## Quantitative Treatment of Micellar Effects upon the Nucleophilicity of Halide Ions

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Nucleophilic attack upon methyl benzenesulfonate (1) by Cl<sup>-</sup> or Br<sup>-</sup> occurs readily in aqueous cetyltrimethylammonium chloride or bromide (CTACl or CTABr, respectively). The increase of rate constant with [surfactant] can be analyzed in terms of the concentration of 1 and halide ion in the micellar pseudophase, and the second-order rate constants in micellar and aqueous pseudophases are similar.

The enhancement of the rates of bimolecular reactions by micelles is due largely to increased concentration of the two reactants in the micellar pseudophase,<sup>1</sup> and the variations of rate constants with [surfactants] can often be treated quantitatively in these terms.<sup>3-6</sup> It is generally relatively easy to examine the partitioning of hydrophobic reactants between aqueous and micellar pseudophases, but the problem is more difficult with hydrophilic ions. A very useful, and widely used, approach is to assume that counterions compete for ionic sites on the micellar surface, and that the fraction,  $\beta$ , of these sites which are neutralized by counterions is approximately constant.<sup>7</sup> This general approach has been applied successfully to rate and equilibrium constants of many reactions in aqueous micelles.<sup>8-10</sup> However, the treatment involves several parameters, e.g.,  $\beta$ , whose values are not known with certainty. In addition, interionic competition between, for example, an inert anion, Y<sup>-</sup>, and a nucleophile, X<sup>-</sup>, may not be described accurately in terms of an ion-exchange model (Scheme 1, where subscripts W and M denote aqueous and micellar pseudophase, respectively).

## Scheme I

$$X_{M}^{-} + Y_{W}^{-} \rightleftharpoons X_{W}^{-} + Y_{M}^{-}$$
(1)

$$K_{\rm Y}^{\rm X} = [{\rm X}_{\rm W}^{-}][{\rm Y}_{\rm M}^{-}]/[{\rm X}_{\rm M}^{-}][{\rm Y}_{\rm W}^{-}]$$

The problem of interionic competition can be eliminated by using a reactive-ion surfactant, in which ionic reagent is the micellar counterion.<sup>11</sup> Therefore its concentration in the micellar pseudophase should be constant, provided that  $\beta$  is constant, and the first-order rate constant,  $k_{\psi}$ , for the overall reaction, should increase with increasing [surfactant] and become constant once substrate is fully

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Scheme II

TABLE I: Reaction in the Absence of Surfactant<sup>a</sup>

[salt], M	NaCl	NaBr	
0.1	1.3	1.7	
0.2	1.6	2.2	
0.3	2.1	3.0	

<sup>a</sup> Values of  $10^{5}k_{\psi}$ , s<sup>-1</sup> at 25.0 °C. In water  $10^{5}k_{\psi} = 1.1$  $s^{-1}$ , 14

TABLE II:	Reactions in	n Surfactant	in	Absence
of Added Sa	lt <sup>a</sup>			

[CTAX], M	X = Cl	X = Br
0.01	4.70 (3.70)	16.6 (15.6)
0.02 0.04	6.25(5.25) 8.25(7.35)	29.9(28.9) 41.0(40.0)
0.06	0.20 (1.00)	45.9 (45.0)
0.08	10.3 (9.5)	51.6 (50.8)
0.10 0.15	126(118)	51.1 (50.3)
0.20	13.0 (12.3)	

<sup>a</sup> Values of  $10^5 k_{\cup}$ , s<sup>-1</sup> at 25.0 °C, in the absence of surfactant  $10^{5}k_{\psi} = 1.1 \text{ s}^{-1}$ ; values in parentheses are  $10^{5}k_{\psi}^{c}$ , s<sup>-1</sup>.

micellar bound. This behavior has been observed for reactions involving hydrogen ions<sup>11a</sup> for nucleophilic addition by CN<sup>-</sup>,<sup>11b</sup> and for substitution by Br<sup>-</sup>.<sup>12</sup>

However, for reactions of very hydrophilic anions, e.g., OH<sup>-</sup> or F<sup>-</sup>, values of  $k_{\psi}$  increase with [surfactant], even when the substrate is fully micellar bound.<sup>11a,c,12a,13</sup>

The aim of the present work was to examine micellar effects upon nucleophilic substitution by Cl<sup>-</sup> or Br<sup>-</sup> upon methyl benzenesulfonate (1), in solutions of cetyltrimethylammonium chloride or bromide (CTACl or CTABr respectively) (Scheme II).

