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# Solvolysis of Benzoyl Halides in AOT/Isooctane/Water Microemulsions. Influence of the Leaving Group

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A kinetic study was carried out on the solvolysis of benzoyl bromide, BzBr, benzoyl chloride, BzCl, and benzoyl fluoride, BzF, in microemulsions of AOT/isooctane/water at 25 °C, where AOT is sodium bis(2-ethylhexyl)sulfosuccinate. In all cases, the pseudo-first-order rate constant,  $k_{\text{obs}}$ , increases together with the [AOT] as a consequence of incorporating the substrates into the interface of the microemulsion. The application of a kinetic model based on the formalism of the pseudophase, which considers the distribution of the reagents between the continuous medium and the interface and that the reaction is taking place only at the interface, has enabled us to obtain the intrinsic values of the rate constant at the interface of the microemulsion for the three benzoyl halides,  $k_i^{\text{BzX}}$ . The values of  $k_i^{\text{BzX}}$  vary together with the water content of the microemulsion. The study of the variation of  $k_i^{\text{BzX}}$  with  $W$  ( $W = [\text{H}_2\text{O}]/[\text{AOT}]$ ), the correlations with the  $E_T$  polarity parameter, and the effect of the leaving group have allowed us to conclude that a mechanistic displacement has occurred along with the variation in  $W$ . For high water contents, the reaction occurs by an associative and dissociative path simultaneously, the relative weights of which depend on the leaving group, with the dissociative character increasing as the salient group of the benzoyl halide improves. As  $W$  diminishes, the associative path is favored as a consequence of an increase in the nucleophilicity of the water, and the dissociative path is disfavored due to the reduction in the capacity of the interfacial water to solvate the leaving group,  $\text{X}^-$ . Consequently, a displacement of the reaction mechanism takes place from a dissociative extreme to an associative one as the water content of the microemulsion is reduced, which causes the sensitivity of the reaction to the nature of the leaving group to vary with  $W$ .

## Introduction

The use of microemulsions as new reaction media has been in the forefront of research in recent years. Microemulsions have a peculiar molecular heterogeneity caused by the amphiphilic nature of the surfactant that resides in an interface between water and the nonpolar solvent. Three different compartments are available for the localization of small solutes:<sup>1,2</sup> (a) the internal aqueous core or water pool, (b) the micellar interface formed by a monolayer of surfactant molecules with their polar head-groups oriented toward the water pool, and (c) the external organic phase. This compartmentalization of the reactives allows the solubilization of a large variety of compounds, which constitutes the basis of the majority of the technological applications for microemulsions. The most intensively studied three-component water in oil (w/o) microemulsions have been systems of the form water/AOT/oil, where AOT is sodium bis(2-ethylhexyl)sulfosuccinate.<sup>3</sup> An important property of these systems is the highly structured nature of the water at the interface when the  $[\text{H}_2\text{O}]/[\text{AOT}]$  ratio  $W$  is small.<sup>3</sup> In dilute systems, the structure of microemulsions is accounted for by the "droplet model",<sup>4</sup> which considers the disperse phase to

be formed by monodisperse spherical droplets, each one surrounded by a layer of surfactant molecules.<sup>5</sup>

In our laboratory, work has centered for some time on the study of the chemical reactivity in microemulsions of three and four components.<sup>6</sup> Recently we have shown that the change in the properties of the water of the microemulsions, as  $W$  varies, has important kinetic repercussions, which not only alter the rate of the reaction but also even modify its mechanism.<sup>7</sup> In this study, we will examine the solvolysis of benzoyl bromide (BzBr), benzoyl chloride (BzCl), and benzoyl fluoride (BzF) in AOT/isooctane/water microemulsions with the purpose of evaluating whether the changes in the properties of the water can modify the mechanism of these reactions as the nature of the leaving group varies.

The solvolysis reactions of benzoyl halides have been widely studied in water and in solvent mixtures.<sup>8</sup> The mechanisms for acyl transfer are (1) dissociative, with an acylium ion intermediate; (2) concerted displacement, which can have associative or dissociative character; and (3) associative, or addition–elimination, with a tetrahedral addition intermediate, see Scheme 1. In water, the change from a dissociative to an associative reaction path with increasingly electron-withdrawing substituents occurs much later for benzoyl chlorides than for benzoyl fluorides

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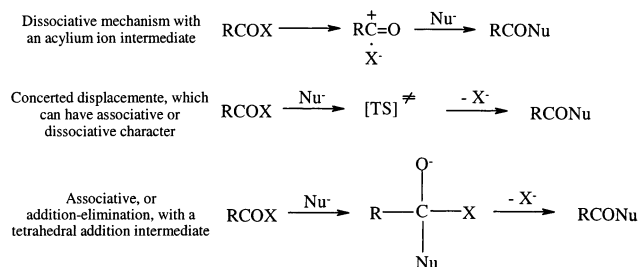
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## Scheme 1



because the rate of the associative reaction is independent of the leaving group, while the dissociative reaction is strongly dependent on the leaving group. The obtained results indicate that as  $W$  decreases a displacement of the mechanism occurs from one extreme with a high dissociative character to another where the associative character increases.

## Experimental Section

**Materials.** AOT (Aldrich) was dried in a vacuum desiccator for 2 days and then used without further purification. Benzoyl halides (all from Aldrich) were of the highest available purity and were used as supplied; all of them were dissolved in isooctane (Aldrich).

**Methods.** Microemulsions were prepared by mixing isooctane, water, and 1.00 M AOT/isooctane solution in appropriate proportions. The solvolysis reactions were followed by monitoring the UV absorbance of substrate solutions (concentration range  $(1-2) \times 10^{-4}$  M) using a Spectronic 3000 diode-array spectrophotometer fitted with thermostated cell holders. The wavelengths used for the kinetic studies fell in the range of  $\lambda = 280-300$  nm. The integrated first-order rate expression was fitted to the absorbance-time data by linear regression ( $r > 0.999$ ) in all cases. The rate constants,  $k_{\text{obs}}$ , could be reproduced with an error margin of  $\pm 5\%$ . In all cases, it was observed that the final spectrum of the product of the reaction coincided with another obtained in pure water, guaranteeing that the presence of microemulsions would not alter the product of the reaction. All experiments were carried out at  $(25.0 \pm 0.1)^\circ\text{C}$ .

