Solvolysis of Substituted Benzoyl Chlorides in Nonionic and Mixed Micellar Solutions

P. Campos-Rey,[†] C. Cabaleiro-Lago,^{*,†,‡} and P. Hervés[†]

Department of Physical Chemistry, Faculty of Chemistry, University of Vigo, 36310 Vigo, Spain, and Department of Biochemistry and Structural Biology, Center for Molecular Protein Science, 22100 Lund University, Lund, Sweden

Received: August 10, 2010; Revised Manuscript Received: September 21, 2010

The solvolysis of substituted benzoyl chlorides is sensitive both to substituent electronic effects and to medium effects. The solvolysis reactions of substituted benzoyl chlorides have been analyzed in the presence of nonionic micelles. The reaction is inhibited or catalyzed depending on the reaction mechanism, dissociative or associative, respectively. The micellar effects observed can be related to the low water content and low polarity of the interface as well as an increase of the nucleophilic character of the interfacial water. Moreover, the effect of the micellar surface charge on the solvolysis mechanism with high associative character was systematically studied. Mixed micelles of nonionic—ionic surfactants with a variable ionic content were prepared and characterized regarding charge and polarity. A correlation between the net charge of the micelles and the rate constants at the micellar interface was observed. The results suggest that the transient state for this mechanism is highly stabilized in a positively charged environment while the negative surface given by anionic micelles strongly inhibit the solvolysis reaction.

Introduction

The solvolysis of benzoyl chlorides has been shown to proceed via different mechanisms depending on both the electronic group at the aromatic ring and the solvent. Diverse mechanisms have been proposed through the years,¹⁻⁴ but, as a summary (see scheme 1), we can classify the solvolysis mechanism into two limiting cases: (a) associative mechanism (association-elimination) with the formation of a tetrahedral intermediate and (b) dissociative mechanism with varying extents of nucleophilic solvation of the developing carbocationlike species (S_N1-S_N2 like mechanism with bond-breaking ahead of bond-forming). Benzoyl chlorides with electron-donating substituents react through a dissociative pathway that is generally affected by the polarity and water content of the medium. Electron-withdrawing groups favor an associative mechanism poorly affected by polarity and strongly dependent on solvent nucleophilicity. The percentage of dissociative or associative character in the mechanism is defined by the nature of the substituent as well as by the properties of the reaction medium.

Micelles are highly dynamic, often polydisperse aggregates, formed from single-chain surfactants⁵ beyond the critical micelle concentration, cmc. Micellization is primarily driven by bulk hydrophobic interactions between the alkyl chains of the surfactant monomers and usually results from a favorable entropy change.⁶ Kinetically, micelles make a highly appealing reaction medium. Because of their physical and chemical characteristics, they can inhibit chemical reactions or they can catalyze reactions by acting as microreactors.^{7–11} Most of the hydrolysis reactions provide an excellent opportunity for comparisons of micellar medium effects. On the basis of the mechanisms of these hydrolytic processes, one expects that properties of the micelles, such as the lower local water concentration in the micellar Stern region, the polarity of the

SCHEME 1



micelles, and the local charge in the micellar Stern region resulting from incomplete counterion binding, play an important role in the catalysis or inhibition of these processes.¹² Hence, spontaneous hydrolyses that are accelerated by an increase in solvent polarity are inhibited^{13–16} in micellar solutions and those hydrolytic processes that are accelerated by a decrease in solvent polarity^{13,17} or an interfacial dehydration¹⁸ are micellar-accelerated.

Solvolysis reactivity of benzoyl chlorides is highly dependent upon media properties. These reactions have been studied in different microheterogenous media such as ionic micelles, 13-16,18-20 vesicles,^{21,22} and microemulsions.^{23–25} In this article, a kinetic study for a series of substituted benzoyl chlorides (see Scheme 1) in the presence of nonionic micelles of Brij35 was performed. This approach allows us to evaluate the effect of the nature of the substituents on the potential catalytic/inhibitory effect of the nonionic surfactant. Besides, we have used mixed micelles Brij35/CTAC and Brij35/STS to systematically study the effect of the variation of the micellar surface charge on the acceleration/inhibition of solvolysis reactions. The purpose of the present work was to gain insight into the interfacial effects on the reactivity of organic chemical processes in micellar systems and extend our work on hydrolysis reactions to different microheterogeneous media, viz., nonionic micelles and mixed micelles of nonionic/ionic surfactant.

^{*} Corresponding author. E-mail: Celia.Cabaleiro-Lago@biochemistry.lu.se. Phone: +46462228252.

[†] University of Vigo.

^{*} Lund University.

Experimental Section

Materials. All the reagents, substituted benzoyl chlorides (XBz, X = 4-Me, 3-Cl, 3-CF₃, 4-CF₃, 3-NO₂, and 4-NO₂), polyoxyethyleneglycol dodecyl ether (Brij35), cetyl trimethylammonium chloride (CTAC), and pyrene from Aldrich, and sodium tetradecyl sulfate (STS) from Alfa Aesar, were used as received. The stock solutions of benzoyl chlorides were prepared in acetonitrile (Aldrich). For aqueous solutions, double distilled and deionized water was used and reactions were carried out in dilute HCl (0.1 M) to eliminate reaction with adventitious base.

Surface Tension. The critical micelle concentration values were determined by surface tension measurements with a Krüss Digital Tensiometer K9 at 25.0 ± 0.1 °C.