There is also a reaction of methyl benzenesulfonate with water, but it is inhibited by cationic micelles of, for ex-

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<sup>(13)</sup> Bunton, C. A.; Frankson, J.; Romsted, L. S. J. Phys. Chem. 1980, 84, 2607.

TABLE III: Effect of Added Halide Ion on Micellar Reactions<sup>a</sup>

[NaX], M	0.02 M CTACl	0.2 M CTACI	0.02 M CTABr
	6.25	13.0	29.9
0.02	7.53	14.6	32.7
0.04			34.2
0.06	8.21	15.3	35.3
0.08			36.5
0.10	8.61	16.7	37.8

<sup>a</sup> Values of  $10^{5}k_{\psi}$ , s<sup>-1</sup> at 25.0 °C, with added common halide ion.

Scheme III

$$S_W + D_n \xrightarrow{K_S} S_M$$
  
 $x_w \xrightarrow{k_W} x_{M} \xrightarrow{k_M}$   
products

ample, cetyltrimethylammonium mesylate, and should make only a minor contribution in surfactant solutions of CTACl or CTABr.14

## **Experimental Section**

*Materials*. The reagents and surfactants were prepared or purified by standard methods.<sup>10,14</sup>

Kinetics. Reactions were followed spectrophotometrically at 25.0 °C by the decrease of absorbance at 262 nm.<sup>14</sup> The solvent was redistilled deionized water. Addition of 10<sup>-3</sup> M HCl or HBr to the more concentrated surfactant solutions did not change the rate constant, so that there was no contribution from reaction with OH-. The first-order rate constants,  $k_{\psi}$ , are in reciprocal seconds.

## **Results and Discussion**

Reactions in Aqueous Salts. In hydroxylic solvents bromide is a better nucleophile than chloride ion, because hydrogen bonding reduces nucleophilicity of anions, and the effect is greatest with small, hydrophilic, anions of high charge density.<sup>15,16</sup> We see this behavior in our reactions (Table I), and the second-order rate constants are  $2.7 \times$  $10^{-5}$  and  $6 \times 10^{-5}$  M<sup>-1</sup> s<sup>-1</sup> for reactions of Cl<sup>-</sup> and Br<sup>-</sup>, respectively. (No correction is made for the salt effects upon these reactions.) The difference between these second-order rate constants is slightly smaller than that for the corresponding reactions with methyl bromide,<sup>17</sup> but very similar to that for reaction of ethyl tosylate in aqueous dioxane.<sup>18</sup>

Micellar Effects. The first-order rate constants increase smoothly with increasing [CTACl] or [CTABr] (Table II). Under some conditions addition of the common halide ion to the surfactant solution increases  $k_{\psi}$  (Table III).

Values of  $k_{\psi}$  tend to reach limits with increasing [surfactant], and, as for reaction in water, Br appears to be a better nucleophile than Cl<sup>-</sup>. This difference is understandable because counterions are extensively hydrated in the water-rich Stern layer of a normal micelle.<sup>19</sup>

Quantitative Treatment of Rate Effects. It is generally assumed that reaction can take place in the aqueous or

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micellar pseudophase<sup>20</sup> (Scheme III).

In Scheme III S denotes substrate and D<sub>n</sub> the micellized surfactant.