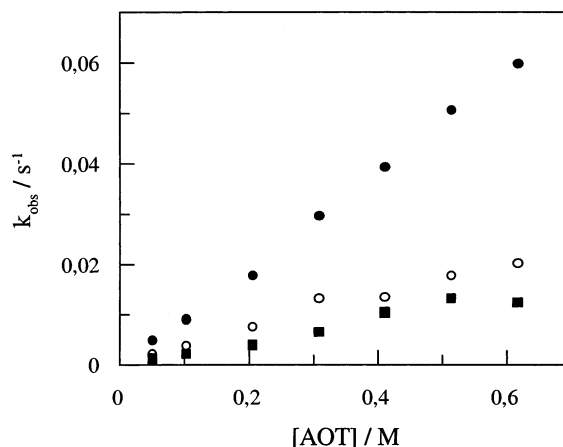
## Results

A study was carried out on the influence of the composition of the microemulsion on the rate constant of pseudo-first-order,  $k_{\text{obs}}$ , varying the surfactant concentration, AOT, between 0.05 and 0.6 M and keeping the molar relationship constant,  $W = [\text{H}_2\text{O}]/[\text{AOT}]$ ,  $W = 18$ . Figure 1 shows that  $k_{\text{obs}}$  increases with the surfactant concentration for the solvolysis of BzBr, BzCl, and BzF. This increase of  $k_{\text{obs}}$  as the concentration of AOT increases is due to the incorporation of benzoyl halide at the interface of the microemulsion.

To carry out a quantitative interpretation of the influence of the microemulsion on the reactivity, it is necessary to know the concentrations of the reagents in the various phases of the microemulsion and the corresponding rate constants. We have recently devised a kinetic model based on the formalism of the pseudophase to explain the reactivity in microemulsions, which has been satisfactorily applied to solvolytic processes.<sup>9</sup>

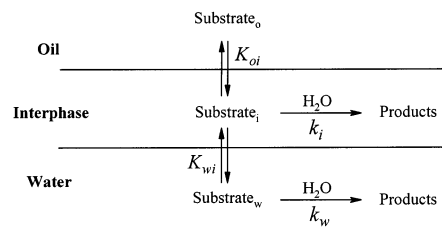
**Intrinsic Rate Constants in the Microemulsion.**

In a first approximation, we can suppose that substrate is distributed between the three pseudophases of the microemulsion (Scheme 2), so that the solvolysis process can take place both at the interface and the aqueous pseudophase.



**Figure 1.** Influence of the [AOT] on  $k_{\text{obs}}$  for the solvolysis of benzoyl halides at  $W = 18$  and  $T = 25^\circ\text{C}$ : (○)  $k_{\text{obs}}$  for solvolysis of BzBr, (●)  $10^2 k_{\text{obs}}$  for solvolysis of BzCl, and (■)  $10^3 k_{\text{obs}}$  for solvolysis of BzF.

## Scheme 2



On the basis of this reactant distribution and the two possible loci of reaction, we can obtain the following equation:

$$k_{\text{obs}} = \frac{k_i K_{oi} K_{wi} + k_w K_{oi} W}{K_{oi} K_{wi} + K_{oi} W + K_{wi} Z} \quad (1)$$

This equation can be transformed into

$$\frac{1}{k_{\text{obs}}} = \frac{K_{oi} K_{wi} + K_{oi} W}{k_i K_{oi} K_{wi} + k_w K_{oi} W} + \frac{K_{wi}}{k_i K_{oi} K_{wi} + k_w K_{oi} W} Z \quad (2)$$

On the basis of eq 2, the following equation is obtained for the quotient intercept/slope:

$$\frac{\text{intercept}}{\text{slope}} = K_{oi} + \frac{K_{oi}}{K_{wi}} W \quad (3)$$

This relationship predicts that the intercept/slope of the representation of  $1/k_{\text{obs}}$  versus  $Z$  should vary with  $W$ . Table 1 displays the results of this relationship for the solvolysis of the BzCl and other substrates. As we can see, the intercept/slope remains independent of the value of  $W$ , which shows that the substrate is distributed solely between the continuous medium and the interface, and therefore, the reaction will take place at the interface alone, even for values of  $W$  as high as  $W = 50$ . Other studies<sup>10</sup> show that if the association constant of a substrate from the continuous phase to the interface is independent of  $W$ , the possibility of the existence of the substrate in the aqueous pseudophase can be discarded.

In this way, the previous model must be modified considering the distribution of the substrate, benzoyl halide, between the continuous medium and the interface

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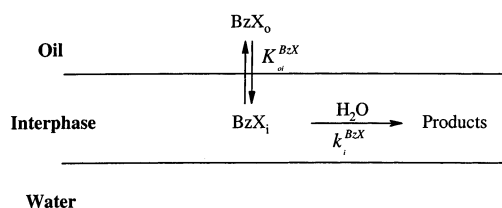
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**Table 1. Influence of  $W$  on the Ratio Slope/Intercept According to Equation 3 for Solvolysis of Benzoyl Chloride (BzCl), 4-Methoxybenzoyl Chloride (4-CH<sub>3</sub>O), and Diphenylmethyl Chloride (DPhMeCl) in Microemulsions of AOT/Isooctane/Water at 25 °C<sup>a</sup>**

$W$	slope/intercept			$W$	slope/intercept		
	BzCl	4-CH <sub>3</sub> O	DPhMeCl		BzCl	4-CH <sub>3</sub> O	DPhMeCl
2	2.2	12.6		13	3.4	9.1	3.1
3	1.8	10.4		18	4.1	8.6	2.5
4	2.5	17.8	3.2	23	5.5	8.8	1.9
5	2.5	13.3	3.3	30	3.3		1.5
6	4.0	10.2	2.6	40	4.0		2.1
7	4.2	10.7	2.2	50	3.7		2.2
10	6.5	8.9	3.3	55	4.2		

<sup>a</sup> Data are from ref 9.

**Scheme 3**



of the microemulsion, where the reaction will take place (Scheme 3). On the basis of this kinetic diagram, we can obtain the following expression for the pseudo-first-order rate constant,  $k_{\text{obs}}$ , according to the composition of the microemulsion.

$$k_{\text{obs}} = \frac{k_i^{\text{BzX}} K_{\text{oi}}^{\text{BzX}}}{K_{\text{oi}}^{\text{BzX}} + Z} \quad (4)$$

where  $k_i^{\text{BzX}}$  is the rate constant of solvolysis at the interface of the microemulsion,  $K_{\text{oi}}^{\text{BzX}}$  is the distribution constant of the benzoyl halide between the continuous medium and the interface,  $K_{\text{oi}}^{\text{BzX}} = ([\text{BzX}]_i Z)/[\text{BzX}]_o$ , and  $Z$  is the composition parameter of the microemulsion, which is defined as  $Z = [\text{isooctane}]/[\text{AOT}]$  by analogy with the parameter  $W$ . The subscripts o and i refer to the continuous medium and the interface, respectively. The concentrations refer to the total volume of the microemulsion.

