The Hammett Equation and Micellar Effects on S_N2 Reactions of Methyl Benzenesulfonates − The Role of Micellar Polarity

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Substituent effects on the reaction of H_2O, OH^-, and Br^- with *p*-substituted methyl benzenesulfonates in cationic micelles of cetyl trialkylammonium ion surfactants (n-$C_{16}H_{33}NR_3X$, X = OH, Br, R = Me, Et, *n*Pr, *n*Bu) and in water were analyzed by using the Hammett equation. Values of ρ in the various media confirm that micellar interfacial regions are less polar than water and polarities decrease with increasing bulk of the surfactant head-group.

Introduction

Aqueous micelles and other association colloids can incorporate reactive solutes and behave as microreactors. Rate effects on spontaneous reactions depend on the distribution of substrates between water and micelles and first-order rate constants in the aqueous and micellar *pseudo*-phases. The latter depend on the properties of the interfacial region, whose polarity and water-content appear to be slightly lower than those of water, and this region, in some respects, behaves like a mixed aqueous-organic solvent.[1] For bimolecular reactions, the distributions of both the reactants between water and micelles have to be considered.[1,2] The concentration of reactive counterions at the surfaces of ionic micelles increases the reaction rates and has to be included in any quantitative treatment. In some cases, ionic-transfer equilibria can be monitored experimentally,[3] but for OH^-, for example, we have to use theoretical treatments to estimate local interfacial concentrations.

For the reactions of a substrate S with an added nucleophile, Nuc, the first-order rate constant of the overall reaction, k_{obs}, is given by Equation 1 or Equation 2:[1]

$$k_{obs} = \frac{k_W\,[Nuc_W] + k_2^m\,K_S\,Nuc_M\,[Dn]}{1 + K_S\,[Dn]} \qquad (1)$$

$$k_{obs} = \frac{k_W\,[Nuc_W] + k_M\,K_S\,[Nuc_M]}{1 + K_S\,[Dn]} \qquad (2)$$

In these equations, subscripts W and M denote aqueous and micellar *pseudo*-phases, respectively, and the quantities in squared brackets are the molar concentrations in the total solution volume. However, Nuc_M without brackets, Equation 1, is the *local* molar concentration in the interfacial region. The second-order rate constants k_W and k_2^m, Equation 1, have dimensions $\text{M}^{-1}\text{s}^{-1}$, but in Equation 2, k_M has a unit of s^{-1} and is written with the concentration of the nucleophile as a mole ratio, $[Nuc_M]/[Dn]$. [Dn] is the concentration of surfactant (detergent) less the critical micelle concentration, cmc, which is taken as the concentration of monomeric surfactant.[4] The association constant, K_S, with respect to *S*, is written in terms of the concentration of micellized surfactant.[5]

Second-order rate constants, k_M, in s^{-1}, and k_2^m in $\text{M}^{-1}\text{s}^{-1}$, are related by

$$k_2^m = k_M V_M \qquad (3)$$

where V_M is the molar volume of the interfacial reaction region[1] which is assumed to be in the range 0.14−0.37 M^{-1}. As a result, comparisons of values of k_w and k_2^m depend on uncertainties regarding local concentrations. Local ion concentrations can be estimated by solving the Poisson-Boltzmann equation in the appropriate symmetry,[3c,6] but this method also involves assumptions. Dediazonization-trapping provides estimates of local ion concentrations, but cannot be used in basic solutions.[3a,3b]

Reactions are often followed in solutions of a surfactant with both inert and reactive counterions and their competition has to be considered.[1] In this work we avoided the complications of inter-ionic competition by using reactive-ion micelles and defining the transfer of the nucleophile between water and the micelles in terms of Equation 4, which has the form of a Langmuir isotherm:[7,8]

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$$K'_{\mathrm{Nuc}} = \frac{[\mathrm{Nuc_M}]}{[\mathrm{Nuc_W}]([\mathrm{Dn}] - [\mathrm{Nuc_M}])} \quad (4)$$