There is also a reaction with water, which makes a (minor) contribution,  $k_{\rm H,O}$ , to the observed rate constant.<sup>14</sup> We correct for it by assuming that it will be the same as in solutions of cetyltrimethylammonium mesylate,<sup>21</sup> giving

$$k_{\psi}^{c} = k_{\psi} - k_{H_{2}O} \tag{2}$$

$$k_{\psi}^{c} = \frac{k'_{W} + k'_{M}K_{S}[D_{n}]}{1 + K_{S}[D_{n}]}$$
(3)

where  $K_{\rm S}$  is the binding constant of substrate to micelles, written in terms of the concentration of micellized surfactant, and  $k'_{W}$  and  $k'_{M}$  are respectively the first-order rate constants in the aqueous and micellar pseudophases. These rate constants can be written in terms of the second-order rate constants,  $k_{\rm W}$  and  $k_{\rm M}$ , and the concentration of  $Cl^-$  of  $Br^-$  in each pseudophase, eq 4 and 5.

$$k'_{\rm W} = k_{\rm W}[{\rm X}_{\rm W}^{-}] \tag{4}$$

$$k'_{\rm M} = k_{\rm M} m_{\rm X}^{\rm s} = k_{\rm M} [{\rm X}_{\rm M}^{-}] / [{\rm D}_{\rm n}] = k_{\rm M} \beta$$
 (5)

The rate constant,  $k_{\rm M}$ , is defined by using concentration written as a mole ratio,  $m_{\rm X}$ <sup>s</sup>, which for a reactive ion surfactant is  $\beta$ .

The quantitative treatment of the rate data therefore involves estimation of the distribution of substrate between water and micelles, which depends on  $K_{\rm S}$ , and estimation of the concentration of Cl<sup>-</sup> or Br<sup>-</sup> in the micellar pseudophase.

The binding constant,  $K_{\rm S}$ , cannot be measured directly, because of reaction between substrate and halide ion, but comparison with the binding of similar, but unreactive, solutes suggests that  $K_{\rm S} \approx 10^2 {\rm M}^{-1}$ , for both CTACl and CTABr.<sup>2,3-5</sup> However, addition of salts to surfactant solutions may increase  $K_{\rm S}$ , by "salting-out" nonionic solutes from the aqueous pseudophase, and we considered this possibility in fitting the rate data.<sup>10,11c</sup>

The rate surfactant profiles for hydrogen ion mediated reactions in micellized sulfonic acids and cyanide addition in micellized CTACN can be analyzed on the assumption that  $\beta$  is constant.<sup>11a,b</sup> However, this assumption fails when the counteranion is small and of high charge density, e.g.,  $OH^-$  or  $F^-$ , but the distribution of counterion  $X^-$  between aqueous and micellar pseudophases can be fitted to eq 6, i.e., to a mass action model.<sup>11c</sup>

$$K'_{X} = [X_{M}^{-}] / [X_{W}^{-}] ([D_{n}] - [X_{M}^{-}])$$
(6)

Equation 6 predicts that the fraction,  $\beta$ , of micellar head groups neutralized by counterions will increase with increasing [surfactant], although  $\beta$  will not vary much with [surfactant] if  $K'_X$  is large, e.g., >10<sup>3</sup> M<sup>-1</sup>. Thus the approximation of a constant  $\beta$  is probably satisfactory for an ion such as Br<sup>-</sup>, which binds strongly to cationic micelles, but it may fail for Cl<sup>-</sup>, which binds less strongly than Br<sup>-</sup> to micelles.<sup>8,10,26</sup> Therefore, in treating our data we con-

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<sup>(22)</sup> The concentration of monomeric surfactant is assumed to be given by the critical micelle concentration,<sup>20</sup> i.e.,  $[D_n] = [CTAX] - cmc$ .

<sup>(23)</sup> The concentration of a reagent in the micellar pseudophase can be defined in terms of the mole ratio of bound reagent to micellar head

groups, allowing definition of a second-order rate constant without de-fining the volume element of reaction in the micellar pseudophase.<sup>24</sup> (24) Bunton, C. A.; Carrasco, H.; Huang, S. K.; Paik, C. H.; Romsted, L. S. J. Am. Chem. Soc. **1978**, 100, 5420.



