammonium bromide (DoTABr; $C_{12}H_{25}NMe_3Br$) and rate constants reach limiting values when 1 is fully bound to micelles of CTABr. Limiting values are not reached in DoTABr, but the data can be fitted to a simple model for the distribution of reactants between water and micelles. Estimated second-order rate constants at the micellar surface are similar to values in water, but this model cannot explain the observed rate enhancements on addition of NaBr to CTABr. Inert anions such as nitrate, mesylate, n-butanesulfonate, phenylmethanesulfonate and camphor-10-sulfonate inhibit reaction in CTABr by competing with Br^- at the micellar surface. Other n-alkanesulfonate ions (RSO_3^-, R = n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}, n-C_8H_{17}) and arenesulfonate ions (benzene-, toluene-, naphthalene-1- and naphthalene-2-sulfonate) behave anomalously. These ions expel Br^- from the micelle, as shown electrochemically, but there are maxima in plots of rate constant against mole fraction of Br^-. These rate extrema are apparently due to perturbation of the micellar surface structure that overcomes the inhibition due to competition with Br^-. These results show that the simple pseudo-phase, ion-exchange model can be applied only in dilute electrolyte and in the absence of hydrophobic anions

INTRODUCTION

Aqueous ionic micelles speed reactions of hydrophobic substrates and counter ions by bringing reactants together at the micellar surface.[1] The rate–surfactant profiles can often be treated quantitatively by estimating the concentration of each reactant at the micellar surface and calculating the second-order rate constant at that surface.[2] For many reactions, values of second-order rate constants at the surfaces of micelles and other colloidal assemblies are similar to those in water, so that observed rate enhancements are due largely to concentration of reactants at colloidal surfaces.

Added inert counter ions decrease micellar rate enhancements of bimolecular reactions involving reactive counter ions because of inter-ionic competition.[1,2] Inhibition increases with increasing polarizability and decreasing charge density of the competing ion, because these properties control the interaction of an ion with the micellar surface.

Micellar effects on the rates of bimolecular ionic reactions have been treated quantitatively in terms of the pseudo-phase ion-exchange (PIE) model.[2] Competition between anions is described in terms of the equation

$$K_X^Y = [Y_W][X_M]/([Y_M][X_W])$$

where concentrations of X^- and Y^- are written as molarities in terms of total solution volume and the subscripts W and M denote aqueous and micellar pseudo-phases, respectively. Fractional charge neutralization of the micellar head groups, β, is assumed to be constant and the concentrations of micellar-bound counter ions can be calculated from a mass-balance relation in terms of K_X^Y and β. The rate–surfactant profiles can then be simulated by using substrate binding constants to the micelle, the distribution of counterions and second-order rate constants in aqueous and micellar pseudo-phases.[2a]

The PIE model also includes the assumption that changes in micellar properties on addition of electrolyte have no effect on K_X^Y, β or the second-order rate constants. These assumptions are reasonable if the properties of the micellar surface are insensitive to changes

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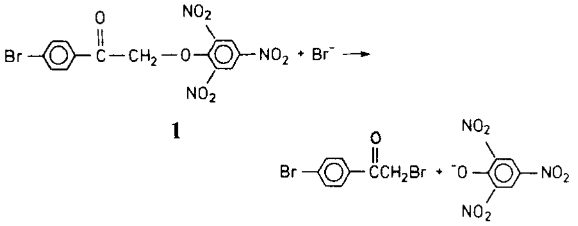
in micellar shape or size. This model fits a great deal of data, although it has been criticized on theoretical and experimental grounds,[3] and it fails for concentrated electrolyte solutions.[4] Kinetic values of K_X^Y for OH$^-$ or F$^-$ in cationic micelles of cetyltrimethylammonium bromide (CTABr) do not agree with values from fluorescence quenching.[5]

A variant of the PIE model expresses ionic distributions in terms of Langmuir isotherms.[6,7] This, unlike the PIE model, is applicable to higher concentrations of electrolyte, but both models lead to similar overall conclusions. Another variant of the pseudo-phase model estimates the coulombic interaction by solving the Poisson–Boltzmann equation with a term for specific ion–micelle interactions.[8–10] It fits data for bimolecular ionic reactions and allows for size changes in spherical micelles.

A major question is the extent to which ions at the micellar surface may affect second-order rate constants at that surface. The success of the various models for reactions in dilute solutions of hydrophilic ions suggests that changes in second-order rate constants at micellar surfaces can be neglected. However, added salts affect the rate constants of some spontaneous reactions in micelles,[2a,c,11] even though inter-ionic competition is unimportant, so salts are affecting these rate constants at micellar surfaces. For example, polarizable, hydrophobic anions sharply speed anionic decarboxylations in cationic micelles,[11] so an assumed constancy of second-order rate constants at micellar surfaces may also be incorrect if salts change micellar surface properties.

