

Spontaneous Hydrolyses in Sulfobetaine Micelles. Dependence of Micellar Charge Effects Upon Mechanism*

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Rate constants of spontaneous hydrolyses in zwitterionic micelles of *N*-hexadecyl-*N,N*-dimethyl-3-ammonio-propanesulfonate (SB3-16) are compared with those in cationic (*n*-C₁₆H₃₃NMe₃X, X = Cl, Br, OMe; CTACl, CTABr, CTAOMe) and anionic (*n*-C₁₂H₂₅OSO₃Na, SDS) micelles. Substrates are methyl benzenesulfonate, 2-adamantyl and pinacolyl 4-nitrobenzenesulfonate, 4-bromo- and 4-nitrobenzoyl chloride, phenyl and 4-nitrophenyl chloroformate and bis(4-nitrophenyl) carbonate. Hydrolyses are micellar inhibited, except for the nitro substituted acid chlorides. Reactions with extensive bond-breaking in the transition state (S_N1 hydrolyses) are faster in SDS than in cationic and sulfobetaine micelles, but the other hydrolyses, which involve significant bond-making, are slower in SDS. Rate constants are similar in cationic and sulfobetaine micelles. These micellar charge effects are ascribed to interactions of the polar transition states with the asymmetrically charged interfacial region which complement effects of the lower polarities of micelles relative to water.

Key words: hydrolysis, deacylation, S_N1-S_N2 reactions, sulfonyl chlorides, surfactants, pseudophase treatments.

* Dedicated to Professor Smiljko Ašperger on the occasion of his 80th birthday.

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INTRODUCTION

Surfactants are amphiphiles with polar organic residues and polar or ionic groups. At concentrations above a critical micelle concentration, c.m.c., they self-assemble to form micelles which, with dilute surfactant and electrolyte, are approximately spherical with head groups in contact with water. The structures are dynamic with monomeric surfactant entering the micelles at diffusion-controlled rates. Micelles solubilize apolar solutes and ionic micelles attract counterions from bulk solution, and can perturb reaction rates and equilibria.¹⁻⁶

Zwitterionic surfactants are formally neutral, but, because they have ionic centers their effects on reactivity are different from those derived from nonionic polyethylene oxides, for example. The sulfobetaine and other betaine surfactants can have varied length alkyl tails and alkyl tethers, but trimethylene tethers are commonly used, and we designate them as: SB3-*n*, where *n* denotes the length of the alkyl tail and typically the cationic center is Me₂N⁺.⁷

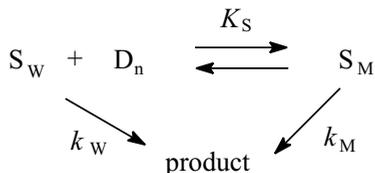
In the present work, we compare rate constants of spontaneous hydrolyses in solutions of the following ionic and sulfobetaine micellized surfactants: *n*-C₁₆H₃₃NMe₃X (X = Cl, Br, OMes), CTAX; *n*-C₁₂H₂₅OSO₃Na, SDS; *n*-C₁₆H₃₃N⁺Me₂(CH₂)₃SO₃⁻, SB3-16.

The charge of ionic micelles is partially neutralized by counter ions that are attracted to the surface and the fractional micellar charge, α , decreases from approximately 0.4 for small, high-charge density, ions to 0.2 for low-charge density ions, *e.g.*, Br⁻.^{5,6,8,9} Although sulfobetaine micelles carry no net charge they attract anions because the positive charge-density is higher than the anionic charge-density and there are specific interactions between the ammonium ion centers and polarizable, low charge-density, anions, *e.g.*, Br⁻ and ClO₄⁻.^{7,10-12} These interactions have been treated theoretically and are consistent with experimental evidence.