Figure 1. Reaction in CTABr, . The solid line is predicted by both model i (constant  $\beta$ ) and model li. The open points are for effect of NaBr in 0.02 M CTABr. The broken line is calculated for model i by assuming a salt effect on substrate binding and the solid line for model ii.

TABLE IV: Rate and Equilibrium Constants for Reaction in CTACl or CTABr<sup>a</sup>

medium	model <sup>b</sup>	$\begin{array}{c} K'_{\mathbf{X}},\\ \mathbf{M}^{-1} \end{array}$	К <sub>S</sub> , М <sup>-1</sup>	$10^{4}k_{\rm M},$ s <sup>-1</sup>	$rac{k_2^{\mathbf{m}}}{k_{\mathrm{W}}}$
CTACI	i		50	1.6	0.8
CTACl	ii	220	70	1.5	0.8
0.02 M CTACl + NaCl	ii	220	70	1,4	0.7
0.2 M CTACl + NaCl	ii	220	70	1.6	0.8
CTABr	i		55	7.3	1.7
CTABr	ii	2200	65	6.1	1.4
0.2 M CTABr + NaBr	i		65 <sup>c</sup>	6.5	1.5
0.02 M CTABr +	ii	2400	65	6.1	1.4

 $^a$  Calculated with cmc of  $1.3\times10^{-3}$  and  $8\times10^{-4}$  M for CTACl and CTABr, respectively.  $^b$  Model i assumes a constant  $\beta$  of 0.8, and model ii is a mass action treatment with variable  $\beta$ . <sup>c</sup> The fit assumes a salt effect on substrate binding, see text.

sidered two possibilities: (i) that  $\beta$  is constant over a wide range of surfactant or halide ion concentration, as is often assumed;<sup>7</sup> (ii) that  $\beta$  increases with increasing halide ion concentration, based on a model applied to micellar binding of relatively hydrophilic anions.<sup>11c</sup>

The simplest assumption is that of a constant  $\beta$ , so that equ 3-5 give

$$k_{\psi}^{c} = \frac{k_{\rm W}[{\rm X}_{\rm W}^{-}] + k_{\rm M}K_{\rm S}\beta[{\rm D}_{\rm n}]}{1 + K_{\rm S}[{\rm D}_{\rm n}]}$$
(7)

$$=\frac{k_{\rm W}([{\rm X}_{\rm T}^{-}] - \beta[{\rm D}_{\rm n}]) + k_{\rm M}K_{\rm S}\beta[{\rm D}_{\rm n}]}{1 + K_{\rm S}[{\rm D}_{\rm n}]}$$
(8)

$$=\frac{k_{\rm W}([{\rm X}_{\rm T}^{-}] - [{\rm X}_{\rm M}^{-}]) + k_{\rm M}K_{\rm S}[{\rm X}_{\rm M}^{-}]}{1 + K_{\rm S}[{\rm D}_{\rm n}]} \tag{9}$$

where subscript T denotes the total concentration of X<sup>-</sup>. With fully micellar bound substrate eq 8 simplifies to

$$k_{\psi}^{c} = k_{\rm M}\beta \tag{10}$$

Equation 8, with a constant  $\beta$ , fits the variation of  $k_{\mu}^{c}$ with [CTACl] or [CTABr] (Figures 1 and 2) in terms of the parameters in Table IV. We note that the rate data can be fitted to other combinations of these parameters provided that the variations are small.<sup>10b</sup>

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Figure 2. Reaction in CTACI, . The broken line is calculated for model i, and the solid line for model ii. Open points, O and O, are for effect of NaCl in 0.02 and 0.2 M CTACl, respectively, and the solid lines are calculated for model ii.