This treatment has been applied to a number of reactions of nucleophilic anions, e.g., OH^- and Br^-, and the values of K'_{OH} and K'_{Br} are those used earlier.[9]

We were interested in bimolecular anionic reactions mediated by cationic micelles of quaternary ammonium ion surfactants and, in particular, how changes in the structure of the head-group affected the reactivities in the interfacial region. For example, if we replace the N^+Me_3 head-group of a cetyl trimethylammonium ion surfactant (n-$C_{16}H_{33}N^+Me_3$) by bulkier alkyl groups, we change both the affinity for anions and the properties of the interface as a reaction region,[10] e.g., by making it less polar. Therefore, effects on the observed rate constants can be due to changes in the partitioning of reactants between water and micelles, as well as to changes in the rate constants in the micellar *pseudo*-phase. As a result, a comparison of the values of k_M or k_2^m, for a variety of cationic micelles with different head-groups involves approximations and assumptions whose validities are uncertain.

It is difficult to decide whether changes in the calculated values of k_2^m or k_M (Equations 1 and 2), with changes in reaction mechanism or surfactant structure, for example, are significant, or if they are due to limitations in our kinetic treatment. One way to improve the situation is to choose a parameter whose values are relatively independent of the imperfections of the *pseudo*-phase treatments, and we use the Hammett equation for this purpose. Substituent effects on the reaction rates and equilibria are typically analyzed by using linear free-energy relationships, e.g., the Hammett equation (Equation 5) which applies to substitutions on a phenyl group:[11]

$$\log k/k_0 = \sigma\rho \quad (5)$$

where k_0 is the rate constant for the phenyl derivative, σ is a substituent parameter and ρ is characteristic of the reaction. Values of ρ are positive for S_N2 reactions at alkyl centers and increase as the polarity and water-content of solvents are decreased. Values of ρ for the reactions of aryl benzoates with OH^- [12a,12c] or thiolate ion[12b] are higher in cationic micelles of CTABr than in water, and, for the reaction of OH^-, increase with increasing bulk of the cationic head-group,[12c] showing that the micellar interfacial region is less polar than water and that polarity decreases with increasing bulk of the head-group. However, these experiments involved mixtures of inert and reactive anions, and in some cases, buffers,[12a,12b] which complicated the estimation of rate constants in the micellar *pseudo*-phase because of inter-ionic competition.[1] As a simpler system, we examined the reactions of *para*-substituted methyl benzenesulfonates, p-Z-$C_6H_4SO_3Me$, with OH^-, Br^-, and H_2O in water and micelles, which allowed us to obtain values of ρ over a range of conditions and nucleophiles, as shown in Scheme 1 for the reactions with OH^- and Br^-:

$$\underset{\mathbf{1}}{p\text{-Z-}C_6H_4SO_3Me} + Nuc^- \longrightarrow p\text{-Z-}C_6H_4SO_3^- + NucMe$$

Nuc= OH, Br; Z=MeO, **1a**; Me, **1b**; H, **1c**; Cl, **1d**; Br, **1e**; NO_2, **1f**

Scheme 1

Reactions of OH^- with **1c** and **1f** had been examined in cationic micelles and the electronic effects on the reactivity appeared to be higher than those in water,[13] in agreement with other evidence which shows that values of ρ are more positive for reactions in micelles than in water.[12] Substituent effects on the solvolysis of substituted alkyl benzenesulfonates fit the Hammett equation and ρ becomes more positive as the solvent polarity is decreased.[14] The bromide ion is an effective nucleophile in S_N2 reactions at alkyl centers, and although it is less reactive than OH^- in water, its higher affinity for cationic micelles means that its micellar reactions can easily be followed over a range of conditions. With both nucleophiles, we avoid complications of inter-ionic competition and micellar effects on buffer equilibria. In addition, spontaneous hydrolyses of sulfonic esters can be followed in both micelles and homogeneous solvents without complications by buffer effects which have to be considered in many deacylations. We can therefore use methyl benzenesulfonates to evaluate substituent effects on the reactions of H_2O, OH^-, and Br^- in various media.