One test of the PIE model is to use a reactive ion micelle so that only reactive ion is in solution and there is no inter-ionic competition.[6,12] Rate constants should increase with increasing surfactant concentration and become constant when substrate is fully bound. This prediction is fulfilled reasonably well for reactions of dilute CN$^-$, N$_3^-$, Cl$^-$ and Br$^-$, but not for reactions of more hydrophilic anions where modification of the simple models is required.[2a,c,6] However, the treatment is not completely satisfactory, even for S$_N$2 reactions of Br$^-$,[12b] because addition of Br$^-$ slightly speeds reaction with methyl arenesulfonates even when they appear to be fully micellar bound. This increase may be due to a structural change in the micelle because CTABr micelles undergo a change from sphere to rod at high NaBr concentrations.[13] Other anions, especially arenesulfonate ions, that induce this change consistently have striking effects on the rates of spontaneous decarboxylations.[11]

Reaction of Br$^-$ with α-picryl-*p*-bromoacetophenone (**1**) gives picrate ion and we could follow it readily in aqueous micelles of CTABr or dodecyltrimethylammonium bromide (DoTABr) in the visible spectral region with no spectral interference from arenesulfonate ions.[14]



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We examined the reaction of Br$^-$ with **1** in aqueous CTABr or DoTABr in the presence and absence of various inert anions, e.g. nitrate and alkane- and arenesulfonate ions of various hydrophobicities. We also used a specific bromide-ion electrode to examine the competition between Br$^-$ and inert anions at the micellar surface.[15]

RESULTS

Micellar reactions

First-order rate constants increase to constant values with increasing [CTABr] (Figure 1). This result is consistent with substrate being incorporated into a

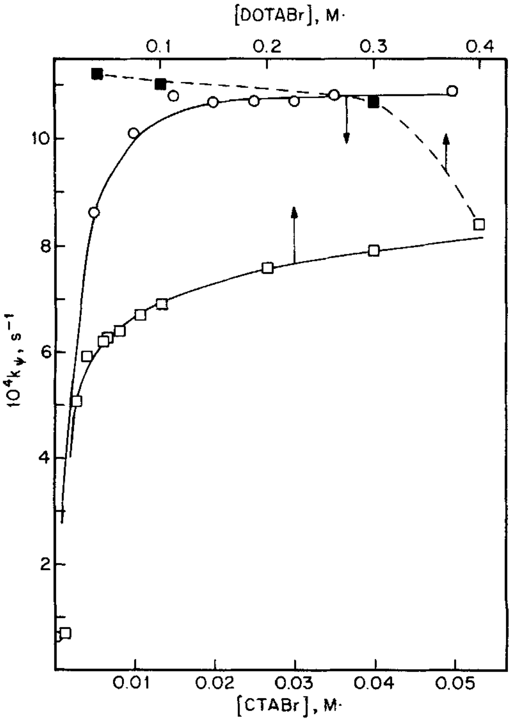
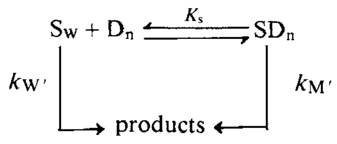


Figure 1. Reaction of 1 in (○) CTABr, (□) DoTABr and (■) 0·4 M DoTABr + NaBr



Scheme 1

micelle whose surface is saturated with Br^-, i.e. in which β is constant,[2a,c,12] as for other S_N2 reactions of Br^- and reactions of other dilute nucleophilic anions.[12]

Micelles of DoTABr also speed reaction, but rate constants do not reach limiting values, even at high [DoTABr] (Figure 1). The results for reaction in CTABr and DoTABr can be described in terms of Scheme 1, where S is substrate, D_n is micellized surfactant, subscripts W and M denote aqueous and micellar pseudo-phases, respectively, and $k_{W'}$ and $k_{M'}$ are first-order rate constants.[2,16] The observed first-order rate constant is given by

$$k\psi = (k_{W'} + k_{M'}K_s[D_n])/(1 + K_s[D_n]) \qquad (2)$$

These rate constants can be written in terms of second-order rate constants and concentrations of Br^- in the two pseudo-phases:

$$k_{W'} = k_W[Br_W^-] \qquad (3)$$

$$k_{M'} = k_M[Br_M^-]/[D_n] \qquad (4)$$

In equation (4), the concentration of micellar-bound Br^- is written as a mole ratio which, in the absence of added anions, should be given by β.[2a,c] Therefore, for a strongly bound substrate, reaction occurs wholly in the micellar pseudo-phase and equations (2)–(4) in the limit of constant β simplify to[2a,c,12]

$$k\psi = \beta k_M \qquad (5)$$

The interaction of Br^- with micelles of DoTABr (or CTABr) can alternatively be described by

$$K_{Br'} = [Br_M^-]/([Br_W^-]([D_n] - [Br_M^-])) \qquad (6)$$

i.e. β is regarded as constant only if $K_{Br'}$ is large. Equation (6) fits data for a variety of micellar reactions in dilute electrolyte.[2a,c,6,7] The data for reaction in DoTABr (Figure 1) were fitted with $K_s = 500\ l\ mol^{-1}$, $K_{Br'} = 150\ l\ mol^{-1}$, critical micellar concentration (cmc) $= 5 \times 10^{-3}$ *M*, $k_M = 9 \times 10^{-4}\ s^{-1}$ and $k_W = 1{\cdot}6 \times 10^{-4}\ l\ mol^{-1}\ s^{-1}$,[14b] but can probably be fitted with other combinations of these parameters.[17]