The interfacial region at a micellar surface can act as a reaction medium, which can be regarded as a pseudophase distinct from bulk solvent, *e.g.*, water.^{1-6,13} Quantitative analyses of bimolecular reactions in terms of this pseudophase model require estimation of local concentrations of both reactants in the micellar and aqueous pseudophases and second-order rate constants in each region.^{2-6,8,9,13} Micellar effects on many bimolecular rate constants have been treated quantitatively in terms of this model, which shows that micellar accelerations of counter-ionic reactions are, to a large extent, due to concentration of reactants in the small volume of the interfacial region.

Treatment of micellar rate effects upon spontaneous, including water-catalyzed hydrolytic, reactions, is very simple, provided that we account for

the partitioning of the substrate between water and micelles as illustrated in Scheme 1 and Equations (1) and (2) for thermal reactions slower than substrate transfer between water and micelles.



Scheme 1.

$$K_S = \frac{[S]_M}{[S]_W [D_n]} \quad (1)$$

$$k_{\text{obs}} = \frac{k_W + k_M K_S [D_n]}{1 + K_S [D_n]} \quad (2)$$

The concentration of micellized surfactant (detergent) $[D_n]$ is the total concentration less that of monomeric surfactant, given by the critical micelle concentration,¹⁴ c.m.c., and k_W and k_M are first-order rate constants in water and micelles respectively.

This treatment has been applied to spontaneous deacylations and S_N1 and S_N2 hydrolyses, largely in ionic micelles.¹⁴⁻¹⁸ With few exceptions hydrolyses are micellar-inhibited, which is understandable because polarities at micellar surfaces, as given by apparent dielectric constants, or values of E_T , are lower than those of water,¹⁹ as are concentrations of water.²⁰ However, these micellar rate effects cannot be explained solely in terms of polarity, or water and salt contents, in the interfacial region. There is also an effect of micellar charge. Regardless of values of k_M/k_W , hydrolyses of carboxylic anhydrides and diaryl carbonates are faster in cationic micelles of CTAX than in anionic micelles of SDS, but for S_N1 hydrolyses reactions are faster in SDS.¹⁵⁻¹⁸ There is less evidence on the effect of sulfobetaine micelles on rates of spontaneous hydrolyses, but they appear to behave similarly to cationic micelles.^{18,21,22} However, nonionic polyoxyethylene derived micelles modestly inhibit deacylation.¹⁶

The substrates are: methyl benzenesulfonate, (MeOBs), pinacolyl and 2-adamantyl 4-nitrobenzenesulfonate (PinONos and 2-AdONos), 4-bromo- and 4-nitrobenzoyl chloride, phenyl and 4-nitrophenyl chloroformate and bis-(4-nitrophenyl) carbonate. Some results on the hydrolysis of methyl naphthalene-2-sulfonate (MeONS)²¹ are included for comparison.

EXPERIMENTAL

Materials were generally commercially available, and had been used earlier.^{17,21,22} Reactions were followed in redistilled water and substrates, dissolved in MeCN, were added to stirred solutions with a spring-loaded Hamilton syringe so that the final solutions contained only 1.5% MeCN (vol. fraction). Reactions were followed at 25.0 °C (298 K) in Beckman or HP diode array spectrophotometers, depending on the reaction rate, and were cleanly first-order. Substrate concentrations were *ca.* 10⁻⁴ mol dm⁻³ and 10⁻³ mol dm⁻³ strong acid, corresponding to the surfactant counter-ion, was added to suppress any reaction with OH⁻. A few experiments with the acid chlorides were also followed in 10⁻² mol dm⁻³ acid, values of *k*_{obs} agreed within 5% and means are quoted in the Tables of rate data for the 4-nitro derivatives. Reactions were followed at the following wavelengths/nm: MeOBs, 262; PinONos and 2-AdONos, 255; 4-BrC₆H₄COCl, 245; 4-NO₂C₆H₄COCl, 260; PhOCOCl, 270; 4-O₂NC₆H₄OCOCl, 346; (O₂NC₆H₄O)₂CO, 320.