However, the increase of  $k_{\psi}$  with added salt is inconsistent with a constant value of  $\beta$ , eq 6–9. One possibility is that added halide ion increases  $K_{\rm S}$ , by "salting-out" the substrate from the aqueous pseudophase. There is precedence for such an effect,<sup>10</sup> but it is small in other systems, and too small to explain all our salt effects. Therefore, at least for reaction of Cl<sup>-</sup>, we cannot accomodate all our data in terms of a constant  $\beta$ .<sup>27</sup>

The alternative explanation is that  $\beta$  increases with increasing halide ion, eq 6 (model ii). Equation 6 places formal limits on 0 and 1 on  $\beta$ , although the lower limit cannot be reached because there is always counterion present in the aqueous pseudophase, and the upper limit of 1 is reached only at counterion concentrations beyond any reasonable limit.<sup>11c</sup> In practice  $\beta$  would vary little with  $[X^{-}]$  if  $K'_X > 10^3 M^{-1}$ .

Equations 3 and 6 were combined by a simple computer program which allowed us to simulate the variation of  $k_{\mu}^{c}$ with [CTAX] or [NaX], and we were able to fit all the rate data for reactions in surfactant, and with added salt (Figures 1 and 2), using the parameters given in Table IV, based on model ii.

For reaction in 0.02 M CTABr + NaBr the rate constants could be fitted to model i (Figure 1), assuming constant  $\beta$ , provided that we assumed that NaBr increased the binding constant of the substrate to the micelles, following eq 11, i.e., with  $b = 8 \text{ M}^{-1}$ , assuming that NaBr

$$K_{\rm S} = 65(1 + b[{\rm NaBr}])$$
 (11)

"salts out" the substrate from the aqueous pseudophase, cf. ref 10. However, the data could be fitted reasonably well to the mass action model ii, without making this assumption (Figure 1).<sup>28</sup> (A slightly better fit is obtained with  $K'_{\rm Br} = 2200 \text{ M}^{-1}$ ,  $k_{\rm M} = 5.7 \times 10^{-4} \text{ s}^{-1}$ , and b = 4 for NaBr in 0.02 M CTABr.)

Although assumption of a constant  $\beta$  (model i) is satisfactory for reactions in CTACl, CTABr, and CTABr + NaBr, we could not fit the rate data for reaction in CTACl + NaCl in terms of this model without taking unreasonably high values of b, eq 11, of greater than 40  $M^{-1}$ .

We therefore conclude that  $\beta$  for CTACl increases with added Cl<sup>-</sup>, although the effect is much smaller than that

<sup>(25)</sup> Almgren, M.; Rydholm, R. J. Phys. Chem. 1979, 83, 360.

<sup>(27)</sup> Low solubility prevented our using high [NaBr] in CTABr. (28) We quote values of  $K_{\rm Br} \approx 2000 {\rm M}^{-1}$  in Table IV, but over the range of surfactant examined this result is equivalent to  $\beta$  being constant. Alternatively our results (Figure 1) can be fitted to a range of values of  $K'_{\rm Br}$ , eq 6.

apparently observed with CTAOH and CTAF.<sup>11a,c</sup> Some variation of  $\beta$  with added counterion is not unreasonable, if only because there is a distribution of micellar sizes in any given surfactant solution.<sup>20</sup> The larger micelles should be the more effective at attracting counterions and, if added salt skews the size distribution toward larger micelles, it should also increase  $\beta$ . Micellar growth depends upon the balance of surfactant-surfactant and surfactant-counterion interactions, and one would expect variation of micellar size to be largest when the counterions interact the least with the micellar head groups, as with such hydrophilic ions as OH<sup>-</sup> or F<sup>-</sup>.

Rate-surfactant profiles for bimolecular reactions involving hydrophilic counterions can readily be interpreted in terms of an ion-exchange, pseudophase, model assuming constant  $\beta$ .<sup>7-10</sup> However, the data can be fitted to various combinations of parameters, including  $\beta$ , so that the fit, of itself, is not a reliable test of the model, and independent verification of the parameters, especially of the ion-exchange constant,<sup>26</sup> is desirable.