Although these simple treatments fit the rate data in the absence of added anions, they fail on addition of Br^- and of inert anions, added either as CTAX, DoTAX or NaX. In the following section we denote alkanesulfonate ions as RSO_3^-, where R = n-C_4H_9 (n-Bu), n-C_5H_{11} (n-Pe), n-C_6H_{13} (n-Hex), n-C_7H_{15} (n-Hep), n-C_8H_{17} (n-Oct), $PhCH_2$ or 10-camphor, and arenesulfonate ions as arene = benzene (OBs), toluene (OTos), naphthalene-1-[ONs(1)] or naphthalene-2-[ONs(2)].

Effect of added Br^-

The simple pseudo-phase model in equation (5)[2a,c,12] predicts that $k\psi$ for reaction in CTABr will become constant with fully bound substrate and be independent of added Br^-. This prediction fails, because $k\psi$ increases markedly on addition of NaBr (Table 1). Added NaBr also affects $k\psi$ for reaction in DoTABr with total $[Br^-] = 0{\cdot}4$ M and variable DoTABr (Figure 1). Paradoxically, $k\psi$ is higher in 0.05 M DoTABr + 0·35 M NaBr than in 0·4 M DoTABr.

Table 1. Effect of NaBr on reaction in CTABr (values of $10^4\ k\psi\ s^{-1}$ at pH 3 and 25·0 °C)

	[CTABr]/M		
[NaBr]/M	0·01	0·02	0·03
—	10·1	10·7	10·7
0·001	10·1	10·7	10·7
0·005	11·1	11·3	11·2
0·009	11·8	12·0	12·4
0·013	12·4	12·5	12·8
0·017	13·1	13·6	13·5
0·021	14·3	14·3	14·7
0·029	14·6	15·4	15·3
0·037		16·8	

Reactions in mixtures of anions

The simplest approach is to examine reactivity in mixtures of CTABr and CTAX with constant surfactant concentration. The results are simple for a mixture of CTABr and $CTANO_3$ because $k\psi$ decreases linearly with decreasing mole fraction of Br^- (x_{Br}) (Fig. 2). These rate effects are shown as k_{rel}, i.e. relative to the value with no adduct. Mixtures of CTABr and cetyltrimethylammonium mesylate (CTAOMs) also give a monotonic decrease of k_{rel} with decreasing x_{Br}, but the situation is different for mixtures containing cetyltrimethylammonium benzenesulfonate and tosylate (CTAOBs and CTAOTos) (Figure 2). The plots of k_{rel} against mole fraction of Br^- are curved and, at high x_{Br}, reaction is faster in mixtures of CTABr + CTAOTos than in CTABr alone. However, values of k_{rel} are very low in CTAX, and are similar to those of the residual reaction with water (see Experimental). These general conclusions are not very sensitive to changes in total surfactant concentration (Figure 2).

The dependence of rate constant on x_{Br} in a mixture of DoTABr and DoTAOMs (Table 2) is similar to that in CTABr + CTAOMs.

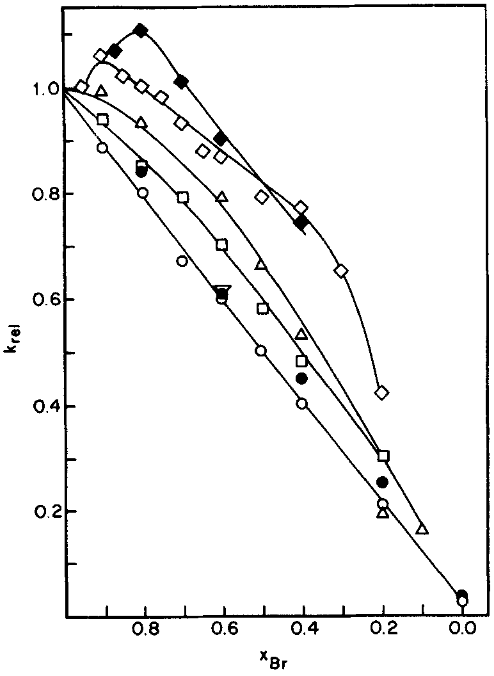


Figure 2. Dependence of rate constants in CTABr on mole fraction or concentration of Br^- with 0·03 M CTABr + CTAX (open symbols) or 0·02 M CTABr + CTAX (closed symbols). X = (○, ●) NO_3; (□) OMs; (△) OBs; (◇ , ◆) OTos