RESULTS AND DISCUSSION

Rate Constants in Micelles

Values of *k*_{obs} for hydrolyses of the less hydrophobic substrates are in Figure 1, together with data for reactions in ionic micelles.¹⁷ Results for S_N1 and S_N2 hydrolyses are in Table I. Values of *k*_{obs} for the nitrobenzene sulfonates are too low in surfactant solutions to be shown conveniently in a Figure. Data for deacylations in SB3-16 are in Table II.

The pseudophase treatment, Scheme 1, is often used to calculate values of *k*_M, and it is necessary to consider the impact of a variety of approximations and assumptions. We assume that values of *K*_S, *k*_W and *k*_M are unaffected by incorporation of substrate in the micelles or by micellar growth induced by substrate or an increase in [surfactant]. Analysis of rate data in dilute surfactant is complicated by possible substrate-induced micellization, or reaction in premicelles,²³ and the concentration of monomeric surfactant, as given by the c.m.c., is often treated as a disposable parameter.⁵

Equation (2) can be rearranged as:¹⁴

$$\frac{1}{(k_W - k_{\text{obs}})} = \frac{1}{(k_W - k_M)} + \frac{1}{K_S (k_W - k_M) [D_n]} \quad (3)$$

which allows estimation of *k*_M and *K*_S, but requires reliable values of *k*_W and c.m.c., and is unsatisfactory when *k*_W ≫ *k*_M.¹⁴ We therefore initially used data obtained with [surfactant] such that *K*_S[*D*_n] ≫ 1 and Eq. (2) simplifies to:

$$k_{\text{obs}} = \frac{k_W}{K_S [D_n]} + k_M \quad (4)$$

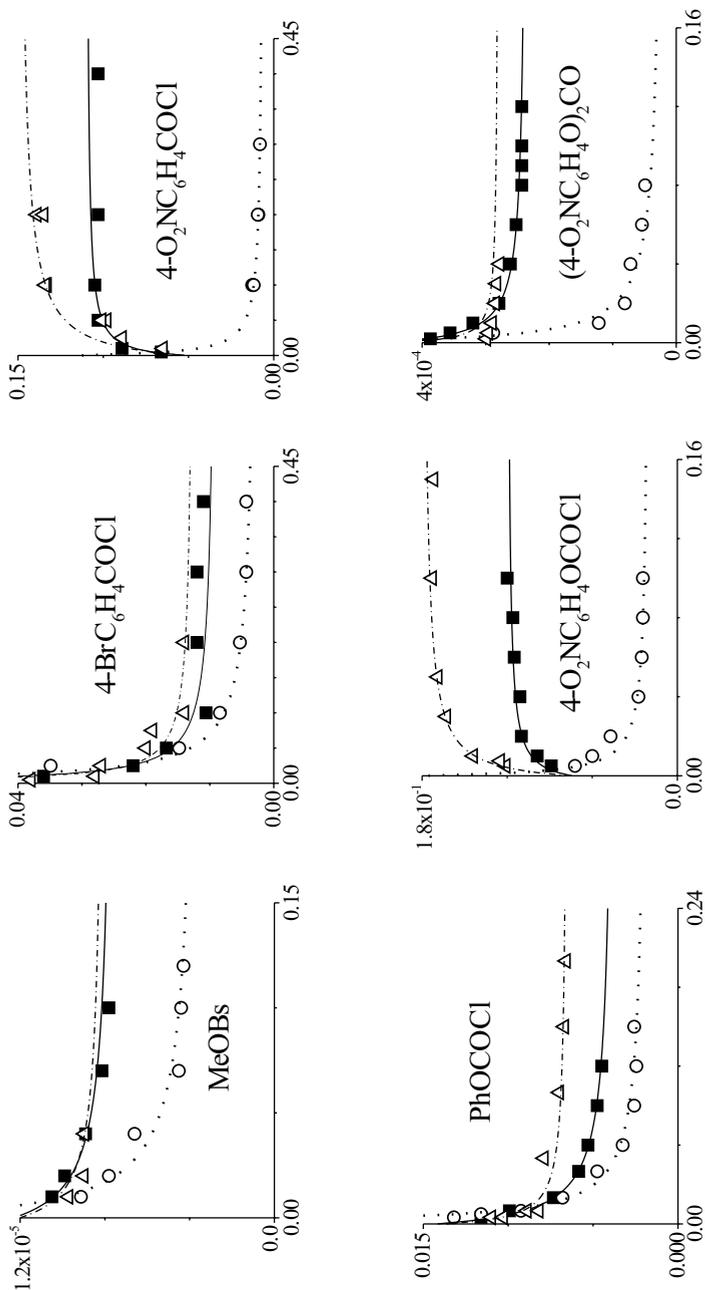


Figure 1. Plots of k_{obs} / s^{-1} , against [surfactant] / mol dm⁻³ (x-axis): ■, CTAX; △, SDS; O, PhOCOCl; △, 4-BrC₆H₄COCl; △, 4-O₂NC₆H₄COCl; △, 4-O₂NC₆H₄CO; △, (4-O₂NC₆H₄O)₂CO. Data for reactions in CTAX and SDS are from Ref. 17 and the other data are in Tables I and II.

TABLE I
S_N hydrolyses in SB3-16

[SB3-16] mol dm ⁻³	10 ⁴ <i>k</i> _{obs} / s ⁻¹		
	MeOBs	PinONos	2-AdONos
	0.12	700	95
0.001			1.81
0.003			1.68
0.005			0.884
0.01	0.09h	17.8	0.224
0.02	0.090	12.5	0.152
0.025			
0.03		8.19	0.155
0.04	0.090		
0.05		6.23	
0.075		4.25	
0.16		4.55	

With very hydrophobic substrates, *e.g.*, the nitrobenzene sulfonates, rate constants decrease very sharply in dilute surfactants, even at concentrations close to, or below, the c.m.c. In these cases we use Eq. (4) to estimate *k*_M, and values of *k*_{obs} level-off at high [surfactant].

Fits of variations of *k*_{obs} with [surfactant] are shown in Figure 1 and values of *k*_W and *k*_M, and *K*_S for the less hydrophobic substrates, are in Table III. Those with ionic micelles are from data in Ref. 17, and for reactions in SB3-16 are from data in Tables I and II. Results on the hydrolysis of methyl naphthalene-2-sulfonate (MeONs)²¹ are compared with those for the less hydrophobic MeOBs.

Values of *K*_S are consistent with those for chemically inert solutes that have otherwise similar structures to our substrates,²⁴ and treatments of micellar binding show the importance of solute hydrophobicity.²⁵ Fits are insensitive to the value of the c.m.c, except in very dilute surfactant, and, as in many reactions, there are rate effects at [surfactant] below the c.m.c. in water.^{6, 23} We used the following fitting values of the c.m.c. / mmol dm⁻³: CTABr, 0.6; CTACl, CTAOMes, 1.0; SDS, 6.0; SB3-16, 0.1. Inhibition of hydrolyses in very dilute surfactant can be ascribed to reactant-induced micellization or to reaction in premicelles.²³ Except for nitro compounds reactions are slower in micelles than in water, especially for S_N1 reactions. These observations are consistent with extensive work on spontaneous hydrolyses at acyl and alkyl

TABLE II
Deacylations in SB3-16

[SB3-16] mol dm ⁻³	10 ⁴ <i>k</i> _{obs} / s ⁻¹				
	O ₂ NC ₆ H ₄ COCl	BrC ₆ H ₄ COCl	O ₂ NC ₆ H ₄ OCOC	PhOCOC	(O ₂ NC ₆ H ₄ O) ₂ CO
	530	1900	760	136	4.50
0.002					2.99
0.005		380	1210	106	2.96
0.0075			1250	86	
0.01	650	280	1440		2.90
0.02					2.85
0.025	890	270			
0.03			1630		2.83
0.04					2.78
0.05	995	200	1690	79	
0.075	1050	190			
0.10	1340	140	1730	70	
0.15			1720	67	
0.20	1370	140	1730	66	