 ζ -Potential Measurements. Micellar electrophoretic mobilities were measured using a Malvern Zetasizer 2000. The ζ -potentials were calculated using the Smoluchowski equation. All samples were used in a concentration over the cmc and filtered previous to the measurement. Measurements were done in filtered water at 25.0 \pm 0.1 °C. Size measurements were performed simultaneously to ensure homogeneity of the micellar solution.

Pyrene Fluorescence Spectra. Pyrene (from Aldrich) was dissolved in ethanol to a concentration of 2 mM. An aliquot of 10 μ L was dried in vials for total ethanol evaporation. The required volume of 0.1 M HCl or acid micellar solution was added to a final concentration of 1 μ M pyrene. The fluorescence emission spectra were recorded using a FluoroMax-3 fluorometer. The ratio between the intensities of the first and third vibronic peaks in the fluorescence emission spectrum of the polarity of the local environment of pyrene. Pyrene was excited at $\lambda = 310$ nm, and the ratio between the intensities and of the first (I₁) and third (I₃) vibronic peaks located at 373 and 383 nm, respectively, was used to calculate micropolarity.

Kinetics. Faster solvolysis reactions (4-MeBz, 4-HBz, and 4-ClBz) were followed spectrophotometrically in an Applied Photophysics SX-18MV Stopped-Flow Reaction Analyzer thermostatted with a Polyscience water bath and a 1:25 asymmetric mixing kit. Slower solvolysis reactions (3-ClBz, 3-CF₃Bz, 4-CF₃Bz, 3-NO₂Bz, and 4-NO₂Bz) were followed in a Hewlett-Packard 8453 UV-vis spectrophotometer. All experiments were carried out at 25.0 \pm 0.1 °C The percentage of acetonitrile in the reaction mixture was always less than 4% by volume. The wavelengths used were between 240 and 265 nm. The concentration range of the different benzoyl chlorides was usually 8 \times 10⁻⁵ M. Kinetic data were always satisfactorily fitted by the first-order integrated rate equations, and therefore k_{obs} denotes the pseudo-first-order rate constant. Experiments were reproducible to within 3%. Rate constants were not affected by the addition of HCl.

Results

1. Solvolysis of Substituted Benzoyl Chlorides in Nonionic Micelles. The solvolysis reaction of different substituted benzoyl chlorides is affected by the presence of nonionic micelles of Brij 35. Figure 1 shows the influence of micellized Brij 35 surfactant $[D_n]$, varied between 0.2 and 20 mM, on the normalized pseudo-first-order rate constant (k_{obs}/k_w) for the solvolysis of the different substituted benzoyl chlorides. Cmc of Brij 35 in HCl (cmc = 0.11 mM) was obtained by surface tension and was subtracted from the total surfactant concentration to give $[D_n]$. As shown in Figure 1, the effect of the micelles depends on the substituent on the aromatic ring. In general, the rate constant decreases when the micellar concentration in-



Figure 1. Normalized observed rate constant (k_{obs}/k_w) vs the concentration of micellized surfactant $[D_n]$ for the different benzoyl chlorides. The solid lines represent the best fit of eqs 1 or 2 to the experimental data (see text).

SCHEME 2



creases. However, in the case of 4-NO₂Bz an increase of k_{obs} is observed, and the observed rate constant for 3-NO₂Bz does not change significantly.

The kinetic effect on the pseudo-first-order rate constant can be analyzed on the basis of the pseudophase model^{26,27} which considers the system divided in two different regions (see Scheme 2): a micellar pseudophase and an aqueous pseudophase. The substrate is distributed between the continuous medium and the interface, and the solvolysis reaction can take place in both pseudophases.

On the basis of this reactant distribution, we can obtain eq 1.

$$k_{\rm obs} = \frac{k_{\rm w} + k_{\rm m} K_{\rm S}[{\rm D_n}]}{1 + K_{\rm S}[{\rm D_n}]} \tag{1}$$

The substrate, S, associates with micellized surfactant, D_n , with an association constant, K_S . k_m and k_w are the first-order



Figure 2. Inverse of the normalized observed rate constant (k_w / k_{obs}) vs micelles concentration for (\bullet) 4-MeBz and (\bigcirc) 3-CF₃Bz. The solid line shows the best linear fit of eq 3 to experimental data for 4-MeBz.

TABLE 1: Kinetic Parameters for Solvolysis of Benzoyl Chlorides in Brij 35 Micelles at 25 °C Obtained by the Fitting of Eqs¹ and ²

substrate	$k_{\rm w}/{ m s}^{-1}$	$k_{\rm m}/{\rm s}^{-1}$	$K_{\rm S}/{ m M}^{-1}$	$k_{\rm m}/k_{\rm w}$
4-MeBz	6.44 ± 0.15		472 ± 27	
4-HBz	1.10 ± 0.04		187 ± 18	
4-ClBz	0.175 ± 0.005		411 ± 37	
3-ClBz	0.093 ± 0.003	0.009 ± 0.001	764 ± 100	0.10
3-CF ₃ Bz	0.048 ± 0.001	0.013 ± 0.002	1089 ± 145	0.28
4-CF ₃ Bz	0.059 ± 0.001	0.028 ± 0.001	534 ± 41	0.48
3-NO ₂ Bz	0.044^{a}			1^a
$4-NO_2Bz$	0.080 ± 0.001	0.089 ± 0.001	2444 ± 1111^{b}	1.11

^{*a*} Value from the reaction in absence of micelles. $k_{\rm m}$ is assumed to be equal to $k_{\rm w}$ (see text). ^{*b*} Uncertain association constant due to the small difference between $k_{\rm w}$ and $k_{\rm m}$.

rate constants in the micellar and aqueous pseudophases, respectively.