Table 2. Reaction in mixtures of DoTABr and DoTAOMs at 25·0 °C in 0·1 M total surfactant

x_{Br}	1·00	0·80	0·60	0·40	0·20	0·00
$10^4 k\psi\,s^{-1}$	6·90	5·59	4·28	3·04	1·73	0·48

Effects of added inert salts

The mole fraction of Br^- can also be decreased by adding NaX to a fixed concentration of CTABr. We used $NaNO_3$ and sodium salts of alkane- and arenesulfonic acids (Figures 3–6). At high concentrations, salts inhibit reaction, but some of the more hydrophobic sulfonates speed reaction at low concentrations. The behaviors of $NaNO_3$, NaOMs and n-$BuSO_3Na$ in CTABr fit the qualitative predictions of the PIE model in that NO_3^- and $BuSO_3^-$, which should compete with Br^- with ion-exchange parameters [equation (1)], of close to unity,[2,5] give rate decreases which closely follow x_{Br} (Figure 3). Mesylate ion is, as expected, a less effective inhibitor than NO_3^-.[2] These results accord with those for mixtures of CTABr and CTAX (Figure 2).

The situation is very different for salts of the hydrophobic sulfonic acids in CTABr. The solutions

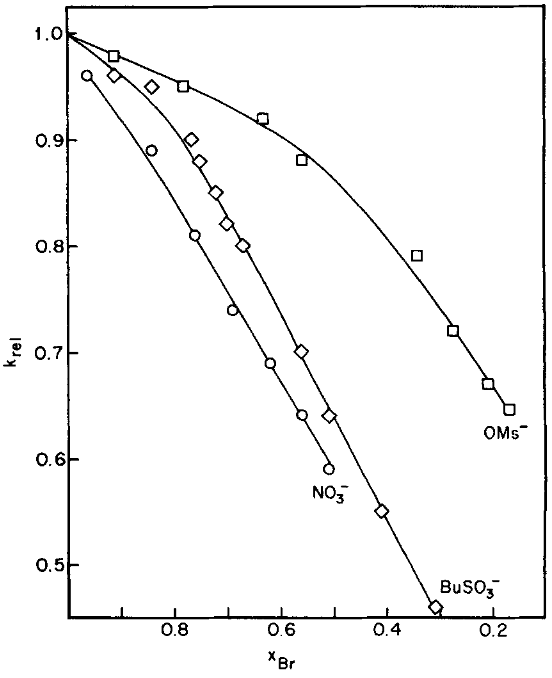


Figure 3. Rate constants relative to $k\psi$ in 0·03 M CTABr. Effect of NaX: X = (○) NO_3; (□) OMs; (◇) n-$BuSO_3$

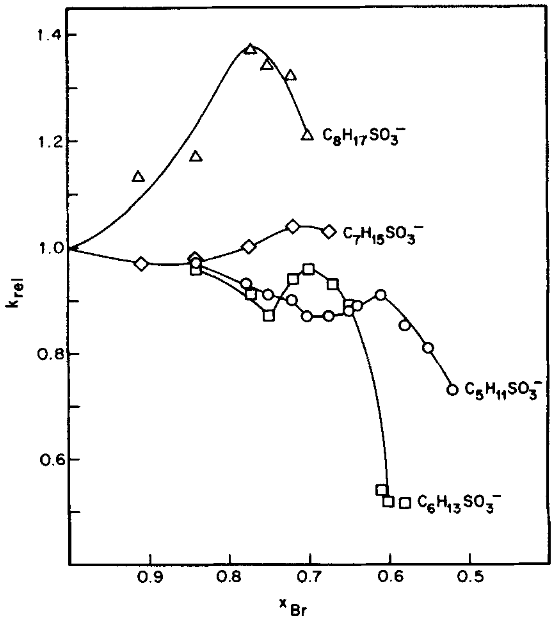


Figure 4. Rate constants relative to $k\psi$ in 0·03 M CTABr. Effect of RSO_3Na: R = (○) Pen; (□) Hex; (◇) Hep; (△) Oct

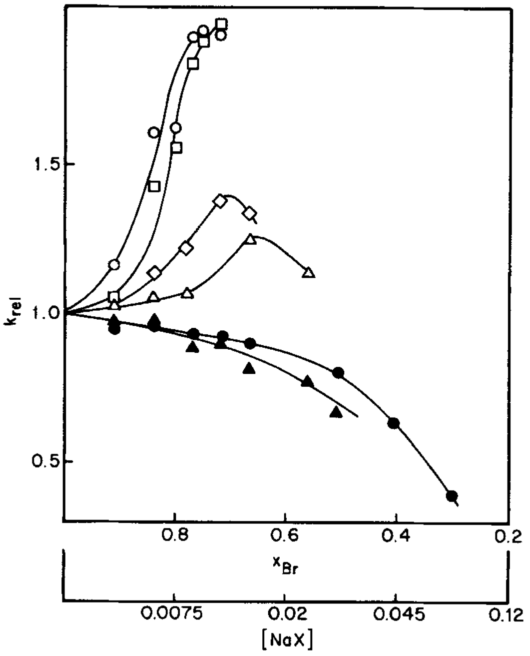


Figure 5. Effect of hydrophobic sulfonate ions on rate constants relative to k_ψ in 0·03 M CTABr. △, NaOBs; ◇, NaOTos. RSO_3Na: R = (▲) $PhCH_2$; (□) ONs(1); (o) ONs(2); (●) 10-camphor