TABLE III
Fitting parameters in micellar-mediated hydrolyses^a

Substrate	10 ⁴ <i>k</i> _w / s ⁻¹	10 ⁴ <i>k</i> _M / s ⁻¹		
		CTAX	SDS	SB3-16
MeOBs	0.12	0.075(60) ^b	0.035(80)	0.080(80)
MeONs	0.125	0.073 ^b	0.028	0.070 ^c
PinONos	700	3.5 ^d	6.5	3.2
2-AdONos	95	0.10 ^d	0.33	0.15
4-BrC ₆ H ₄ COCl	1900	900(500) ^d	250(350)	1250(650)
4-O ₂ NC ₆ H ₄ COCl	530	1100(100) ^d	62(80)	1500(50)
PhOCOC	136	37(90) ^e	18(120)	65(170)
4-O ₂ NC ₆ H ₄ OCOC	760	1200(160) ^e	200(160)	1800(180)
(O ₂ NC ₆ H ₄ O) ₂ CO	4.5	2.35(200) ^e	0.20(240)	2.8

^a Values in parentheses are *K*_S / mol⁻¹ dm³; ^b X = OMe; ^c SB3-14, Ref. 21; ^d X = Cl; ^e X = Br.

centers¹⁴⁻¹⁸ and with evidence that reaction is in an interfacial region whose polarity and water content are modestly lower than those of water.^{19,20} The S_N1 reactions are significantly inhibited because they are very sensitive to solvent polarity and water content,^{26,27} and the hydrophobic substrates may be incorporated somewhat more deeply in the micelle than the other substrates.

The higher reactivities of the nitro substituted acid chlorides in cationic and sulfobetaine micelles, relative to water, require comment, but the modest micellar inhibitions of deacylation and the larger effects on S_N1 reactions by SB3-16 are as expected on the basis of rate data in ionic micelles.¹⁴⁻¹⁸ In some cases rate constants of hydrolysis in micelles are qualitatively similar to those in mixed aqueous-organic solvents of relatively high water content.

Chloroformates are typically less reactive than the corresponding acyl chlorides, which is ascribed to initial state stabilization due to resonance.²⁸ However, in both water and micelles 4-nitrophenyl chloroformate is more reactive than 4-nitrobenzoyl chloride (Tables II and III), due to resonance interaction between the nitro and aryloxy moieties and the consequent inductive effect.

Source of Micellar Charge Effects

Relative rate constants of hydrolyses in water and cationic, anionic and sulfobetaine micelles are summarized in Table IV, with rounded-off values of relative rate constants. Rate constants in water and micelles are related qualitatively to mechanism and, for a given class of compounds, *e.g.*, the acid chlorides, to substituent electronic effects, especially for 4-NO₂. Substrate hydrophobicity is not of major importance, although it affects overall rate constants by changing K_S (Scheme 1).

The charges of the head groups of ionic micelles are partially neutralized by counterions creating electrical asymmetry in the double-layer interfacial region.^{1-6,8,9} Transition state formation in hydrolyses of nonionic substrates involves charge separation and interactions of these partial charges with the ionic interfacial region will affect hydrolysis rates. For example, in an S_N1 reaction positive charge developing on the organic residue^{26,27} interacts unfavorably with cationic head groups.^{14,17,18} Conversely, in hydrolysis of carboxylic anhydrides, for example, negative charge develops on the organic moiety and interactions will be unfavorable with anionic and favorable with cationic, head groups.