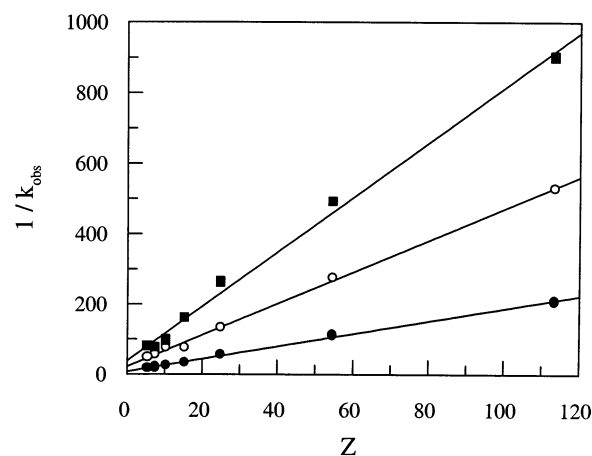
Equation 4 can be rewritten as

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_i^{\text{BzX}}} + \frac{Z}{k_i^{\text{BzX}} K_{\text{oi}}^{\text{BzX}}} \quad (5)$$

This equation predicts the existence of a linear dependency between  $1/k_{\text{obs}}$  and the  $Z$  parameter of composition of the microemulsion. Figure 2 shows the realization of eq 2 for the solvolysis of the BzX in microemulsions of  $W = 18$ . On the basis of the ordinates and gradients of Figure 2, we can obtain the values  $K_{\text{oi}}^{\text{BzX}}$  and  $k_i^{\text{BzX}}$ . The values obtained for  $K_{\text{oi}}^{\text{BzX}}$  are  $K_{\text{oi}}^{\text{BzBr}} = 4.9$ ,  $K_{\text{oi}}^{\text{BzCl}} = 4.6$ , and  $K_{\text{oi}}^{\text{BzF}} = 5.0$  for the solvolysis of the benzoyl bromide, benzoyl chloride, and benzoyl fluoride, respectively. These values are very near to each other, indicating that the change in the nature of the leaving group does not significantly affect the distribution of the benzoyl halides through the phases of the microemulsion.

#### Influence of $W$ on the Intrinsic Rate Constant.

When the value of  $K_{\text{oi}}^{\text{BzX}}$  is known, we can obtain the value of  $k_i^{\text{BzX}}$  for each  $W$  on the basis of eq 4, without knowing any more than the value  $k_{\text{obs}}$  for this water content of



**Figure 2.** Linearization of the data of Figure 1 according to eq 5: (○)  $1/k_{\text{obs}}$  for solvolysis of BzBr, (●)  $1/(10^2 k_{\text{obs}})$  for solvolysis of BzCl, and (■)  $1/(10^3 k_{\text{obs}})$  for solvolysis of BzF.

**Table 2. Values of  $k_i^{\text{BzX}}$  for Solvolysis of Benzoyl Halides in Microemulsions of AOT/Isooctane/Water at 25 °C**

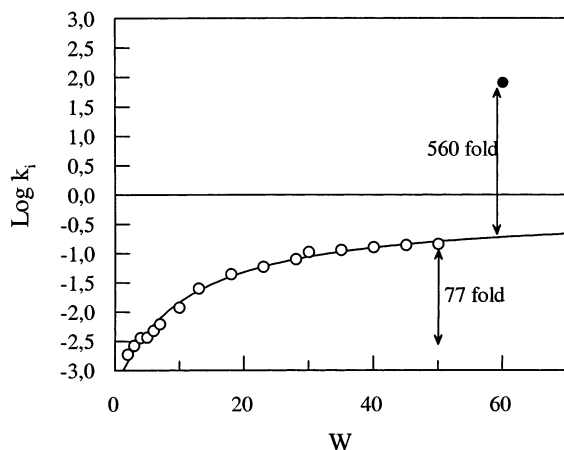
$W$	$k_i^{\text{BzX}}/\text{s}^{-1}$		
	BzBr	BzCl	BzF
2	$1.87 \times 10^{-3}$	$3.97 \times 10^{-4}$	$2.09 \times 10^{-5}$
3	$2.64 \times 10^{-3}$	$3.69 \times 10^{-4}$	$1.93 \times 10^{-5}$
4	$3.59 \times 10^{-3}$	$3.54 \times 10^{-4}$	$1.80 \times 10^{-5}$
5	$3.65 \times 10^{-3}$	$3.64 \times 10^{-4}$	$1.69 \times 10^{-5}$
6	$4.73 \times 10^{-3}$	$4.11 \times 10^{-4}$	$1.72 \times 10^{-5}$
7	$6.20 \times 10^{-3}$	$4.86 \times 10^{-4}$	$1.83 \times 10^{-5}$
10	$1.18 \times 10^{-2}$	$6.44 \times 10^{-4}$	$2.16 \times 10^{-5}$
13	$2.51 \times 10^{-2}$	$9.00 \times 10^{-4}$	$2.40 \times 10^{-5}$
18	$4.39 \times 10^{-2}$	$1.31 \times 10^{-3}$	$2.61 \times 10^{-5}$
23	$5.86 \times 10^{-2}$	$1.73 \times 10^{-3}$	$2.77 \times 10^{-5}$
28	$7.93 \times 10^{-2}$	$2.19 \times 10^{-3}$	$3.01 \times 10^{-5}$
30	$1.05 \times 10^{-1}$	$2.31 \times 10^{-3}$	$3.03 \times 10^{-5}$
35	$1.14 \times 10^{-1}$	$2.86 \times 10^{-3}$	$3.27 \times 10^{-5}$
40	$1.27 \times 10^{-1}$	$3.29 \times 10^{-3}$	$3.82 \times 10^{-5}$
45	$1.38 \times 10^{-1}$	$3.64 \times 10^{-3}$	$3.81 \times 10^{-5}$
50	$1.44 \times 10^{-1}$	$4.14 \times 10^{-3}$	$4.16 \times 10^{-5}$
water	80.8	1.10	$1.78 \times 10^{-3}$

the microemulsion. Indetermination in calculating  $k_i^{\text{BzX}}$  values is not greater than 15%. The values calculated for  $k_i^{\text{BzX}}$  are shown in Table 2. As can be observed, the values of  $k_i^{\text{BzX}}$  vary as much in accordance with the nature of the substrate as with the water content of the microemulsion. Figures 3–5 show the  $W$ -dependence of the intrinsic rate constant for solvolysis of benzoyl halides at the interface of the microemulsion. This result contrasts with the fact that the rate constant for nitroso group transfer at the interface of AOT microemulsions is independent of  $W$ .<sup>6a,11</sup> The variation of  $k_i^{\text{BzX}}$  with  $W$  is due to the high sensibility of this type of solvolytic process to the changes in the solvent properties, whereas in the nitroso group transfer reactions studied previously the rate constant presents a small variation with the polarity of the dissolvent.<sup>12</sup>