If no reaction in the micellar interface occurs, the equation can be simplified and arranged as follows,

$$k_{\rm obs} = \frac{k_{\rm w}}{1 + K_{\rm S}[{\rm D_n}]} \tag{2}$$

$$\frac{1}{k_{\rm obs}} = \frac{1}{k_{\rm w}} + \frac{K_{\rm s}}{k_{\rm w}} [\mathrm{D_n}] \tag{3}$$

Equations 2 and 3 are distinct presentations of the same equation. Equation 3 can provide information about the extent of the reaction in the micellar medium. A linear relationship between the inverse of k_{obs} and micelle concentration indicates that the reaction in micelles is nonexistent or negligible with respect to the reaction in water.

This type of linear relationship was observed for 4-MeBz, 4-HBz, and 4-ClBz. The rest of the substrates deviate strongly from the linear trend. Figure 2 shows two examples of different behavior. According to the deviation from linearity, either eq 1 or 2 was applied to the different experimental data set in order to obtain the kinetic parameters for the reaction. Table 1 summarizes the kinetic parameters obtained from the best fittings shown graphically in Figure 1.

The decrease of the observed rate constant with the addition of micelles can be explained by the partitioning of the substrates between the aqueous and micellar pseudophases. Substrates tightly associate to the micelles because of their low solubility in water. In the case of no reactivity in the micellar aggregates (or extremely slow reaction with respect to the reaction in water, e.g., 4-MeBz, 4-HBz, and 4-ClBz), sequestering of the substrates leads to the decrease of the observed reaction rate. For substrates that react at the micellar interface, the decrease in the observed reaction rate is not so sharp (3-ClBz, 3-CF₃Bz, 4-CF₃Bz, 3-NO₂Bz). Furthermore, an increase in k_{obs} can be observed (4-NO₂Bz) if the rate constant at the micellar interface is higher than the rate constant in bulk water.

Table 1 shows the values of the association constants of the different benzoyl chlorides to Brij 35 micelles. We find larger values of the association constants in Brij 35 micelles than those reported for ionic micelles¹⁹ although the same order of magnitude is observed for studies of solvolysis of benzoyl chloride in vesicles performed with similar experimental resources. Discrepancies can originate from inaccurate determination of rate constants at low surfactant concentration for fast reactions.

The differences in the reactivity at the micellar interface can be explained within the framework of the competition between reaction mechanisms (associative and dissociative) for the solvolysis reaction of the studied substrates (see Introduction).^{1,3,4} Both mechanisms are affected by the polarity and water content of the media. However, in the case of a reaction proceeding via a dissociative mechanism, the polarity effects are more significant and the reaction rate decreases sharply as the concentration of water and polarity decreases.⁴ The dissociative mechanism with bond-breaking preceding bond-forming and with possible nucleophilic assistance proceeds through a carbocation-like intermediate. The developed positive charge at the carbonyl center is stabilized by electron-donating substituents. Therefore, benzoyl chlorides with electron-donating substituents react preferentially by means of a dissociative mechanism in highly aqueous media. 4-MeOBz reacts via a dissociative pathway over a full range of solvents while 4-MeBz, parent compound, and 4-ClBz can react by either the dissociative or associative mechanism depending on the properties of the solvent. For example, the mechanism changes occur at different ethanol contents in ethanolic mixtures depending on the benzoyl chloride (90-95%, 80-60%, and 50-60% ethanol for 4-MeBz, 4-HBz, and 4-ClBz, respectively).²

Nonzero values for the reaction rate at the interface are reported in similar systems for the solvolysis of 4-MeOBz, 4-MeBz, 4-HBz, and 4-CIBz.^{19,21} These reported reaction rates indicate that the substrates react at the Brij 35 micellar interface but with a very low reaction rate with respect to the reaction in water. Unfortunately, because of the limitations of the fitting procedure and experimental data, if we fit eq 1 to our data set, we obtain values for the reaction constant in micelles (4-MeBz $k_m = 0.0151 \text{ s}^{-1}$, 4-HBz $k_m = 0.013 \text{ s}^{-1}$, 4-Cl $k_m = 0.003 \text{ s}^{-1}$) with a high error. Both the error and the confirmation of the linearity of the inverse constant prevent us from performing a quantitative analysis of these data. Nevertheless, from a qualitative point of view, we can see that the rate constant at the interface is several orders of magnitude lower than the rate constant in water (see Table 1).

The polarity of the Brij 35 interface was calculated using pyrene as a micropolarity probe.²⁸ The ratio between the vibronic bands of the fluorescence spectra of the pyrene in Brij 35 micelles ($I_1/I_3 = 1.27$) is lower than that of pyrene in bulk water ($I_1/I_3 = 1.87$), indicating a more apolar environment. The low reactivity of 4-MeBz, 4-HBz, and 4-ClBz in Brij 35 micelles is consistent with the hypothesis that those substrates react

primarily by means of a dissociative mechanism. Similar effects were observed in DPPC vesicles²¹ and ionic micelles.¹⁹ In vesicles, the rate constant at the vesicular interface is higher than that for the Brij 35 micellar interface, suggesting a more hydrated environment. The disparities with the values of CTAC and SDS micelles can come from both the different polarity and the weak micellar electronic effects.