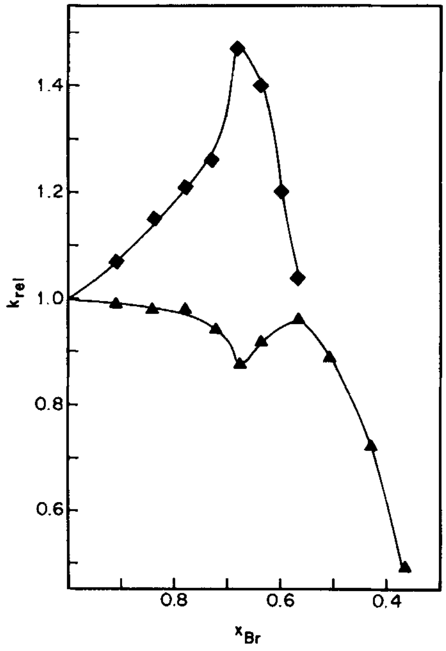


Figure 6. Rate constants relative to k_ψ in 0·02 M CTABr. Effect of (▲) NaOBs and (◆) NaOTos

often become viscous on addition of the salt,[11] which limits the amount that can be added, and there are rate maxima in dilute salt (Figures 4–6). For a series of n-alkanesulfonates the extent and position of these maxima depend on the length of the n-alkyl group (Figure 4).

Results for mixtures of 0·03 M CTABr and sodium arenesulfonates are shown in Figure 5. There are also striking rate enhancements to extrema on addition of NaOTos and NaOBs to 0·02 M CTABr (Figure 6). Although sodium arenesulfonates give unexpected rate extrema, sodium phenylmethanesulfonate and sodium camphor-10-sulfonate give the predicted monotonic rate decreases (Figure 5).

Salt effects on reaction in DoTABr (0·1 or 0·2 M) (Figure 7) are qualitatively similar to those in CTABr, except that NaOBs did not give a rate maximum.

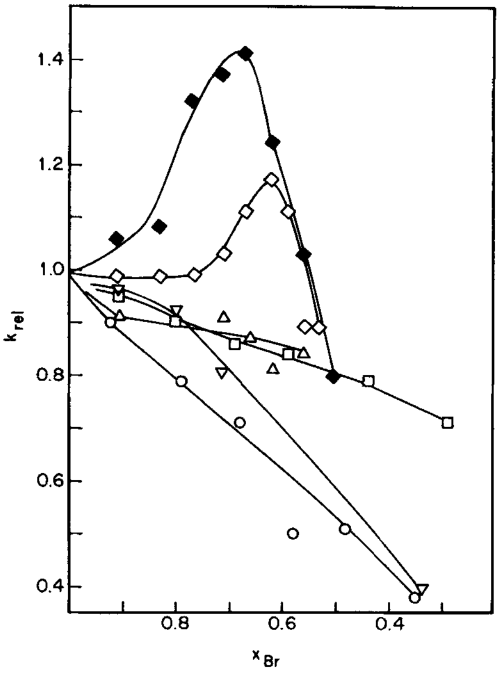


Figure 7. Effect of NaX on rate constants relative to k_ψ in 0·1 M DoTABr (open symbols) and in 0·2 M DoTABr (closed symbols). X = (o) NO_3; (□) OMs; (△) OBs; (◇, ◆) OTos; (▽) $PhCH_2SO_3$

Binding of Br^-

Specific ion electrodes are assumed to sense ions that are free in the water rather than bound to the micelle.[15] Their response depends on mean ion activity rather than concentration, so there is a question of the activity correction in solutions of ionic surfactants with mixed anions. We therefore used the data only qualitatively

Table 3. Salt effect on the binding of Br^- in CTABr micelles[a]

[Salt]/M	$NaNO_3$	NaOMs	NaOBs	NaOTos
0·002				0·015
0·004	0·015	0·016	0·016	0·013
0·008	0·013	0·015	0·012	0·010
0·012	0·011	0·013		0·007
0·016	0·009	0·012	0·006	0·004
0·018				0·003
0·020	0·008	0·012	0·005	0·002
0·024	0·007	0·011	0·004	
0·028	0·006	0·01	0·003	
0·032	0·006	0·011		
0·036	0·006		0·002	
0·04	0·004		0·001	

[a] Values of $[Br_M^-]$ in 0·02 M CTABr, calculated from $[Br_W^-]$ estimated by using a specific ion electrode. In 0·02 M CTABr with no added salts $[Br_M^-] = 0{\cdot}017$ M

(Experimental) and values of $[Br_M^-]$ in Table 3 are given by $[CTABr] - [Br_W^-]$ on the assumption that $[Br_W^-]$ is given by the electrode after calibration in aqueous NaBr. This assumption neglects the decrease in concentration of monomeric surfactant due to added salt (the cmc is very low in added salt), but the results show that all the ions displace Br^- from the micelle in the expected sequence, $OTos^- > NO_3^- > OMs^-$.[2,5] Arenesulfonate ions are especially effective in displacing Br^-.