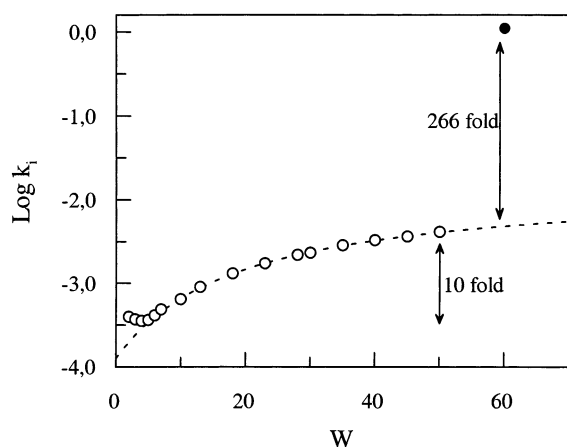
From Figures 3–5, it is important to analyze both the decrease of the solvolysis rate constant on going from bulk water to the interface of AOT/isooctane/water microemulsions of high water content ( $W = 50$ ) as well as the decrease in the rate constant when the water content of the microemulsion decreases from  $W = 50$  to  $W = 2$ . Table 3

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**Figure 3.** Variation of  $\text{Log } k_i^{\text{BzBr}}$  with the water content of the microemulsion,  $W$ , for the solvolysis of BzBr in microemulsions of AOT/isooctane/water at 25 °C (○) and the solvolysis rate constant in bulk water (●).

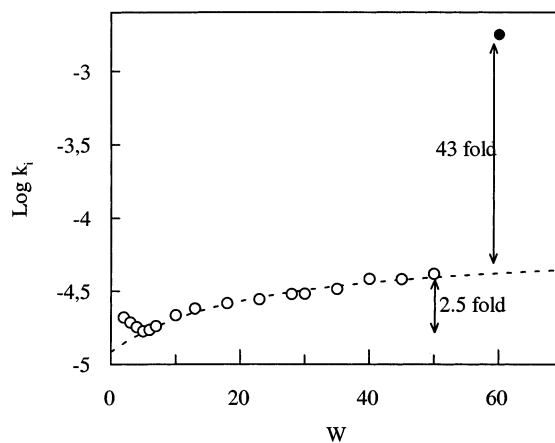


**Figure 4.** Variation of  $\text{Log } k_i^{\text{BzCl}}$  with the water content of the microemulsion,  $W$ , for the solvolysis of BzCl in microemulsions of AOT/isooctane/water at 25 °C (○) and the solvolysis rate constant in bulk water (●).

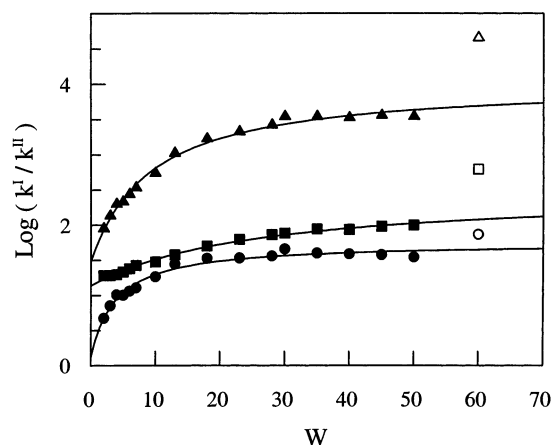
**Table 3**

Substrate	AOT / Isooctane / water			$\frac{k_i(\text{bulk water})}{k_i(W=50)}$	$\frac{k_i(W=50)}{k_i(W=2)}$
	$k_i(\text{bulk water})$	$k_i(W=50)$	$k_i(W=2)$		
<chem>COc1ccc(cc1)C(=O)Cl</chem> Dissociative mechanism	$58.2 \text{ s}^{-1}$	$0.158 \text{ s}^{-1}$	$4.85 \times 10^{-4} \text{ s}^{-1}$	368	326
<chem>c1ccccc1C(=O)Br</chem>	$80.8 \text{ s}^{-1}$	$0.144 \text{ s}^{-1}$	$1.87 \times 10^{-3} \text{ s}^{-1}$	560	77
<chem>c1ccccc1C(=O)Cl</chem>	$1.14 \text{ s}^{-1}$	$4.14 \times 10^{-3} \text{ s}^{-1}$	$3.97 \times 10^{-4} \text{ s}^{-1}$	275	10
<chem>c1ccccc1C(=O)F</chem>	$1.78 \times 10^{-3} \text{ s}^{-1}$	$4.16 \times 10^{-5} \text{ s}^{-1}$	$2.09 \times 10^{-5} \text{ s}^{-1}$	42	2
<chem>[O-][N+]([O-])c1ccc(cc1)C(=O)Cl</chem> Associative mechanism	$0.079 \text{ s}^{-1}$	$2.84 \times 10^{-3} \text{ s}^{-1}$	$8.32 \times 10^{-3} \text{ s}^{-1}$	27	0.34

shows the observed behavior for solvolysis of BzBr, BzCl, and BzF as well as for solvolysis of 4-methoxybenzoyl chloride, whose solvolysis takes place through a dissociative mechanism, and for 4-nitrobenzoyl chloride, where solvolysis takes place by an associative mechanism.<sup>13</sup>



**Figure 5.** Variation of  $\text{Log } k_i^{\text{BzF}}$  with the water content of the microemulsion,  $W$ , for the solvolysis of BzF in microemulsions of AOT/isooctane/water at 25 °C (○) and the solvolysis rate constant in bulk water (●).



**Figure 6.** Variation of (●)  $k_i^{\text{BzBr}}/k_i^{\text{BzCl}}$ , (▲)  $k_i^{\text{BzBr}}/k_i^{\text{BzF}}$ , and (■)  $k_i^{\text{BzCl}}/k_i^{\text{BzF}}$  with  $W$  for the solvolysis of BzX in microemulsions of AOT/isooctane/water. Empty symbols correspond to the same ratios in bulk water.