As we move in the scale of electronegativity, benzoyl chlorides with less electron-donating substituents show a significant reactivity in the micellar interface even though lower than in water (due to the lower polarity of the media). Nevertheless, the ratio k_m/k_w progressively increases (Table 1). In the case of 3-NO₂Bz, no significant variation of k_{obs} is observed. This could give the impression that the solvolysis of 3-NO₂Bz is not affected by micelles because no adsorption at the micellar interface occurs. However, if we consider the trend observed for the rest of substrates, we can postulate that 3-NO₂Bz reacts at the micellar interface but the rate constant is very similar to the rate constant in water. Therefore, partitioning has no effect on the observed kinetic constant.

In the case of 4-NO₂Bz, the rate constant in micelles is higher than the rate constant in water. This substrate generally reacts via an associative mechanism weakly affected by polarity. In a wide range of solvents, 4-NO₂Bz reacts predominantly via an associative mechanism. Just for 97% hexafluoro-2-propanol, a significant contribution of an ionization pathway can be postulated.² An associative mechanism for the solvolysis reaction could explain a mild decrease of the observed rate constant upon micelle addition but not an increase. Normally, the solvolysis of benzoyl chlorides decreases with the decrease of polarity and ionizing power of the medium. This decrease can be counteracted by a secondary associative mechanism that works in the opposite direction, making the rate constant decrease less prominent.¹⁹ Nevertheless, in other media, such as alcohol/water mixtures,²⁹ vesicles,²¹ ionic and nonionic microemulsions,^{23,24} and cationic micelles,¹⁹ similar catalytic effect was observed. In the case of alcohol water mixtures, the anomalous behavior was attributed to the reactivity of the alcohol as a nucleophile. The same behavior was explained as an increase of the nucleophilic character of the water in microemulsions.

The change in the properties of the water due to the presence of organic solutes is not only observed in colloidal systems. Ethers and monofunctional alcohols are known to cause disruption of the water structure at high mole fraction of organic cosolvent in aqueous solutions.³⁰ These interactions can produce more unbound and more reactive water molecules, increasing the nucleophilic character. In similar fashion, ether groups of the polyoxyethylene surfactants interact with interfacial water.²⁴ It is reported that polyoxyethylene surfactants have water molecules trapped in the polyoxyethylene headgroup with 5.2 to 10.5 water molecules per ethylene oxide unit, with two of these molecules hydrogen bonded to the ether oxygen.³¹ In the case of microemulsions of an analogous surfactant, Brij 30 (shorter headgroup), enhancement of the nucleophilic character of the interfacial water at low interface hydration was confirmed by NMR studies and correlated with the catalysis observed for the solvolysis of 4-NO₂Bz. We propose a similar effect in the case of Brij 35. Brij 35 micelles offer an environment with a concentration of water significantly lower than that in the aqueous phase³² and can be compared with a highly hydrated nonionic microemulsion. In fact, the extent of catalysis observed for the 4-NO₂Bz in Brij 35 micelles corresponds to the catalysis observed in Brij 30 microemulsions with a high content of water.24



Figure 3. Hammett plots for the solvolysis of substituted benzoyl chlorides in (\bullet) water (k_w) and (\bigcirc) Brij35 micelles (k_m). Lines are a guide for the eye. Asterisks indicate rate constant values with significant error.

On the other hand, the effect of DPPC vesicles and cationic micelles was attributed to an electrostatic stabilization of the transition state of the reaction. Vesicles of DPPC²¹ favor the associative mechanism, and the rate constants in the vesicular interface for 4-NO₂Bz, 4-CF₃Bz, and 3-CF₃Bz are higher than in nonionic micelles because of electrostatic stabilization. Electronic effects also apply in the case of ionic micelles. Positively charged CTAB micelles accelerate the 4-NO₂Bz solvolysis reaction while negatively charged SDS micelles inhibit the reaction.¹⁹ In Brij 35 micelles the rate values are intermediate between the values for the ionic micelles because the electrostatic interactions do not occur.

In mixtures of solvents^{3,4} and other microheterogenous systems^{21,23,24} the log of the reaction constants follows the Hammett correlation showing a sharp change of the slope. This change indicates a change in the solvolysis mechanism. Figure 3 shows the Hammett plots in water and in the micellar interface. Values for the electron-donating substituted benzoyl chlorides are included for qualitative information because they are obtained with high error (see above). A slight shift in the mechanism turning point can be inferred. While in water the turning point occurs around 3-CF₃Bz, the 3-ClBz mechanism still shows a significant associative character in micelles. Therefore, the micellar environment favors the associative pathway and shifts the overall mechanism toward the associative end of the mechanistic spectra. From the observed trend we can see that the substrates that show significant reactivity in micelles are those with the certain character of the associative mechanism. Substrates on the lower part of the σ Hammett scale react via a dissociative mechanism mainly affected by polarity. Therefore, the rate constant is strongly reduced at the micellar interface. For substrates on the other side of the Hammett scale (associative mechanism), a secondary micellar effect, enhanced water nucleophilicity, counteracts the decrease because of polarity yielding to significant rate constant values at the micellar interface. To conclude, the micellar effects observed in Brij 35 micelles are possibly due to the low polarity and low water content of the interface and the enhanced nucelophilic character of the interfacial water.