Reactions of OH^- and thiolate ions with aryl benzoates, and S_N2 reactions of methyl benzenesulfonates are known to be "well-behaved" in that electronic effects on these reactions in both water and micelles fit the Hammett equation reasonably well.[12,14] However, in some spontaneous reactions, the electronic effects of the substituents on the reactions in both homogeneous solvents and micelles do not fit linear free-energy relationships. For example, substituent effects on the spontaneous solvolyses of benzoyl and benzenesulfonyl chlorides[15,16] are complex in that plots of log-k_{obs} against σ are curved and may go through minima, indicating that electronic redistributions in the transition state vary with changes in substrate structure and reaction medium. Changes in mechanism can also generate extremes in these linear free-energy plots.[17]

The surfactants are: n-$C_{16}H_{33}NMe_3X$, X=OH, Br, CTAOH, and CTABr; n-$C_{16}H_{33}NEt_3Br$, CTEABr; n-$C_{16}H_{33}N(n\mathrm{Pr})_3OH$, CTPAOH; and n-$C_{16}H_{33}N(n\mathrm{Bu})_3Br$ CTBABr. We examined spontaneous hydrolyses in (n-$C_{16}H_{33}N^+Me_3$)$MeSO_3^-$, cetyl trimethylammonium mesylate, CTAOMs. In these reactions, where we compared the values of ρ under different conditions, errors introduced in the fitting procedures, e.g., in values of K'_{OH} or K'_{Br}, cancelled out, to a first approximation, in the estimation of Hammett parameters. Selection of the values of the molar volume, V_M, of the interfacial reaction region is a vexing problem, in part because they may depend on the reaction under consideration, but this problem should be less serious when mechanisms and substrate structures are similar.

Results and Discussion

Reactions in the Absence of Surfactant

Values of k_{obs} for spontaneous hydrolyses in water and in mixed solvents[18] are listed in Table 1, and second-order rate constants for reactions with OH^- and Br^- are listed in Table 2.

Table 1. Solvolyses in the presence and absence of CTAOMs

Medium	Substituent[a] p-NO_2	p-Br	p-Cl	H	p-Me	p-OMe	ρ[b]	
H_2O[c]	7.20	1.93	1.84	1.10[d]	0.823	0.607	1.13	(0.991)
MeOH[e]	14.0	3.45		1.63	1.06		1.36	(0.999)
EtOH[f]	65.3	15.5		7.04	4.51	3.16	1.43	(0.999)
EtOH:H_2O (1:1, v:v)[e]	61.7			6.60	4.41		1.36	(0.996)
dioxane/H_2O (1:1, v:v)[e]	32.3	10.5		3.62	2.29		1.44	(0.999)
CTAOMs	5.30[g]	1.70	1.63	0.73[g]	0.43	0.27	1.41	(0.996)

[a] Values of $10^5\ k_{obs}$, s^{-1}, and $10^5\ k'_m$, s^{-1}, in CTAOMs. – [b] Values of correlation coefficients in parentheses. σ values used are −0.268, −0.160, 0.227, 0.232 for OCH_3, CH_3, Cl, and Br, respecively; for NO_2 see text. – [c] ρ=1.10 at 25°C and 1.05 at 50°C, ref. [18b]. – [d] ref. [19]. – [e] at 50°C, ref. [18a]. – [f] at 70°C, ref. [18a]. – [g] ref. [13].

Table 2. Nucleophilic reactions in the presence and absence of surfactants

Medium	Substituent[a] p-NO_2	p-Br	p-Cl	H	p-Me	p-OMe	ρ	r
OH^-, H_2O	39.6[b]	15.8	14.8	10.3[b]	6.58	5.42	0.94	0.998
CTAOH	140 (140)[b]	50.0 (55.0)	47.0 (51.0)	18.0 (18.0)[b]	12.0 (14.0)	7.10 (7.30)	1.41 (1.40)	0.993 (0.984)
CTPAOH	165 (165)[b]	48.0 (53.0)	44.0 (47.0)	14.0 (14.0)[b]	8.20 (8.80)	4.75 (4.75)	1.72 (1.72)	0.992 (0.988)
Br^-, H_2O	3.80	1.37	1.15	0.600	0.575	0.469	1.00	0.982
CTABr	70.0	23.0	21.0	6.0	5.10	2.50	1.58	0.984
CTEABr	95.0 (120)	34.5 (40.0)	21.0 (32.0)	9.80 (11.0)	7.60 (8.60)	3.90 (4.25)	1.52 (1.58)	0.984 (0.986)
CTBABr	200 (300)	60.0 (87.0)	54.0 (78.0)	14.0 (19.0)	10.0 (13.5)	4.80 (6.20)	1.79 (1.56)	0.986 (0.985)