These inhibitions are compatible with that observed for nitroso group transfer in water in oil microemulsions as compared with bulk water.<sup>6a</sup>

The solvolysis rate constant decreases on going from bulk water to the interface of the microemulsion because of the insufficient hydration of the interface. The magnitude of the inhibition decreases with a decrease in the ability of the leaving group. In the same way, the rate constant decreases with a decrease in the water content of the microemulsion and the magnitude of the inhibition between  $W=50$  and  $W=2$  is also leaving group dependent. The magnitude of the inhibition is smaller for BzX than for 4-methoxybenzoyl chloride, and for 4-nitrobenzoyl chloride we observe the opposite behavior: increase of the solvolysis rate constant when  $W$  decreases. The fact that the magnitude of the inhibition on going from bulk water to  $W=50$  and on going from  $W=50$  to  $W=2$  depends on the leaving group is indicative that the transition state for the reaction is different when we change the halide leaving group.

Figure 6 also supports the hypothesis that the transition state for the reaction is different on changing the leaving group. The ratios  $k_i^{\text{BzBr}}/k_i^{\text{BzF}}$ ,  $k_i^{\text{BzCl}}/k_i^{\text{BzF}}$ , and  $k_i^{\text{BzBr}}/k_i^{\text{BzCl}}$  are used as indicative of the nature of the transition state. In bulk water, the obtained values of  $k_i^{\text{BzBr}}/k_i^{\text{BzF}} = 4.5 \times 10^4$ ,  $k_i^{\text{BzCl}}/k_i^{\text{BzF}} = 617$ , and  $k_i^{\text{BzBr}}/k_i^{\text{BzCl}} = 73$  are different from

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those obtained in microemulsions with high water content ( $W = 50$ ):  $k_1^{\text{BzBr}}/k_1^{\text{BzF}} = 3.4 \times 10^3$ ,  $k_1^{\text{BzCl}}/k_1^{\text{BzF}} = 99$ , and  $k_1^{\text{BzBr}}/k_1^{\text{BzCl}} = 35$ . These ratios of solvolysis rate constants in the microemulsion also decrease as  $W$  decreases, and the magnitude of the inhibition is depending on the leaving groups. The quotient  $k_1^{\text{BzBr}}/k_1^{\text{BzF}}$  decreases 39-fold, the quotient  $k_1^{\text{BzCl}}/k_1^{\text{BzF}}$  decreases 5.5 times, and we observe a decrease of 7.4-fold in the quotient  $k_1^{\text{BzBr}}/k_1^{\text{BzCl}}$  on going from  $W = 50$  to  $W = 2$ .

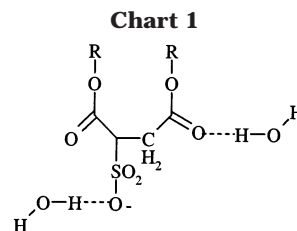
### Discussion

The solvolysis of benzoyl halides occurs by means of an associative or dissociative mechanism depending on the substituents of the benzoyl halide and the solvent in which the reaction takes place.<sup>8</sup> The results shown in Table 2 indicate that the values of  $k_1^{\text{BzX}}$  are strongly affected by both the leaving group and the water content of the microemulsion.

**Reaction Mechanism in Water in Oil AOT-Based Microemulsions.** Figures 3–5 show how  $k_1^{\text{BzBr}}$ ,  $k_1^{\text{BzCl}}$ , and  $k_1^{\text{BzF}}$ , for the solvolysis of the benzoyl bromide, chloride, and fluoride, respectively, decrease continuously as does the water content of the microemulsion. Those decreases are parallel with the reduction of the polarity of the interface with the water content of the microemulsion. A possible example of the changes in the polarity of the interface as a consequence of the variation of  $W$  is the analysis of the variation of dielectric constant values of the interface.<sup>14</sup> These values range from  $\epsilon = 31$  (for  $W = 1$ ) to  $\epsilon = 47$  (for  $W = 45.2$ ) as the water content varies. So the dependence of  $k_1^{\text{BzBr}}$ ,  $k_1^{\text{BzCl}}$ , and  $k_1^{\text{BzF}}$  on  $W$  is a consequence of the reduction of the capacity of the interfacial water to solvate the leaving group  $\text{Br}^-$ ,  $\text{Cl}^-$ , or  $\text{F}^-$ . As  $W$  decreases, the interfacial water content does too, and it is fundamentally implicated in the solvation of the headgroup of the AOT, which brings about a reduction in its electrophilic character.

The 77-fold reduction observed for  $k_1^{\text{BzBr}}$  as  $W$  decreases is larger than the 10-fold and 2.5-fold reductions observed for solvolysis of  $\text{BzCl}$  and  $\text{BzF}$ , respectively,<sup>15</sup> but much lower than the 300-fold reduction observed for the rate constant at the interface of the microemulsion, between the same values of  $W$ , for the solvolysis of 4-methoxybenzoyl chloride (see Table 3 for comparison). These results seem to indicate that the solvolysis of  $\text{BzBr}$  in microemulsions of AOT/isooctane/water does not behave like a completely dissociative process. In a previous study, we showed that the solvolysis of substituted benzoyl chlorides undergoes a change of mechanism, favoring an associative process as the water content of the microemulsion decreases.<sup>13</sup> The change from a predominantly dissociative mechanism to an associative one as  $W$  decreases could explain why the dependence of  $k_1^{\text{BzBr}}$  on  $W$  is weaker than in the solvolysis of 4-methoxybenzoyl chloride.

Two competing reaction channels have been proposed for solvolysis of benzoyl chloride.<sup>8,16</sup> One of these channels



is predominantly dissociative in character and the rate depends directly on the solvent polarity, whereas the competing reaction channel is much less sensitive to changes in solvent polarity. As aqueous binary mixtures cover a wide range of solvent polarities, a mechanistic change from one reaction channel to the other can be seen as the solvent composition is varied. Recent studies<sup>17</sup> showed that the solvolysis mechanism of benzoyl chlorides is mainly dissociative in highly aqueous media. The solvolysis of the  $\text{BzCl}$  presents, therefore, a change from an eminently dissociative process at high  $W$  values to an eminently associative one at low  $W$  levels. To explain the magnitude of the inhibition in Figure 4 in comparison with that observed in Figure 3, it is necessary to be aware of the influence of the changes in the composition of the microemulsion on the associative and dissociative processes.