Comparison of the Models. The rate–surfactant profiles can be fitted to either model i or ii<sup>30</sup> (Table IV and Figures 1 and 2). The variation of  $k_{\psi}$  with [NaBr], for a given [CTABr], can be fitted to the mass action model, eq 6, by taking  $K'_{\rm Br} \approx 2 \times 10^3 \,{\rm M}^{-1}$ . The values of  $K'_{\rm X}$  for Cl<sup>-</sup> (Table IV) are reasonable, in comparison with  $K'_{\rm OH} \approx 55 \,{\rm M}^{-1}$  and  $K'_{\rm F} \approx 40 \,{\rm M}^{-1}$ , and  $K' \approx 80 \,{\rm M}^{-1}$  for formate and acetate ion,<sup>11</sup> because less hydrophilic ions, such as Cl<sup>-</sup> or Br<sup>-</sup>, should have larger binding constants.

The values of  $K_{\rm S}$  and  $k_{\rm M}$  are similar for both models. These comparisons suggest that estimation of  $k_{\rm M}$  is relatively straightforward and insensitive to the model chosen for treatment of the data.

The second-order rate constants for reaction in the micellar and aqueous pseudophases,  $k_{\rm M}$  and  $k_{\rm W}$ , have different dimensions; but they can be compared by defining the volume element of reaction in the micelles, which we assume to be that of Stern layer, with a molar volume of ca. 0.14 L.<sup>24</sup> Therefore, the second-order rate constant,  $k_2^{\rm m}$ , M<sup>-1</sup> s<sup>-1</sup>, is given by<sup>32</sup>

$$k_2^{\rm m} = 0.14k_{\rm M} \tag{12}$$

The values of  $k_2^m$  for reactions in the micellar Stern layer are almost identical with those of  $k_W$  in water (Table IV). The close similarity is probably coincidental, because it depends upon our estimated molar volume of the Stern layer. However, the overall volume of the micelle is probably approximately twice that of the Stern layer,<sup>7</sup> so our overall conclusion would be little affected by choice of a different volume element of reaction.

The similarity of  $k_2^m$  and  $k_W$  is understandable, because both substrate and halide ion should be located near the water-rich micellar surface.<sup>7,19</sup> There are many examples of reactions for which second-order rate constants in micelles are similar to those in water, and the differences in constants are probably due to the properties of the micelle as a kinetic solvent, or to a different location of the two reactants in the micelle.<sup>33</sup>

Validity of the Pseudophase Model. Most treatments of micellar rate enhancements assume that there is no reaction across the shear surface of the micelle.<sup>2-11,20</sup> Reaction across this surface was invoked to explain rate effects in cationic micelles having hydroxide as counterion,<sup>11a</sup> but an alternative explanation was subsequently given.<sup>11c</sup> However, reactions of OH<sup>-</sup> with organic chlorides in micelles of CTABr fit the ion-exchange model in dilute, but not in more concentrated, OH-, and it was suggested that there was a reaction of OH<sup>-</sup> across the micellar shear surface at higher [OH<sup>-</sup>].<sup>35</sup> Alternatively, one could suppose that the assumptions of the ion-exchange model break down in these solutions of relatively concentrated OH<sup>-</sup>, and it is difficult to distinguish between a reaction across the micellar shear surface and an increase of concentration of reactive ion at the micellar surface.

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<sup>(30)</sup> Treatment of the data, assuming a constant  $\beta$ , gives values of  $\beta k_{\rm M}$ , and assignment of a value of  $k_{\rm M}$  depends on  $\beta$ . This parameter is generally in the range 0.7–0.9 for micellized quanternary ammonium halides.<sup>7-10,31</sup>

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<sup>(32)</sup> If the volume element of reaction is taken to be the molar volume of the micelle, the second-order rate constant,  $k_2^M$ , would be approximately doubled.<sup>7-9</sup>

<sup>(33)</sup> So far as we are aware, nucleophilic aromatic substitution by azide ion is the only major exception to this generalization.<sup>34</sup>