[a] Values of second-order rate constants $10^4\ k_w$, $\text{M}^{-1}s^{-1}$, in water and $10^4\ k_m$, s^{-1}, in surfactant; values of k_m in parentheses are in 0.1 M NaOH or NaBr. Values of K_s, M^{-1}, are: p-NO_2, 58 (50 in CTABr); p-Br, 130; p-Cl, 120; H, 65; p-Me, 120; p-OMe, 90 (100 in CTAOH, and 120 in CTPAOH). – [b] ref. [13].

Micellar Reactions

The spontaneous hydrolyses are modestly inhibited by CTAOMs micelles (Table 1), and $k_{obs} = k'_M$ (Equation 2), when the substrates are fully micellar-bound. These observations are consistent with earlier results,[13,19] and evidence that micellar interfacial regions are less polar than water.[1,20]

Cationic micelles accelerate the reactions of OH^- and Br^-, and values of k_{obs} increase monotonically without reaching limiting values, especially for systems with hydroxide as counterion, as already observed in other cases.[1b,9] When NaX is added (X = OH or Br), the values of k_{obs} tend towards limiting values, and k_{obs} increases relative to values without any added salt. These effects can be related to a change in local anion concentration, when the surfactant concentration is increased, or when salt is added, as observed in cetyl trialkylammonium bromide surfactants by Soldi et al.[21b] The rate−surfactant profiles are fitted to Equation 2 with experimental values of k_W (Table 2) and with literature values of K'_{OH} and K'_{Br} (in units of M^{-1}) which are 55 and 25 for OH^- in CTAOH and CTPAOH, respectively, and 2000, 1500, 750 for Br^- in CTABr, CTEABr, and CTBABr respectively.[9] Values of k_{obs} are corrected for the minor contribution of the reaction with H_2O measured in CTAOMs (Table S9 and ref.[19]). Values of K_S are typical of compounds containing one phenyl group and are increased by relatively hydrophobic substituents.[5] Some values of K_S had been estimated earlier and are similar to those used here.[13] Values of k_M and K_S are given in Table 2. Values of K'_{OH} and K'_{Br} decrease with increasing bulk of the head-group, consistent with physical evidence (e.g., NMR spectroscopy, conductivity)[1c][1d] of affinities of anions for micelles. Examples of the fits are shown in Figure 1 and Figure 2 for OH^- and Br^- respectively, and all the kinetic data are available as supplementary material.

Values of k_M for reactions of OH^- with a given substrate are not very sensitive to the addition of 0.1 M NaOH, but 0.1 M NaBr accelerates the reactions with Br^- (Table 2). Structures of bromide ion micelles are sensitive to the addition of Br^-, which increases aggregation numbers and therefore may change the properties of the interfacial regions, e.g., by inducing a sphere-to-rod transition;[21] added bromide may also produce an increase in interfacial bromide concentration, as observed by Soldi et al.[21b]

Fits to the Hammett Equation

The original σ_m and σ_p values were calculated from the dissociation constants of substituted benzoic acids in water and involved an interplay between inductive (field) effects and mesomeric (resonance) effects. There is extensive work