These interactions may reinforce or oppose the inhibitions of spontaneous hydrolyses due to the low polarity and decreased water content of the micellar interfacial region, relative to water, depending on the sensitivity of a given reaction to solvent.^{26,27} The plots in Figure 1 show that SB3-16 and

TABLE IV
Effects of micellar charge upon hydrolyses

Substrate	k^+ / k_W	k^- / k_W	k^{SB} / k_W	k^+ / k^-	k^{SB} / k^+
MeOBs	0.63	0.29	0.67	2.1	1.1
MeONs	0.58	0.22	0.56	2.6	1.0
PinONos	0.005	0.009	0.0046	0.54	0.9
2-AdONos	0.001	0.0035	0.0016	0.4	1.5
4-BrC ₆ H ₄ COCl	0.47	0.13	0.66	3.6	1.4
4-O ₂ NC ₆ H ₄ COCl	2.1	0.12	2.8	18	1.3
PhOCOCl	0.27	0.13	0.48	2.1	1.8
4-O ₂ NC ₆ H ₄ OCOCl	1.6	0.26	2.4	6.0	1.5
(4-O ₂ NC ₆ H ₄ O) ₂ CO	0.5	0.044	0.62	12	1.2
4-MeOC ₆ H ₄ SO ₂ Cl	0.014	0.012	0.012	1.1	0.9
4-MeC ₆ H ₄ SO ₂ Cl	0.026	0.009	0.026	2.9	1.0
PhSO ₂ Cl	0.052	0.01	0.049	5.2	0.9
4-BrC ₆ H ₄ SO ₂ Cl	0.21	0.038	0.18	5.5	0.9
4-O ₂ NC ₆ H ₄ SO ₂ Cl	0.86	0.041	0.90	21	1.0

cationic micelles have similar effects on rates of hydrolysis, which differ significantly from the effects of SDS, whether micelles accelerate or inhibit hydrolysis, *cf.*, Tables III and IV. The geometry of sulfobetaines creates an electrical double layer at the micellar surface similar, qualitatively, to that at surfaces of cationic micelles.^{7,10-12}

Comparisons of rate constants in sulfobetaine and ionic micelles (Table IV) are consistent with the assumption that charge asymmetry in the interfacial region has major effects on rates of spontaneous hydrolyses in micelles, relative to water.^{18,22,29} This generalization also applies to spontaneous decarboxylation³⁰ and dephosphorylation.³¹ Values of k_M are generally similar in micelles of SB3-16 and CTAX, and for hydrolyses of 4-nitrobenzoyl chloride and 4-nitrophenyl chloroformate, where bond-making should be most important, $k_M / k_W > 1$, despite depletion of water in the interfacial region.

The balance between bond-making and breaking has been analyzed in detail for hydrolyses at alkyl centers which follow the S_N2-S_N1 mechanistic continuum,^{26,27} but the situation is more complex for spontaneous deacylation, especially of acid chlorides and related compounds. Bond-making appears to be dominant in hydrolyses of diaryl carbonates,^{14,16,17} and reactions

are always faster in cationic micelles with quaternary ammonium head groups than in anionic micelles, *e.g.*, of SDS, although, except for hydrolysis of bis(2,4-dinitrophenyl) carbonate,¹⁶ reactions are micellar inhibited. However, hydrolysis of bis(4-nitrophenyl) carbonate is only modestly inhibited by micelles of CTABr and SB3-16 (Table II and Ref. 18).

Spontaneous solvolyses of the chloroformates are well studied, with mechanistic evidence relating to medium and structural effects, and it appears that bond-making is dominant.²⁸ Consistently hydrolyses are faster in cationic and sulfobetaine than in anionic micelles and the presence of a 4-nitro group generates an increase of rate by cationic and sulfobetaine micelles, relative to water (Table II and Ref. 18).

The situation is more complex for hydrolyses of acyl halides where extents of bond-making and breaking appear to be highly dependent on substrate structure and the nature of the reaction medium.^{32,33} Charge development in the organic moiety in the transition state can involve both the leaving anion and the carbonyl oxygen, but, except in special situations, water, or other hydroxy molecule, is involved nucleophilically and probably also as a general base.³²⁻³⁴

Kevill and Wang, in reviewing evidence on the mechanisms of solvolyses of acyl halides, consider, as one limit, addition giving a tetrahedral species, which then rapidly loses halide ion, and, as the other, a concerted S_N1-S_N2 -like reaction.³³ Electron-donation favors loss of halide ion, with build-up of positive charge at the acyl reaction center, within this mechanistic continuum; and electron-withdrawing substituents promote strong nucleophilic participation by water with an increase in electron density adjacent to the reaction center, *e.g.*, on carbonyl oxygen.^{18,32,33}