As  $W$  decreases, so too does the interfacial water capacity of the microemulsion to solvate the leaving  $\text{Cl}^-$ . This decrease is a consequence of the reduction of the quantity of interfacial water and of the fact that water plays an increasingly important role in the solvation of the headgroup of the surfactant. Therefore, we should be able to observe a reduction in the rate constant of the dissociative process in an analogous way to the solvolysis of the  $\text{BzBr}$ . Previously we have studied the solvolysis of 4-nitrobenzoyl chloride,<sup>13</sup> a process which takes place fundamentally by means of an associative mechanism. Its rate constant increases as  $W$  decreases, probably because of the greater availability of the water to react as a consequence of the destruction of its structure of hydrogen bonds. Likewise, to this destruction of the structure of the hydrogen bonds of the interfacial water we have to add the fact that the interaction between the water and the headgroups of the surfactant takes place in such a way that water acts as an electron acceptor, solvating the carbonyl groups and  $\text{SO}_3^-$  (Chart 1), and consequently, the nucleophilic character of solvating water will increase. The smaller the water content of the microemulsion, the greater the increase in the nucleophilic character. Therefore, judging by the results shown in Figure 4, it is logical to believe that a change is taking place gradually in the solvolysis mechanism of the  $\text{BzCl}$  as  $W$  decreases. So, for large  $W$  values the reaction will take place fundamentally by means of a dissociative path, whereas for small  $W$  values the reaction will take place fundamentally by an associative path.

Figure 5 shows the variation of  $k_1^{\text{BzF}}$  with  $W$  for the solvolysis of  $\text{BzF}$ . This behavior shows quantitative differences from that observed in the solvolysis of the  $\text{BzCl}$  and  $\text{BzBr}$ , where the rate constant at the interface shows a dependence on  $W$  which is more pronounced and a greater variation is observed between the rate constant in bulk water and the value obtained at the interface of the microemulsion for  $W = 50$ . The rates of solvolysis of many substituted benzoyl fluorides, between which the non-substituted compound is found, show a large increase with

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(15) As mentioned by one of the reviewers, the minimum observed in the plot  $\text{Log } k_1$  versus  $W$  may be compatible with the error in the determination of  $k_1$ . However, as will be shown, the existence of that minimum is irrelevant, and we will focus our attention on the magnitude of the inhibition of  $k_1$  from bulk water to microemulsions with high water content ( $W = 50$ ) and low water content ( $W = 2$ ). For  $\text{BzF}$ , we observe a 43-fold decrease in the solvolysis rate constant on going from bulk water to  $W = 50$  and a 2.5-fold decrease on going from  $W = 50$  to  $W = 2$ .

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electron-withdrawing substituents and follow a Hammett correlation with  $\rho^+ = 1.65$ . This is evidence for an associative transition state that involves a bimolecular attack of water on the acyl halide.<sup>8</sup> Therefore, the variation of  $k_1^{\text{BzF}}$  with the composition of the microemulsion will be consistent with the solvolysis of the BzF taking place simultaneously by an associative and a dissociative path where the associative character predominates, in such a way that as  $W$  decreases the associative character of the reaction increases.<sup>18</sup>

The fact that the sensitivity of  $k_1^{\text{BzX}}$  to the water content of the microemulsion decreases with the sequence  $\text{BzBr} > \text{BzCl} > \text{BzF}$  is due to two main factors (see Chart 1), namely, the reduction of  $k_1^{\text{BzX}}$  as  $W$  decreases when the reaction occurs by means of a dissociative mechanism, as a consequence of the lower capacity for solvation of the leaving group  $\text{X}^-$ ; and the increase of  $k_1^{\text{BzX}}$  as  $W$  decreases when the reaction occurs by means of an associative mechanism, as a consequence of the increase of the nucleophilicity of the water.

**Influence of the Leaving Group Ability.** Figure 6 shows the variation of the quotients  $k_1^{\text{BzBr}}/k_1^{\text{BzF}}$ ,  $k_1^{\text{BzCl}}/k_1^{\text{BzF}}$ , and  $k_1^{\text{BzBr}}/k_1^{\text{BzCl}}$  with  $W$ , as well as the corresponding values in bulk water. Two apparent anomalous behaviors can be observed: First, the ratios in bulk water and in microemulsions of high water content ( $W = 50$ ) are different. In all cases, the ratios are smaller in the microemulsion than in bulk water. The second apparent anomaly is that these relationships do not remain constant as the water content of the microemulsion varies.

Experimentally obtained values of the quotient  $k_1^{\text{BzCl}}/k_1^{\text{BzF}}$  in AOT-based microemulsions are between  $k_{\text{Cl}}/k_{\text{F}} = 1.2$  for the solvolysis of 4-nitrobenzoyl halides in water, a reaction which takes place through an associative mechanism, and  $k_{\text{Cl}}/k_{\text{F}} = 3 \times 10^7$  for 4-(dimethylamino)-benzoyl halides, a reaction which occurs by a dissociative path.<sup>8</sup> This margin is so wide that it does not allow us to obtain any mechanistic information. The relationships  $k_1^{\text{BzCl}}/k_1^{\text{BzF}} \cong 600$  in bulk water and  $k_1^{\text{BzCl}}/k_1^{\text{BzF}} \cong 100$  for  $W = 50$  are greater than that found for the reaction of methyl halides with water,<sup>19</sup>  $k_{\text{Cl}}/k_{\text{F}} = 35$ , in which case the reaction takes place by means of a  $\text{S}_{\text{N}}2$  process. Likewise, this value is higher than that found in the reaction of methyl halides with hydroxide ion,<sup>20</sup>  $k_{\text{Cl}}/k_{\text{F}} = 11.4$ , and lower than that found in its reaction with iodide ion,<sup>21</sup>  $k_{\text{Cl}}/k_{\text{F}} = 830$ . The obtained value for  $W = 2$ ,  $k_1^{\text{BzCl}}/k_1^{\text{BzF}} \cong 18$ , is close to obtained values for  $\text{S}_{\text{N}}2$  processes. Therefore, the observed behavior for the relationship  $k_1^{\text{BzCl}}/k_1^{\text{BzF}}$  is consistent with a process which occurs where the BzCl reacts eminently by means of a dissociative mechanism whereas the BzF reacts by means of a predominantly associative one.