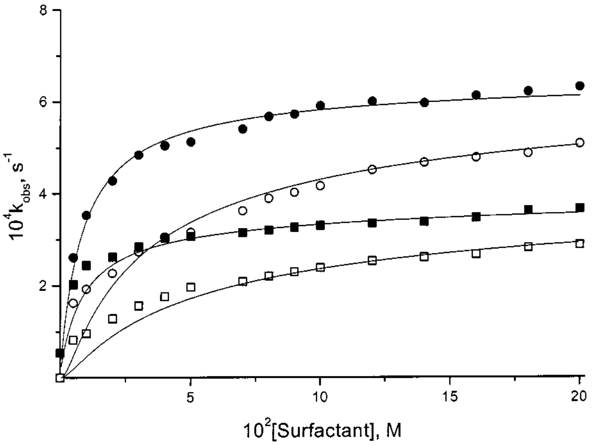

Figure 1. Reaction of methyl *p*-methoxybenzenesulfonate in CTAOH (●, ○), CTPAOH (■, □). Solid and open symbols refer to reaction with and without 0.1 M NaOH, respectively

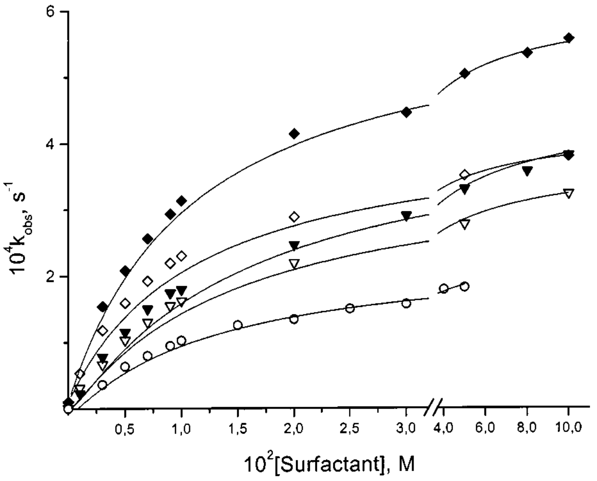

Figure 2. Reaction of methyl *p*-methoxybenzenesulfonate in CTABr (○), CTEABr (▼, ▽), CTBABr (◆, ◇). Solid and open symbols refer to reaction with and without 0.1 M NaBr, respectively

on the separation of these effects, including estimations of σ values for special situations,[11] and Yukawa and Tsuno have introduced an additional parameter to allow for the relative importance of inductive and mesomeric effects.[22]

There were negative deviations with $\sigma_p = 0.78$ for the *p*-NO_2 group in all our micellar reactions. There are deviations from the simple form of the Hammett equation for the *p*-NO_2 group in a number of reactions,[11a,11b] depending to some extent on the reaction medium, and similar deviations were found for other groups, e.g., OR, where resonance interactions were possible. This question is considered later. In our work, fits were improved when we used the σ_I value for *p*-NO_2, which considers only inductive effects, (based on the correlation coefficient, r), and this approach has been applied to electronic effects of *p*-OMe in some reactions[23] which are accelerated by electron donation. Most of the data in the literature are for *p*-substituents, except for reactions in organic or mixed solvents where the *m*-NO_2 derivative was also used.[18] unless specified, data were collected at 25.0 °C.

Values of ρ for reactions of H_2O, OH^-, and Br^- in micelles were found to be more positive than in water. For the spontaneous hydrolysis in CTAOMs, the value of ρ was very similar to those for solvolyses in alcohols or aqueous-organic media, which are included for comparison (Table 1). For reactions of OH^- and Br^-, ρ became more positive with an increase in the bulk of the head-group, as found earlier for ester saponification,[12c] corresponding to a decrease in polarity of the interfacial region. Details of the rate constants and values of ρ calculated by using σ_p for NO_2 are available as Supplementary material.