2. Solvolysis of 4-CF₃-Benzoyl Chloride in Mixed Micelles. In order to estimate the importance of the micellar effects for the solvolysis of benzoyl chlorides reacting by means of an associative mechanism, a study of the solvolysis reaction of

TABLE 2: Cmc, ζ -Potential, and I_1/I_3 Values for Different Mixed Micelles

	cmc/mM			
	water	0.1 M HCl	ζ-potential in water/mV	I_1/I_3^a in 0.1 M HCl
CTAC	5.71	0.59	64 ± 2	1.300 ± 0.005
CTAC/Brij35 3:1	0.38	0.22	40 ± 4	1.295 ± 0.005
CTAC/Brij35 1:1	0.15	0.17	22 ± 5	1.275 ± 0.005
CTAC/Brij35 1:3	0.11	0.11	15 ± 4	1.270 ± 0.010
Brij35	0.10	0.11	-9 ± 7	1.270 ± 0.005
Brij35/STS 3:1	0.11	0.07	-62 ± 2	1.235 ± 0.005
Brij35/STS 2:1	0.12	0.07	-66 ± 4	1.220 ± 0.005
STS ^a	1.58	0.4	-92 ± 4	1.025 ± 0.005

^{*a*} Value in water of the pyrene vibronic bands ratio, $I_3/I_1 = 1.87$.⁴⁹

4-CF₃Bz was carried out in micelles with different superficial charges. Mixed micelles of ionic, CTAC and STS, and nonionic Brij 35 surfactants were prepared and characterized and their kinetic effects studied.

2.1. Characterization of Mixed Micelles. Surface tension measurements were performed in order to determine the cmc of the mixtures of surfactants. Table 2 summarizes the cmc values obtained. In the case of a binary mixture of surfactants, different scenarios can occur. Surfactants can construct two types of micelles formed by individual surfactants, one type of mixed micelles where both surfactants are incorporated or a range of mixed micelles with different ratios for the constituent surfactants.33-35 The scenario can vary depending on the type of surfactant pairs as well as on the concentration of surfactants. In the case where more than one type of aggregate is present in solution, two or more breaking points in the surface tension plots must be observed. Even so, within our concentration limits, only one type of micelle composed by both surfactants is present in solution. In all cases, just one break point was observed (see Supporting Information Figure S1 as an example). The same results were reported previously for a similar system applying different experimental techniques.^{36,37} Cmc's were calculated both in water and in 0.1 M HCl media. For the pure systems in water, the cmc's are similar to those reported in the literature^{27,38} In the presence of HCl, the cmc is reduced drastically for the ionic surfactants because the electrolyte shields the repulsion forces between ionic surfactants head groups, but the cmc is not reduced for the nonionic and mixtures of surfactants.³⁹ For both cases, the absence and presence of HCl, cmc's fall between the values for pure micelles. However, cmc's for the mixed systems do not follow the Clint equation, indicating a nonideal mixing of the two surfactants.^{37,40} Besides, the analysis of the data according to Rubingh model^{41,42} provides negative values for parameter β , indicating a favorable interaction between the surfactants that compose the mixed micelles, as reported in similar systems.43

Properties such as polarity and charge were determined for all the systems. The ζ - potential of the micelles was calculated in the absence of acid because the high ionic strength for the 0.1 M HCl solution was not suitable to perform reliable ζ potential measurements. The charge of the micelles goes as expected from high negative values for the STS micelles, progressively decreases toward zero for the Brij 35 micelles, and reaches a positive value for the CTAC micelles (Table 2). In the presence of HCl, a general drift toward zero of the ζ potential can be observed for all micelles. In all cases, one single peak is observed, supporting the idea that only one type of micelle is formed in the mixed surfactant systems.

Polarity was calculated by means of the ratio between the intensities of the first and third vibronic bands of the pyrene

fluorescence spectra. Series of spectra were recorded for the single surfactant solutions at increasing surfactant concentration. The ratio between the vibronic bands decreases sharply toward a plateau, indicating the formation of micellar aggregates (Figure S2, Supporting Information). In order to obtain values for the polarity of the micellar interface, spectra were taken at a concentration higher than the cmc for all mixed systems. I_1/I_3 values show that polarity is similar between CTAC, Brij 35, and CTAC/Brij35 micelles, even though CTAC micelles are slightly more polar. On the other hand, STS micelles have a much lower I_1/I_3 ratio, indicating a more apolar interface (see Table 2). Our findings agree with previous studies where CTABrich micelles were shown to be less compact, more water accessible, and therefore more polar than SDS-rich micelles.⁴⁴ The size of the headgroup of the ammonium salt surfactant prevents compact packing, yielding a more hydrated interface.

Comparison of polarity values is a bit controversial. Depending on the probe used for assessing the polarity of the interface, different values can be obtained. In the study of SDS micelles with $E_T(30)$ probe, higher polarity for the SDS micelles were found.⁴⁵ In other studies using benzene as a probe, similar dielectric constant values for SDS and CTAB molecules were reported.⁴⁶ The discrepancies in polarity arise from the different loci of solubilization in the micelles depending on the chemical structure of the probe. For our system, benzene or pyrene would probably be a more suitable local environment probe than $E_T(30)$ because of the similarity in size with the studied benzoyl chlorides. Therefore, we assume that the locus for solubilization of the benzoyl chlorides is similar to the one for the polarity probe used, and our data give a fair measure of the micropolarity felt by the substrate.