Bentley<sup>22,23</sup> has studied the influence of the leaving group and solvent effects on  $\text{S}_{\text{N}}1$  reactions of adamantyl substrates. In water, the relationship  $k_{\text{Br}}/k_{\text{Cl}}$  is approximately 25. As the solvent varies, in water/alcohol mixtures the relationship  $k_{\text{Br}}/k_{\text{Cl}}$  for the solvolysis of 1-adamantyl halides varies between  $k_{\text{Br}}/k_{\text{Cl}} = 18$  in a

solvent which contains 97% trifluoroethanol up to a value of  $k_{\text{Br}}/k_{\text{Cl}} = 35$  in a solvent which contains 80% ethanol. Bromide/chloride rate ratios in ethanol<sup>24</sup> are slightly higher for solvolysis of tertiary substrates ( $k_{\text{Br}}/k_{\text{Cl}} = 51$  for *tert*-butyl halide), and the solvolysis of 4-methoxybenzyl halides gives the lowest Br/Cl rate ratio ( $k_{\text{Br}}/k_{\text{Cl}} = 10.5$ ); the latter is not consistent with geminal electronic effects. The values of the relationship Br/Cl found for the solvolysis of benzoyl halides at the interface of AOT-based microemulsions vary from  $k_1^{\text{BzBr}}/k_1^{\text{BzCl}} = 35$  for  $W = 50$  up to  $k_1^{\text{BzBr}}/k_1^{\text{BzCl}} \cong 5$  for  $W = 2$  ( $k_1^{\text{BzBr}}/k_1^{\text{BzCl}} = 73$  in bulk water). The value of the relationship Br/Cl found for  $W = 50$  is typical of solvolytic  $\text{S}_{\text{N}}1$  processes indicating, therefore, that in microemulsions with high water contents both processes take place by means of a predominantly dissociative path.

To explain the variation of the relationships  $k_1^{\text{BzBr}}/k_1^{\text{BzF}}$ ,  $k_1^{\text{BzCl}}/k_1^{\text{BzF}}$ , and  $k_1^{\text{BzBr}}/k_1^{\text{BzCl}}$  with  $W$ , it is necessary to recall the influence of  $W$  on the rate of the associative and dissociative processes. As  $W$  decreases, so too does the interfacial water content and its electrophilic character to solvate the leaving group,  $\text{X}^-$ . Consequently, as the water content of the microemulsion decreases the rate of the dissociative mechanism also ought to decrease. At the same time, the variation of  $W$  entails an increase in the nucleophilicity of water due to the increase in the strength of the interactions between the interfacial water and the headgroup of the surfactant. In these interactions, the water always acts as an electronic acceptor, which brings about an increase in its nucleophilicity and, therefore, an increase in the rate of the associative process. If the processes of solvolysis took place by means of an associative mechanism, the three reactions would show the same dependence on  $W$  and consequently the relationships  $k_1^{\text{BzBr}}/k_1^{\text{BzF}}$ ,  $k_1^{\text{BzCl}}/k_1^{\text{BzF}}$ , and  $k_1^{\text{BzBr}}/k_1^{\text{BzCl}}$  would remain constant.

For a process which takes place by means of a dissociative mechanism, the electrophilic solvation of the dissolvent will be the main determining effect of its rate. There is good evidence that electrophilic effects for fluorides are even greater than for tosylates (OTs).<sup>25</sup> This consistent order of susceptibility to electrophilic effects,  $\text{F}^- > \text{OTs}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ , can be explained by differences of electronegativity between the atoms on which the negative charge is developing.<sup>26</sup> If the processes took place by means of a dissociative mechanism, the greater necessity for solvation of the  $\text{F}^-$  due to its smaller size would mean that its sensitivity to the changes in the electrophilic character of the water would be greater and consequently the relationships  $k_1^{\text{BzBr}}/k_1^{\text{BzF}}$ ,  $k_1^{\text{BzCl}}/k_1^{\text{BzF}}$ , and  $k_1^{\text{BzBr}}/k_1^{\text{BzCl}}$  should increase as  $W$  decreases. The experimental observed behavior is the opposite, and in order to explain this, it is necessary to bear in mind that a displacement from a dissociative to an associative mechanism takes place as  $W$  decreases.

The decrease in the three relationships,  $k_1^{\text{BzBr}}/k_1^{\text{BzF}}$ ,  $k_1^{\text{BzCl}}/k_1^{\text{BzF}}$ , and  $k_1^{\text{BzBr}}/k_1^{\text{BzCl}}$ , with  $W$  is consistent with the increase in the associative character of these solvolytic processes as  $W$  decreases, and with the fact that the weaker the leaving group, the greater the importance of the associative character. The rate of the associative process is less sensitive to solvent polarity than that of

(18) If the reaction took place by means of a dissociative path, the greater necessity of solvation of the  $\text{F}^-$ , by comparison with  $\text{Cl}^-$  and  $\text{Br}^-$ , would mean that the variation of  $k_1^{\text{BzF}}$  with  $W$  would be the most pronounced of the three substrates studied.

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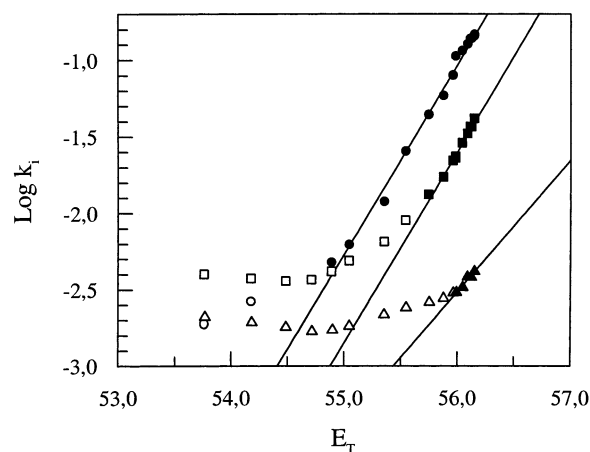
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the dissociative one due to the strong solvation of the leaving group. For example, the rate of solvolysis of the BzBr will decrease constantly as  $W$  does; however, the decrease in the rate of the solvolysis of the BzF with  $W$  is much less, meaning that the relationship  $k_i^{\text{BzBr}}/k_i^{\text{BzF}}$  decreases as  $W$  decreases. An analysis of the results shown in Figure 6 indicates that the relationship  $k_i^{\text{BzCl}}/k_i^{\text{BzF}}$  decreases approximately 5-fold from  $W = 50$  to  $W = 2$ , and the relationship  $k_i^{\text{BzBr}}/k_i^{\text{BzCl}}$  decreases approximately 7-fold, whereas the relationship  $k_i^{\text{BzBr}}/k_i^{\text{BzF}}$  decreases approximately 40-fold. This behavior is consistent with the displacement from a dissociative to an associative character as the capacity of the leaving group decreases. The solvolysis of the BzF presents simultaneously an associative and dissociative character at  $W = 50$ , whereas for the solvolysis of the BzCl and BzBr at  $W = 50$  the percentage of associative character must be lower. As  $W$  decreases, the solvolysis of the BzF shows an increase in the associative character (that increase is less noticeable for BzCl and BzBr).