There is extensive evidence on competition between Br^- and inorganic anions,[2,5] and Lissi *et al.*[18] have estimated the following exchange constants [equation (1)] between Br^- and RCO_2^-: R = Me, 0·06; n-Bu, 0·60; Pen, 1·4; Hex, 4·5; Hep, 10; and Oct, 23. A qualitatively similar series of exchange constants should apply to the competition between Br^- and alkanesulfonate ions.

DISCUSSION

The PIE model

Some of our data are consistent with the PIE model.[2] For example, the constant values of k_ψ for [CTABr] > 0·02 M (Figure 1) fit a constant value of β [equation (5)], and give $k_M = 14 \times 10^{-4}\ s^{-1}$, based on the concentration of Br^- written as a mole ratio, and $\beta = 0{\cdot}78$.[2] If we assume that the molar volume of the reactive region, $V_M = 0{\cdot}14\ l\,mol^{-1}$, and write[2a,c]

$$k_2^m = k_M V_M \qquad (7)$$

where k_2^m has the dimensions $l\,mol^{-1}\,s^{-1}$, we obtain $k_2^m = 1{\cdot}9 \times 10^{-4}\ l\,mol^{-1}\,s^{-1}$. This value is very similar to that of $k_W = 1{\cdot}6 \times 10^{-4}\ l\,mol^{-1}\,s^{-1}$ in water.[14b] Hence the rate enhancement is due largely to an increased concentration of reactants at the micellar surface. Similar conclusions have been drawn from analyses of many bimolecular ionic reactions in micelles.[2,7,9,10,12] For reaction in DoTABr, application of equations (2)–(4) and (6) gives $k_M \approx 9 \times 10^{-4}\ s^{-1}$, which is slightly lower than the value in CTABr but, assuming $V_M = 0{\cdot}14\ l\,mol^{-1}$, $k_2^m \approx 1{\cdot}3 \times 10^{-4}\ l\,mol^{-1}\,s^{-1}$ and is slightly lower than in water.

Despite these fits of the data in the absence of added salt, there are problems with the simple model, even with no inert anion, because added NaBr increases k_ψ with fully bound substrate (Table 2). The increase is by a factor of ca 1·5, so it cannot be explained simply by an increase in the value of $[Br_M^-]/[D_n]$ in equations (2)–(5), if this term is identified with β, because β must be less than 1, and is ca 0.8 for these cationic micelles.[1,2]

The extent of fractional neutralization, β, is generally taken as a measure of the concentration of counter ions in the micellar Stern layer, which is also regarded as the reaction region in the micellar pseudo-phase.[1,2] This description is adequate for reactions in CTABr alone, or with limited amounts of added reactive counter ions,[2a,c] but it apparently fails for high concentrations of counter ions, regardless of their hydrophilicity.[4,6] The ion distribution adjacent to the micellar surface is diffuse and the counter-ion concentrations decrease gradually with distance from the surface rather than changing abruptly at the Stern layer boundary,[8–10] as is implied by the simple kinetic model.[2] Counter-ion binding is governed by coulombic and specific interactions with micellar head groups. The specific interactions should be short-range, but coulombic interactions are long-range and the concentration of anions, e.g. Br^-, in the diffuse layer and adjacent to, but not in, the micellar surface will increase with increasing total anion concentration and with any structural change that increases the micellar surface potential. Ions in this region may react with micellar-bound substrate.

Micelles of CTABr grow and become rod-like on addition of NaBr.[13] This change in shape will bring head groups closer together, and may affect reactivity in various ways. The increase in surface charge density, and the change of shape from sphere to rod, will increase the coulombic interaction with Br^-. The closer packing of head groups will, in effect, decrease V_M [equation (7)], which is equivalent to increasing the concentration of Br^- at the micellar surface.[2,3a] In addition, if water is partially expelled from the surface, the consequent change in micropolarity will also speed reaction, because the non-micellar reaction is strongly inhibited by an increase in the water content of the solvent.[14b] These effects should also apply to reactions in DoTABr. Although the simple treatment [equations (2)–(6)] fits the kinetic data in the absence of salt, it is only a first approximation, and it fails in moderately concentrated NaBr.