The mild effect of the addition of ionic surfactants on the polarity of nonionic micelles can be explained by taking into account the geometry of the individual surfactants and micelles. In the case of ionic-C12E6 (analogous to Brij 35 but with much shorter headgroup) mixed micelles, the ionic head groups are solubilized in the ethylene oxide region of the nonionic surfactant.⁴⁷ SDS is located close to the micellar surface molecules, causing an opening and increasing the water accessibility, while DTAC is located close to the micellar hydrophobic core. According to our data, no significant change in water accessibility is observed. The explanation for this behavior is a result of the larger headgroup size of the Brij 35 that is, most likely, weakly disturbed by the addition of the ionic surfactants. In fact, structural³⁶ and kinetic⁴⁸ studies of mixed systems of



Figure 4. Normalized observed rate constant (k_{obs}/k_w) vs $[D_n]$ for solvolysis of 4-NO₂Bz in the presence of micelles of (\blacksquare) CTAC, (\Box) CTAC/Brij35 3:1, (\bullet) CTAC/Brij35 1:1, (\odot) CTAC/Brij35 1:3, (\blacktriangle) Brij35, (\triangle) Brij35/STS 3:1, (\triangle) Brij35/STS 2:1, and (\blacktriangledown) STS.

TABLE 3: Kinetic Parameters for Solvolysis of 4-CF₃Bz in Mixed Micelles at 25 $^\circ\text{C}$

substrate	$k_{\rm w}/{ m s}^{-1}$	$k_{\rm m}/{\rm s}^{-1}$	$K_{\rm S}/{ m M}^{-1}$	$k_{\rm m}/k_{\rm w}$
CTAC CTAC/Brij35 3:1 CTAC/Brij35 1:1 CTAC/Brij35 1:3 Brij35 Brij35/STS 3:1	$\begin{array}{c} 0.050 \pm 0.002 \\ 0.050 \pm 0.002 \\ 0.050 \pm 0.002 \\ 0.059 \pm 0.002 \\ 0.059 \pm 0.001 \\ 0.059 \pm 0.001 \end{array}$	$\begin{array}{c} 0.055 \pm 0.002 \\ 0.044 \pm 0.001 \\ 0.039 \pm 0.002 \\ 0.032 \pm 0.002 \\ 0.028 \pm 0.001 \\ 0.022 \pm 0.001 \end{array}$	$ \begin{array}{r} 179 \pm 224^{a} \\ 675 \pm 466 \\ 928 \pm 263 \\ 315 \pm 65 \\ 534 \pm 41 \\ 893 \pm 160 \\ \end{array} $	1.1 0.89 0.78 0.54 0.48 0.39
Brij35/STS 2:1 STS ^b	0.057 ± 0.001 0.059 ± 0.002 0.047	0.022 ± 0.001 0.015 ± 0.001 0.0095	605 ± 53 1700	0.26 0.20

^{*a*} High error caused by the small difference between the rate constants in the two pseudophases. ^{*b*} Estimated values due to the low STS solubility (see text).

SCHEME 3



Brij 35 and CTAB show that the headgroups of CTAB are located next to the hydrophobic chains of Brij 35 without disturbing the conformation of the long hydrophilic polyoxyethylene chains.

2.2. *Kinetic Effects.* The solvolysis reaction of benzoyl chlorides is affected by the nature of the micelle.¹⁹ We have studied the solvolysis of 4-CF₃Bz in cationic, anionic, and nonionic surfactants as well as in binary mixtures. Figure 4 shows how the ability of mixed micelles to inhibit the solvolysis decreases as the micellar charge is increased (the surface charge becomes positive) and while for the pure cationic micelle the reaction is catalyzed as reported previously.¹⁹ The same kinetic pseudophase model can be applied for the mixed micelles because, according to the characterization, only one type of

mixed micelles is formed in the concentration range studied. Hence, to obtain the values of the rate and association constants, eq 1 was fitted to the experimental results.

Table 3 summarizes the kinetic parameters obtained from the fitting. The association constant was obtained, but no correlation between the polarity of the micellar surface and the association constant was observed. In fact the variation of the polarity is quite scarce between CTAC, Brij 35, and mixed micelles. Consequently, not much change in association constant is expected. Even though the concentration range for STS is much smaller than for the other micelles because of solubility issues, we can clearly infer from the beginning of the curve that the association constant in STS is higher than for CTAC, Brij 35, and mixed micelles. This can be related to the lower polarity of STS micelles as reported in the previous section. The rate constant in the micellar interface varies considerably for the different micelles. 4-CF3Bz, according to the studies in continuous solvents,⁴ reacts by means of a highly associative pathway (see discussion in section 1). This is confirmed by the fact that in CTAC micelles the solvolysis is catalyzed. The catalysis of solvolysis of benzoyl chlorides can only be explained if the mechanism of the reaction is associative because the dissociative mechanism in a low content water environment is always inhibited.

Different micellar effects can contribute to the behavior observed. The low polarity of the interface would reduce the rate constant in the micellar interface. However, taking into account that the polarity of the interface is alike in all systems (excluding STS), the inhibition exerted by the polarity would be expected to be similar in all cases. However, a variation depending on the composition of the micelles is observed.

A second interaction proposed previously is of electrostatic nature. The associative mechanism goes through the formation of an intermediate with a partial negative charge. This intermediate would be favored in environments where the negative charge is stabilized by means of electrostatic interactions (see Scheme 3). The negatively charged intermediate is expected to stabilized by a positive potential at the micellar interface. In fact, a correlation between the log k_m and both the molar fraction of the ionic surfactant (related directly to the net charge of the micelle) and the ζ -potential of the micelles is observed (Figure 5). This trend indicates that the intermediate of the reaction is highly favorable in positive micelles. As Bunton et al. states,¹⁹ cationic micelles have an affect to an extent that overcomes the inhibition due to the low polarity and water content of the micelles.



Figure 5. (Left) correlation between log k_m and ζ -potential of the micelles. (Right) correlation between log k_m and the molar fraction of ionic surfactants (O) CTAB and (\blacksquare) STS.