Values of ρ (Table 1 and 2) show that S_N2 reactions of the methyl benzenesulfonates are less sensitive to electronic effects than the saponification of phenyl benzoates, for which ρ = 1.86 or 1.76 in water, and 2.6−3.1 in cationic micelles.[12a][12c] These differences are understandable in view of the differences in the relative locations of the reaction centers and substituents in the two sets of reactions, which facilitate the transmission of electronic effects in the reactions of the phenyl benzoates. Attack of OH^- on phenyl benzoates involves a rate-limiting addition to the acyl group, which is accelerated by electron-withdrawing substituents in the benzoate ring, but in S_N2 reactions we have to consider both nucleophilic attack and loss of the leaving sulfonate ion. Comparisons of second-order rate constants in water and micelles depend on parameters whose values are uncertain, e.g., those which describe inter-ionic competition and the volume of the interfacial reaction region.[1] We therefore have to be cautious in using kinetic data for the overall reaction to compare medium properties of water and micellar interfacial regions, because under some conditions, kinetic fits are indeterminate for reactions of weakly interacting ions (e.g., OH^-) in the presence of strongly interacting ions.[3c] However, as discussed above, a comparison of the values of ρ eliminates some of these uncertainties.

The Interfacial Reaction Region

Micellar acceleration of bimolecular reactions is due largely to the concentration of the reactants in the interfacial region where local second-order rate constants are often similar, but not identical, to those in water.[1] If they were identical, substituent effects would be the same in water and micelles, which is not the case.

Comparison of second-order rate constants in water and micelles requires concentrations to be expressed in the same units, and conventionally molar concentrations are used in solution reactions. Elsewhere we have taken $V_M = 0.14$ M^{-1} (Equation 3), although it may depend on the micellar head-group and on the nature of the reactants. Values of k_2^m/k_W calculated with $V_M = 0.14$ M^{-1} for all the surfactants range from approximately 0.1−0.5 for reactions of OH^-, and 0.4−1 for reactions of Br^-. They are not very sensitive to the head-group bulk for reactions of OH^-, but an increase in bulk increases k_2^m/k_W for the reaction of Br^- (assuming $V_M = 0.14$ M^{-1}). These differences are consistent with variations in ρ (Table 2). Reactions of OH^- and Br^- probably differ in the extents of charge dispersion in transition-state formation, but differences in average locations of the very hydrophilic OH^- and the less hydrophilic Br^- in the interfacial region may also affect relative rate constants. The assumption that the micellar interface is a uniform reaction region is applicable only as a first approximation, but it rationalizes extensive rate data.[1] In addition, the increasing (positive) values of ρ for the S_N2 reactions in micelles, or in solvents of lower polarity than water, can be rationalized by considering the reaction region as uniform, and they are understandable in terms of Jencks−More O'Ferrall[24] free-energy diagrams and qualitative descriptions of medium effects on organic reactions which give evidence on the extents of bond-making and -breaking in transition states.[11,12] On the basis of data from dediazonization, Soldi et al. concluded that values of V_M are larger than those used here and increase significantly with increasing bulk of the head-group.[21b] In that event, values of k_2^m would be higher than those quoted here, especially with CTPAOH and CTBABr, but the Hammett parameters should not be affected, provided that V_M is independent of the substrate.

Electronic Effects of the Nitro Groups

We saw negative deviations from Equation 5 when we used the σ_p value of 0.78 for the *p*-nitro group. For example, Robertson's very precise data for solvolyses of substituted methyl benzenesulfonates in water and mixed solvents[18] generally gave slightly better fits to the Hammett equation when the σ_I value of 0.65 for *p*-NO_2 was used, and ρ values then became more positive, by approximately 0.1 units, than for the reactions with OH^- and Br^- (Tables 1, 2, and S10). Some of these values are from rate data at 50° or 70° C, but the quality of the fits for reaction in H_2O at 25° or 50° C with either the σ_I or σ_p parameters for the *p*-NO_2 group were essentially identical, although ρ became slightly less positive with an increase in temperature. Our value of ρ for the hydrolysis in water was similar to that from the earlier data (Table 1). There are examples of reactions in solution for which deviations from linearity of Hammett plots are evident for strongly electron-donating or -withdrawing groups with resonance interactions, when the original σ_p values are used. It is possible that electronic effects of the *p*-NO_2 group are sensitive to the reaction medium, e.g., the asymmetry of the micellar, interfacial, region may orient the *p*-NO_2 group so as to disfavor electron withdrawal by resonance, and a decrease in solvent polarity should have a similar effect. We noted that good fits to the Hammett equation have been obtained for reactions of other *p*-nitrophenyl derivatives in micelles,[12a][12b] although here the positive ρ values were higher than in our work and deviations from linearity would be less evident.