Role of inert anions

It is useful to distinguish between two experimental situations. Inhibition due to an increase in the mole fraction of an inert anion, X^-, in solutions with constant [CTABr] + [CTAX], can be ascribed to replacement of Br^- by X^-, and therefore dilution of Br^- at the micellar surface (Figure 2). Addition of X^- as NaX exchanges an inert anion for Br^-, but it also increases the number of counter ions relative to surfactant head groups and the overall ionic strength (Figures 3–6). The exchanges with inert anions are confirmed by the use of a specific Br^- electrode (Table 3), and the rate inhibition by hydrophilic anions, e.g. NO_3^- or $MeSO_3^-$, is as predicted.[2]

The rate effects of hydrophobic alkane- and arenesulfonate ions are inconsistent with a simple exchange model (Figures 4–6). For example, these anions are more effective than NO_3^- or OMs^- at displacing Br^- (Table 3), and should therefore strongly inhibit reaction, but under some conditions they actually speed it. There must be compensating effects, probably related to changes in micellar structure and surface polarity, that depend on the geometry of the sulfonate ion and on its hydrophobicity. The rate extrema move towards higher mole fractions of Br^- with increasing length of the organic residue, i.e. from C_5H_{11} to C_8H_{17}, and both $C_7H_{15}SO_3^-$ and $C_8H_{17}SO_3^-$ give rate maxima (Figure 4). Arenesulfonate ions added as the sodium salts, or as CTAOTos, also increase k_{rel}, although for surfactant mixtures the rate constants initially increase and then decrease sharply (Figures 2, 5 and 6). Addition of sodium arenesulfonates increases the solution viscosity so much that we observed only a rate increase, but not overall inhibition, in 0.03 M CTABr (Figure 5). Similar, but less extensive, kinetic results were observed with DoTABr (Figure 7).

The overall inhibition by sodium α-toluenesulfonate and camphorsulfonate was unexpected, because both these anions should be as hydrophobic as the arenesulfonates or the longer chain alkanesulfonates. They apparently inhibit reaction by displacing Br^- from the micelle but without inducing the structural change that increases the rate.

Anomalous salt effects are observed only with arenesulfonate ions and the alkanesulfonate ions that have longer alkyl groups. Arenesulfonate and carboxylate ions and aryloxide ions interact strongly with cationic micelles,[11,19] and spectroscopic evidence suggests that they insert between the head groups. This insertion changes the micellar structure from spherical to rod-like, as shown by marked increases in viscosity. Qualitatively sodium phenylmethane- and camphorsulfonate do not markedly increase viscosity, so it appears that they do not induce a transition from sphere to rod. The low solution viscosity allowed the use of relatively high concentrations of these salts.

We cannot explain the rate extrema (Figures 2–7) in terms of any simple quantitative model, but it appears that anions that are linearly symmetrical, e.g. n-alkanesulfonates, or have the anionic residue directly attached to the arene group, e.g. the arenesulfonates, behave differently to the nonlinear phenylmethanesulfonate ion, with angularity at the methylene group, or the bulky bicyclic camphorsulfonate ion, which do not induce the change in surface structure that assists reaction. We tentatively suggest that these last two anions interact with, but do not penetrate, the micellar surface.

Spontaneous anionic decarboxylations[11] are assisted by decreases in water content and polarity, as are bimolecular anionic reactions.[20,21] Reaction of **1** with NaBr is consistently strongly inhibited by an increase in the water content of the solvent. The second-order rate constants at $25{\cdot}0\,^{\circ}C$ are $5{\cdot}09 \times 10^{-3}$ and ca $0{\cdot}16 \times 10^{-3}\,l\,mol^{-1}\,s^{-1}$ in 0·645 and 0 mole fraction of t-BuOH in water, respectively.[14b] Reactivities of Cl^- and Br^- in S_N2 reactions at surfaces of cationic micelles increase as the size of the head group increases in the sequence $Me_3N^+ < Et_3N^+ < n\text{-}Pr_3N^+ < n\text{-}Bu_3N^+$, even though the extent of halide ion binding decreases in this sequence.[22] There is NMR evidence for decreased hydration of Br^- at the surfaces of micelles that have the bulky head groups,[22b] and it should be responsible, at least in part, for the rate increases.

If a transition from sphere to rod is induced by Br^- or a sulfonate ion, the head group spacing should decrease, and water could be partially excluded from the surface, which will be less polar, so that the rate constant of an S_N2 reaction of Br^- should increase at the surface. There is evidence from Dimroth's E_T30 polarity values[23] for a decrease in micellar surface polarity with a transition from sphere to rod and on addition of salts[23] and it correlates qualitatively with our kinetic data. In addition, a decrease in head group spacing, however induced, will increase the surface electrical potential and coulombic attraction of counter ions and partially compensate for the charge neutralization by inert counter ions.