This relationship between micellar charge effects and the extents of bond-making and breaking is not restricted to reactions at alkyl and acyl centers. Micelles inhibit spontaneous hydrolyses of benzenesulfonyl chlorides, but there is a strong dependence on micellar charge which is related to electronic effects of substituents.²² Values of k_W follow the sequence 4-MeO > 4-Me > 4-H > 4-Br < 4-NO₂ indicating a balance between extents of bond-breaking and making in the transition state. This balance is also evident in the values of k^+ / k^- and k^+ / k^{SB} and of k_M / k_W (Table IV).

Although we can rationalize variations of k_M for a given reaction with micellar head-group charge it is more difficult to explain variations of k_M / k_W in simple terms, because of the problem in comparing properties of micellar interfacial regions and solvents at the quantitative level. For example, polarities, or apparent dielectric constants, estimated by using micellar-bound probes can be compared with those of a range of solvents¹⁹ and the local concentrations of water are being estimated by dediazonization trapping.²⁰ Quali-

tatively, polarities are higher at surfaces of anionic than cationic micelles,¹⁹ but there is some dependence on the probe, and analogies between effects of micelles and mixed aqueous-organic solvents on polarities and on rates and equilibria, although qualitatively reasonable, are less useful quantitatively. At the simplest level we can suppose that micellar effects upon rates and equilibria involve dispersive and electrostatic interactions. To the extent that the former should not be very dependent upon charge, comparisons of k^+ with k^- or k^{SB} approximately factor-out the specific dispersive interactions and, to a first approximation, reflect the electrostatic interactions.¹⁷

Rate constants in micelles, relative to those in water, depend on reaction mechanism and substrate structure. Substrate hydrophobicity is not very important in controlling reactivity, although it strongly affects transfer from water to micelles.^{24,25} As a result, MeOBs and MeONs²¹ behave similarly in micelles, provided that transfer equilibria are taken into account (Tables III and IV). This conclusion is reasonable for alkyl derivatives where charge is not dispersed into the organic moiety in formation of the transition state. The data in the last two columns of Table IV show the simple relationship between extents of bond-making and breaking in the transition state and the effect of charge in the micelle or head groups. The structure of the head-group does not appear to be very important, unless a phenyl group is present,¹⁶ and differences in counteranions have only small effects,¹⁷ unless, like the halide ions at alkyl centers, they can react nucleophilically, or change micellar structure. The similar behaviors of cationic and sulfobetaine micelles show that the latter behave like cationic micelles, but with no overall charge, *i.e.*, with zero fractional charge. However, due to differences in charge densities at the cationic and anionic surfaces they interact with even high-charge density anions and specifically with polarizable, low-charge density anions.^{7,10-12}

Garcia-Rio and Leis examined hydrolyses of substituted benzoyl chlorides in water-in-oil microemulsions of AOT-isooctane (AOT = sodium bis(2-ethylhexyl)sulfosuccinate) and concluded that an increase in $W = [\text{H}_2\text{O}] / [\text{AOT}]$ could change the mechanism of hydrolysis, depending on the substituent.³⁵ This conclusion depends on the assumption that reaction is wholly in the interfacial region, rather than in the aqueous microdroplet, which is not always correct, even for very hydrophobic substrates.³⁶

Brønsted-Bjerrum Treatment

In the pseudophase treatment water and micelles are treated as distinct reaction regions, and rate constants in each region are estimated after accounting for transfer equilibria.¹⁻⁶ In an alternative approach, shown for a

spontaneous hydrolysis, rate constants are written in terms of the Brønsted-Bjerrum rate equation (4).³⁷

$$k_{\text{obs}} = k_{\text{W}} \frac{\gamma_{\text{S}}}{\gamma_{\ddagger}} \quad (4)$$