Conclusions

Application of the Hammett equation to S_N2 reactions of H_2O, OH^-, and Br^- with *p*-substituted methyl benzenesulfonates in cationic micelles gave values of ρ which were more informative than simple rate constants because they were less sensitive to assumptions regarding interfacial volumes and transfer equilibria of ions and nonionic substrates. Values obtained in this way were more positive than those in water, indicating that the polarities of the interfacial regions are lower than that of water and decreased with increasing bulk of the head group.

Experimental Section

Materials: Surfactants were samples used earlier,[9b,13] as was **1c**. Compounds **1b** and **1f** were obtained from Aldrich. The other sulfonates were prepared from the sulfonyl chloride in MeOH with Et_3N at 0° C, except for **1a**, where we used NaOMe in MeOH. − For the substrates **1a**, **1d**, and **1e**, ^1H NMR spectra were recorded on a 80 MHz Bruker instrument, in order to confirm the structures. ^1H NMR ($CDCl_3$), δ: **1a:** 3.7 (s, 3 H, CH_3), 3.9 (s, 3 H, CH_3), 7.1 (m, 2 H, 2 CH), 7.9 (m, 2 H, 2 CH); **1d**: 3.7 (s, 3 H, CH_3), 7.5−8.0 (m, 4 H, 4 CH); **1e**: 3.7 (s, 3 H, CH_3), 7.4−7.8 (m, 2 H, 2 CH), 7.8−7.9 (m, 2 H, 2 CH). Melting points: **1d**, m.p. 51−52 °C; **1e**, m.p. 59−60 °C (ref. 60.5 °C)[18a].

Kinetics: Reactions were followed spectrophotometrically at 25.0° C, as described[13,16] on HP8452 or Shimadzu 160 A instruments at the following wavelengths: **1a**, 246; **1b**, 236; **1c**, 266; **1d**,**e**, 242, **1f**, 280 nm. The substrate was added in MeOH, and the reaction mixture contained substrate (10^{-4} M) and MeOH (1 vol%). Good first-order kinetic plots were obtained with all substrates. Reactions were followed in redistilled, CO_2-free water. The least reliable data were for the reaction with Br^- in water, which was not much faster than the spontaneous hydrolysis. There may be a salt effect of NaBr on this reaction, because 0.1 M $MeSO_3Na$ decreases k_{obs} for the hydrolysis of **1a** from $6.07 \cdot 10^{-6}$ to $5.75 \cdot 10^{-6}$ s^{-1}, but it should decrease the second-order rate constants for all the substrates to similar extents. We did not have this problem with the reactions with OH^- or with Br^- in micelles which were much faster than those with water.

Data Fitting: The first-order rate constants were corrected for the minor contribution of reaction with H_2O, based on reactions in CTAOMs (Table S9) and quoted values of k_{obs} refer to reactions with OH^- or Br^-. In fitting the kinetic data to Equation 1, we used literature values of K'_{OH} and K'_{Br}.[9] Values of K_S were 50−130 M^{-1}, as is typical of compounds with this general structure, and we assumed that hydrophobic substituents would modestly increase K_S. Estimated values of k_M were insensitive to changes in K_S of ca. 10%. Values of 10^4 cmc, were taken as: 7, 5, 8, 6, 2.8 M for CTAOH, CTPAOH, CTABr, CTEABr, and CTBAbr, respectively, and as zero in 0.1 M NaOH or NaBr with very little effect on fits, especially in 0.1 M NaOH or NaBr. There were deviations between the observed and predicted rate constants in dilute surfactant, especially with the hydroxide ion surfactants, as in other systems.[9] They are due to several factors, including assumptions regarding concentrations of monomeric surfactant, as given by the cmc, perturbation of micellar structure by the substrate and possible intervention by premicelles. Addition of OH^- or Br^- improves the fits, probably by promoting micellization.

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