Development of the pseudo-phase model for reaction in aqueous micelles led to the generalization that second-order rate constants of most bimolecular reactions are similar in water and at micellar surfaces and that β, in the absence of inert counter ions, gives the concentration of reactive ion at the surface.[2] These generalizations apparently fail at high salt concentrations, especially if the micellar surface is markedly perturbed, for example by addition of hydrophobic counter ions or introduction of bulky head groups.[22] In addition, the original form of the PIE model involved the assumption that reaction occurs in a discrete zone at the surface, often identified with the micellar Stern layer, although the counter-ion concentrations decrease smoothly with distance from the surface.[4,9,10] In dilute electrolyte, counter-ion concentrations at the micellar surface, of the order of 3–5 M,[2a] are so much higher than those in bulk solvent that it appears as if reaction is occurring in a discrete zone at the surface, but this simplification becomes less satisfactory as the counter-ion concentration is increased.[9] It is therefore understandable that the PIE model is generally satisfactory in dilute but not in concentrated solutions of reactive ions, where it may break down for (at least) two reasons. First, the concept of a discrete reaction zone is unsatisfactory at high concentrations of reactive counter ion, as for reaction of Br^- with **1**, and for reactions of OH^-,[4] where rate constants at the micellar surface increase, rather than remain constant, on addition of nucleophilic anion. Second, inert counter ions, e.g. arene- or alkanesulfonate ions, may perturb the properties of the micellar surface so as to assist reaction.

These electrolyte effects on the properties of the micellar surface have unexpected kinetic consequences. For example, although arenesulfonate ions effectively displace Br^- from the micellar surface (Refs 2 and 5 and Table 3), at low concentrations some of them are more effective than Br^- in increasing the reaction rate in CTABr (Figures 5 and 6 and Table 1). The rate in 0·03 M CTABr is increased by factors of 1·5-fold by 0·02 M Br^-, 1·4-fold by 0·013 M $OTos^-$ and ca 1.9-fold by 0·013 M naphthalenesulfonate ion.

EXPERIMENTAL

Materials. α-Picryl-*p*-bromoacetophenone (**1**) was prepared by reaction of equimolar silver picrate with α-bromo-*p*-bromoacetophenone in dry MeCN under reflux for 48 h. The product was recrystallized from MeOH–MeCN, m.p. 163–164·5 °C, and gave picrate ion quantitatively on reaction with dilute I^- in EtOH. The surfactants were commercial samples (Aldrich, CTABr and DoTABr) recrystallized from EtOH–Et_2O or MeOH–Et_2O, or were prepared by exchange of anions ($CTANO_3$, $DoTANO_3$) or by quaternization of *N,N*-dimethyldodecylamine or *N,N*-dimethylhexadecylamine. Quaternization was generally effected in MeOH under reflux and the surfactants were purified as for CTABr,[1,2] until there were no minima in plots of surface tension against surfactant concentration. The critical micelle concentrations (cmc) in Table 4 were determined by surface tension and agree with available literature values.[24]

The sodium salts were commercial samples or were prepared by neutralization of the acid or by reaction of the alkyl bromide with Na_2SO_3 in EtOH–H_2O (1:1, v/v) under reflux.

Kinetic methods. Formation of picrate ion was followed spectrophotometrically at 350–360 nm. Kinetic solutions were prepared by adding 25 μl of a 10^{-3} M solution of **1** in dioxane to the reaction medium (3 ml) at 25·0 °C. Lower concentrations of **1** were used when solubility was a problem. Most experiments were made at pH 3 (HBr) to suppress reaction with OH^-, but the rates were independent of pH from 2 to 5. Reaction is slow in the absence of Br^- at low pH. In water in 10^{-3} M HNO_3 + 0·02 M KNO_3 the first-order rate constant is $k_\psi = 2{\cdot}6 \times 10^{-6}\ s^{-1}$ at 25·0 °C and is unaffected by increase in HNO_3 concentration to 0·006 M at constant ionic strength, and in 0·04 M $CTANO_3$ and a solution pH of 3 (HNO_3) $k_\psi = 3{\cdot}4 \times 10^{-5}\ s^{-1}$. This rate increase with addition of $CTANO_3$ is probably caused by incursion of a micellar reaction with OH^-, despite its low concentration in bulk solvent,[2] and because of the effects of cationic micelles on S_N2 reactions with water molecules.[9]

Table 4. Critical micelle concentrations in water at 25·0 °C

Surfactant	10^4cmc/M	Surfactant	10^4cmc/M
CTABr	8·0	CTAOTos	1·3
$CTANO_3$	9·0	DoTABr	190
CTAOMs	13	DoTAOMs	210
CTAOBs	3·0		

Electrochemical measurements. A Beckman Select Ion electrode, calibrated with aqueous NaBr, was used to estimate the amount of free Br^- in surfactant solutions. If the cmc and the fractional micellar ionization, α, are constant, we obtain

$$[Br_W^-] = \alpha[\mathrm{CTABr}] + (1-\alpha)\mathrm{cmc} \qquad (9)$$

A plot of $[Br_W^-]$ against [CTABr] is linear, but the slope, $\alpha = 0{\cdot}14$, is lower than the generally accepted values of ca 0·2.[1,2] These differences probably stem from activity effects of the surfactant ions and therefore we use values of $[Br_W^-]$ and $[Br_M^-]$ in added salt for purposes of comparison only.

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