The standard state is water and incorporation of substrate in micelles decreases γ_{S} and the overall rate effect depends on stabilization, or destabilization, of the transition, relative to the initial, state.³⁸ Activity coefficients, or transfer free energies, are directly related to partition constants, P_{S} , rather than to K_{S} , but the two are related by:¹³

$$K_{\text{S}} = P_{\text{S}} V_{\text{M}} \quad (5)$$

where V_{M} is the molar volume of the micellar reaction region. Values of V_{M} are assumed to be in the range 0.14–0.37 dm³ mol⁻¹, and probably depend to some extent on the structure of the head group.^{1–5} As a result, the pseudophase treatment (Scheme 1 and Eq. (2)) factors out the initial state stabilization due to substrate binding to the micelles, and the value of $k_{\text{M}} / k_{\text{W}}$ reflects the property of the interfacial region as a reaction environment.

The pseudophase treatment and that based on the Brønsted-Bjerrum equation, or the transition state formalism, are alternative ways of treating micellar rate effects.³⁹ The pseudophase treatment is descriptively convenient for reactions of organic compounds which bind strongly to micelles or other association colloids and reaction in the aqueous medium is relatively unimportant. However, the situation is very different for some interionic reactions which occur largely in the aqueous medium and the Brønsted-Bjerrum equation accommodates the ionic strength effect of micelles which behave as macro-ions.³⁷

In principle it should be possible to predict micellar effects upon activity coefficients of transition states of reactions or organic substrates. Linear free energy treatments are being used to predict transfer free energies of nonionic solutes between water and micelles,²⁵ and coulombic contributions to ion-micelle interactions have been treated theoretically.^{9,37,38}

CONCLUSIONS

For spontaneous hydrolyses at alkyl centers there is an evident relationship between molecularity and the micellar charge effect, because bimolecular attack upon pinacolyl and 2-adamantyl derivatives is excluded sterically and a methyl cation is an unlikely intermediate in aqueous media.^{26,27} The other substrates that we, and others, have examined react with nucleophilic

water with assistance from a general base, which is typically a second water molecule.^{14–16,28,33,34} Participation of the second water molecule disperses the positive charge that builds up on the nucleophilic water molecule. This process is often considered to be a slow proton transfer, but it could involve strong hydrogen bonding which disperses charge.

However, even though hydrolyses of the acid chlorides involve water as a nucleophile in the rate limiting step, values of k^+ / k^- and k^{SB} / k^+ are indicative of major differences in extents of bond-making and breaking in the transition state due to substituent electronic effects.

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SAŽETAK

Spontana hidroliza sulfobetainskih micela. Ovisnost efekata naboja micela o mehanizmu

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Konstante brzine spontane hidrolize u zwitterionskim micelama *N*-heksadecil-*N,N*-dimetil-3-amonio-propansulfonata (SB3-16) usporedene su s onima u kationskim ($n\text{-C}_{16}\text{H}_{33}\text{NMe}_3\text{X}$; X = Cl, Br, OMes; CTACl, CTABr, CTAOMes) i anionskim ($n\text{-C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$; SDS) micelama. Supstrati su metil-benzensulfonat, 2-adamantil- i pinakolil-4-nitrobenzensulfonat, 4-bromo- i 4-nitrobenzoil-klorid, fenil- i 4-nitrofenil-kloroformiat i bis(4-nitrofenil)-karbonat. Hidrolize su inhibirane micelama, osim za nitrosubstituirane kiselinske kloride. Reakcije sa znatnim prekidom veze u prijelaznom stanju ($\text{S}_{\text{N}}1$ hidrolize) brže su u SDS nego u kationskim i sulfobetainskim micelama, no druge hidrolize koje uključuju znatno stvaranje veze polaganije su u SDS. Konstante brzine slične su u kationskim i sulfobetainskim micelama. Ti efekti micelarnog naboja pripisuju se interakcijama polarnih prijelaznih stanja s asimetrično nabijenim područjem na granici faza koje prate efekte smanjene polarnosti micela s obzirom na vodu.