As soon as the micellar potential decreases, the contribution of the stabilization is reduced. In the case of Brij 35 micelles without effective charge, polarity and low hydration of the interface cause the micellar effect. As we move toward more negative potentials, the intermediate of reaction for the associative mechanism becomes increasingly more unstable and k_m drops to lower values. The most negative micelle, STS, produces the highest inhibition. This behavior is consistent with the unfavorable interaction between the negative micellar surface and the negative charge developed at the intermediate of the reaction. We cannot exclude that the low polarity of this micelle means additional inhibition due to the greatly limited water accessibility.

Finally, as discussed previously, a modification of the water properties at the interface cannot be excluded. Bunton et al.¹⁹ reported rate constants for the solvolysis of substituted benzoyl chlorides in water/acetonitrile mixtures. If we compare the rate constant at the micellar interface for the substrates with a highly dissociative mechanism to the reported rate constants, we can conclude that the polarity effect of Brij 35 micelles is similar to that observed in a 40% water/CHCN mixture. By extrapolation of the Hammett plots for that particular water/acetonitrile mixture, the rate constant for 4-CF₃Bz can be interpolated as ca. $0.01-0.015 \text{ s}^{-1}$. However, the value obtained in our study is twice that of the calculated value. This rough estimation could indicate the enhancement of the associative pathway of the solvolysis due to a modification of the properties of the water. As discussed in the previous section, the water at the Brij 35 interface is disturbed in a manner that could enhance its nucleophilic character and therefore be more reactive in the solvolysis reaction of 4-CF₃Bz.

Conclusions

Solvolysis of substituted benzoyl chlorides are affected by the presence of nonionic micelles. Both catalysis and inhibition can be observed and related to the operating solvolysis mechanism. Inhibition of solvolysis can be explained by the low polarity and water hydration of the micellar interface for the dissociative mechanism. The catalysis of substrates reacting by means of a highly associative mechanism can be explained in terms of the enhanced nucleophilicity of bound water. For that type of mechanism, a strong correlation between the charge of the micelles and the rate constant of the solvolysis is observed in binary mixtures of nonionic and ionic surfactants. This observation suggests electrostatic interactions between the surfactant charged head groups and the negatively charged intermediate of the reaction. Cationic micelles strongly stabilize the intermediate of the reaction and catalyze the process. This stabilization decreases with the decrease of the charge toward negative potentials. High negative charge presents the highest inhibition of the solvolysis reaction due to the unfavorable charge-charge interactions. In summary, the overall kinetic effect results from a combination of different contributions: low water polarity and low water content that lead to modification of water properties and enhancement of the reactivity of water as a nucleophile and for electrostatic interactions.

Acknowledgment. C.C.L. acknowledges the Isidro Parga Pondal Program fellowship (Xunta de Galicia, Spain) and the Swedish Research Council. This work has been supported by the Spanish Ministerio de Educación y Ciencia (Project CTQ2007-64758).

Supporting Information Available: Dependence of surface tension on surfactant concentration for mixed Brij 35:CTAC

1:1 solutions and variation of the pyrene I_1/I_3 ratio with the concentration of Brij. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bentley, T. W.; Harris, H. C. J. Chem. Soc., Perkin Trans. 2 1986, (4), 619–24.

(2) Kevill, D. N.; D'Souza, M. J. J. Phys. Org. Chem. 2002, 15 (12), 881–888.

(3) Kevill, D. N.; Wang, W. F. K. J. Chem. Soc., Perkin Trans. 2 1998, (12), 2631–2637.

(4) Song, B. D.; Jencks, W. P. J. Am. Chem. Soc. 1989, 111 (22), 8470–9.

(5) Lindman, B.; Wennerstrom, H.; Gustavsson, H.; Kamenka, N.; Brun, B. Pure Appl. Chem. **1980**, *52* (5), 1307–1315.

(6) Blokzijl, W.; Engberts, J. Angew. Chem., Int. Ed. 1993, 32 (11), 1545–1579.

(7) Bunton, C. A.; Nome, F.; Quina, F. H.; Romsted, L. S. Acc. Chem. Res. **1991**, 24 (12), 357–364.

(8) Fendler, J. F. Membrane Mimetic Chemistry; John Wiley & Sons Ltd.: New York, 1982.

(9) Otto, S.; Engberts, J. *Pure Appl. Chem.* 2000, 72 (7), 1365–1372.
(10) Alvarez, A. R.; García-Río, L.; Hervés, P.; Leis, J. R.; Mejuto,

J. Č.; Pérez-Juste, J. *Langmuir* 1999, *15* (24), 8368–8375.
 (11) García-Río, L.; Hervés, P.; Mejuto, J. C.; Pérez-Juste, J.; Rodríguez-

- Dafonte, P. New J. Chem. 2003, 27 (2), 372–380.
 - (12) Buurma, N. J. Adv. Phys. Org. Chem. **2009**, 43, 1–37.
- (13) El Seoud, O. A.; Ruasse, M. F.; Possidonio, S. J. Phys. Org. Chem.
 2001, 14 (8), 526–532.
 (14) Buurma, N. J.; Herranz, A. M.; Engberts, J. J. Chem. Soc., Perkin
- *Trans.* 2 **1999**, (1), 113–119. (15) Chiarini, M.; Gillitt, N. D.; Bunton, C. A. *Langmuir* **2002**, *18* (10),

3836–3842. (16) Buurma, N. J.; Serena, P.; Blandamer, M. J.; Engberts, J. J. Org.

Chem. 2004, 69 (11), 3899–3906.
(17) Muñoz, M.; Rodríguez, A.; Graciani, M. D.; Moya, M. L. Int. J. Chem. Kinet. 2002, 34 (7), 445–451.

(18) Maximiano, F. A.; Chaimovich, H.; Cuccovia, I. M. *Langmuir* 2006, 22 (19), 8050–8055.

- (19) Bunton, C. A.; Gillitt, N. D.; Mhala, M. M.; Moffatt, J. R.; Yatsimirsky, A. K. *Langmuir* **2000**, *16* (23), 8595–8603.
 - (20) Bunton, C. A. J. Phys. Org. Chem. 2005, 18 (2), 115-120.
 - (21) Cabaleiro-Lago, C.; García-Río, L.; Hervés, P.; Pérez-Juste, J. J.
- Phys. Chem. B 2006, 110 (16), 8524–8530.
 (22) Cabaleiro-Lago, C.; García-Río, L.; Hervés, P.; Pérez-Juste, J. J.
- Phys. Chem. B 2009, 113 (19), 6749–6755.
 (23) García-Río, L.; Leis, J. R.; Moreira, J. A. J. Am. Chem. Soc. 2000,
- 122 (42), 10325–10334.
 (24) Cabaleiro-Lago, C.; García-Río, L.; Hervés, P.; Pérez-Juste, J. J.
- Phys. Chem. B 2005, 109 (47), 22614–22622.
 (25) Campos-Rey, P.; Cabaleiro-Lago, C.; Hervés, P. J. Phys. Chem. B
- **2009**, *113* (35), 11921–11927.
 - (26) Bunton, C. A.; Savelli, G. Adv. Phys. Org. Chem. 1986, 22, 213.
- (27) Romsted, L. S. Surfactants in Solution; Plenum Press: New York, 1984.
- (28) Dong, D. C.; Winnik, M. A. Photochem. Photobiol. 1982, 35 (1), 17–21.
- (29) Bentley, T. W.; Jones, R. O. J. Chem. Soc., Perkin Trans. 2 1993, 2, 2351–2357.

(30) Blandamer, M.; Burgess, J. J. Chem. Soc. Rev. 1975, 4, 55-75.

- (31) Eleini, D. I. D.; Barry, B. W.; Rhodes, C. T. J. Colloid Interface Sci. 1976, 54 (3), 348–351.
- (32) Khan, M. N.; Ismail, E.; Yusoff, M. R. J. Phys. Org. Chem. 2001, 14 (10), 669–676.
- (33) Graciani, M. D.; Rodríguez, A.; Moya, M. L. J. Colloid Interface Sci. 2008, 328 (2), 324–330.
- (34) Muñoz, M.; Rodríguez, A.; Graciani, M. D.; Moya, M. L. Langmuir 2004, 20 (25), 10858–10867.
- (35) Freire, L.; Iglesias, E.; Bravo, C.; Leis, J. R.; Peña, M. E. J. Chem.
 Soc., Perkin Trans. 2 1994, (8), 1887–1894.
 (36) Gao, H. C.; Zhao, S.; Mao, S. Z.; Yuan, H. Z.; Yu, J. Y.; Shen,
- (36) Gao, H. C.; Zhao, S.; Mao, S. Z.; Yuan, H. Z.; Yu, J. Y.; Shen, L. F.; Du, Y. R. *J. Colloid Interface Sci.* **2002**, *249* (1), 200–208.
- (37) Gao, H. C.; Zhu, R. X.; Yang, X. Y.; Mao, S. Z.; Zhao, S.; Yu, J. Y.; Du, Y. R. J. Colloid Interface Sci. 2004, 273 (2), 626–631.

(38) Mukerjee, P.; Mysels, K. J. Critical micelle concentrations of aqueous surfactant systems; NSRDS-NBS-36, U.S. Government Printing Office: Washington, D.C., 1971.

(39) Wennerstrom, H.; Lindman, B. Phys. Rep. 1979, 52 (1), 1-86.

(40) Clint, J. H. J. Chem. Soc., Faraday Trans. 1 1975, 71 (6), 1327–1334.

Solvolysis of Substituted Benzoyl Chlorides

(41) Rubingh, D. In *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum: New York, 1979; Vol. 1.

- (42) Holland, P.; Rubingh, D. In *Mixed Surfactant Systems*; Holland, P.; Rubingh, D., Eds.; American Chemical Society: Washinton, D.C., 1992.
- (43) Rodrigues, M. A.; Alonso, E. O.; Yihwa, C.; Farah, J. P. S.; Quina, F. H. *Langmuir* **1999**, *15* (20), 6770–6774.
- (44) Chakraborty, H.; Sarkar, M. *Langmuir* 2004, 20 (9), 3551–3558.
 (45) Zachariasse, K. A.; Vanphuc, N.; Kozankiewicz, B. J. Phys. Chem. 1981, 85 (18), 2676–2683.

(46) Mukerjee, P.; Cardinal, J. R. J. Phys. Chem. 1978, 82 (14), 1620–1627.

- (47) Baglioni, P.; Dei, L. G.; Rivaraminten, E.; Kevan, L. J. Am. Chem. Soc. **1993**, *115* (10), 4286–4290.
- (48) Khan, M. N.; Ismail, E.; Yusof, N. S. M. Colloids Surf., A 2010, 361 (1-3), 150-161.
- (49) Dong, D. C.; Winnik, M. A. Can. J. Chem. 1984, 62 (11), 2560–2565.

JP107538V