**Correlation with  $E_T$  Polarity Parameter.** A very useful tool for investigating reaction mechanisms is the correlation of rate constants with the solvent polarity by using empirical parameters. There exist only a few systematic studies of the physical properties of the microemulsion as a function of  $W$ , examining mainly properties such as polarity of the interface,<sup>27</sup> viscosity,<sup>28</sup> water penetration, and so forth. Grieser<sup>14</sup> and Silber<sup>29</sup> have studied the variation of  $\lambda_{\text{max}}$  of  $E_T(30)$ <sup>30</sup> with the composition of microemulsions of AOT. On the basis of the values of  $\lambda_{\text{max}}$  obtained by Grieser, we have calculated the variation of the parameter  $E_T$  according to  $W$ . Because of the rather localized negative charge at the phenolic oxygen atom, the standard dye,  $E_T(30)$ , is capable of specific Lewis acid/base interactions. Therefore, in addition to the nonspecific dye/solvent interactions, the betaine dye  $E_T(30)$  preferably measures the specific Lewis acidity of organic solvents. On the other hand, the positive charge of the pyridinium moiety of  $E_T(30)$  is delocalized. Therefore, the solvent Lewis basicity will not be registered by the probe molecules  $E_T(30)$ . If this solvent property is relevant for the system under study, other empirical measures of Lewis basicity should be used. Therefore, the parameter  $E_T$  will be a good measurement to evaluate the capacity of the interfacial water of the microemulsion to solvate the leaving  $X^-$  group and, therefore, to quantify the magnitude of the dissociative mechanism by comparison with the associative one. In Figure 7, we can observe the correlation existing between the logarithm of the rate constant at the interface of the microemulsion and the  $E_T$  polarity parameter for the solvolysis of benzoyl halides.<sup>31</sup>



**Figure 7.** Correlation between  $\text{Log } k_i$  and the  $E_T$  polarity parameter for solvolysis of benzoyl halides in AOT/isooctane/water microemulsions: (●,○)  $\text{Log } k_i$  for solvolysis of BzBr, (■,□)  $(1 + \text{Log } k_i)$  for solvolysis of BzCl, and (▲,△)  $(2 + \text{Log } k_i)$  for solvolysis of BzF. Empty points are not included in the correlation.

The solvolysis of the benzoyl bromide shows a good correlation ( $r > 0.996$ ) for values of  $W > 6$ , which indicates that the reaction takes place predominantly through a dissociative mechanism in the microemulsion interface with a high water content. As the water content of the microemulsion decreases, we can observe a deviation of the correlation. This deviation contrasts with the existence of a perfectly linear correlation between  $\text{Log } k_i$  versus the  $E_T$  polarity parameter for the solvolysis of 4-methoxybenzoyl chloride,<sup>13</sup> a reaction which takes place through a dissociative mechanism, between  $W = 50$  and  $W = 2$ . In solvolysis of BzCl and BzF, there exists a correlation between  $\text{Log } k_i^{\text{BzX}}$  and the  $E_T$  polarity parameter for microemulsions with high water contents, causing a deviation of the correlation as  $W$  decreases. Quantitatively, we can observe that the deviation of the correlation  $\text{Log } k_i^{\text{BzX}}$  versus  $E_T$  is produced at higher water contents, the weaker the leaving group of the benzoyl halide. For the BzBr, a good correlation can be seen for values of  $W > 6$ , while with the BzCl only the values of  $W > 18$  satisfy the correlation. In the case of the BzF, only the values of  $k_i^{\text{BzF}}$  obtained for higher water contents ( $W > 30$ ) satisfy the correlation  $\text{Log } k_i^{\text{BzX}}$  versus  $E_T$ .

As can be observed in Figure 7, the gradients of the correlations  $\text{Log } k_i^{\text{BzX}}$  versus  $E_T$  are very similar. The values obtained ( $1.24 \pm 0.03$ ) for the solvolysis of the BzBr and ( $1.25 \pm 0.06$ ) for the solvolysis of the BzCl indicate that the two processes present the same sensitivity to the changes in the properties of the medium for high water contents of the microemulsion. This result indicates, therefore, for values of  $W > 25$  that both processes should take place with the same percentage of associative and dissociative character. The results obtained with the BzF, gradient =  $(0.9 \pm 0.1)$ , indicate that this process is less sensitive to the changes in the electrophilic character of the interfacial water and hence suggest the existence of a lesser dissociative character in its reaction mechanism. In any case, the value of the gradient of the correlation  $\text{Log } k_i^{\text{BzF}}$  versus  $E_T$  cannot be determined with complete certainty due to the fact that it was only possible to use the values of  $W > 35$ .

The deviations of the correlation between  $\text{Log } k_i^{\text{BzX}}$  versus  $E_T$  are a consequence of the change of solvolysis mechanism from an extreme where the reaction takes place with a high dissociative character to another extreme

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where the associative mechanism is the one which predominates. The rupture in the correlation  $\text{Log } k_1^{\text{BzX}}$  versus  $E_T$  is consistent with the effect of the substituents observed in the solvolysis of benzoyl halides in water.<sup>8</sup> The change from a dissociative to an associative reaction path with increasingly electron-withdrawing substituents occurs much later for benzoyl chlorides than for benzoyl fluorides because the rate of the associative reaction is independent of the leaving group, while the dissociative reaction is strongly dependent on the leaving group.

### Conclusions

A study was carried out on the solvolysis of benzoyl chloride, bromide, and fluoride in microemulsions of AOT/isooctane/water. The application of the formalism of the pseudophase has allowed us to obtain the intrinsic rate constants for solvolysis at the interface of the microemulsion. The observed behavior indicates that for high water contents in the microemulsion,  $W=50$ , the three processes take place simultaneously by an associative and a dissociative path, the relative importance of which depends on the capacity of the leaving group. The stronger the

leaving group, the greater the percentage of the dissociative character. As the water content of the microemulsion decreases, the dissociative process becomes difficult due to the lesser capacity of the interfacial water to solvate the leaving group  $X^-$ , but the associative process is favored due to the increase in the nucleophilicity of water as a consequence of its interaction in the solvation of the headgroups of the AOT. The combination of these two factors means that a displacement occurs from an eminently dissociative mechanism at high  $W$  values to one that is eminently associative as the water content of the microemulsion decreases. These results enable us to suggest the existence of a new field of application of the microemulsions as an alternative to the solvent mixtures in carrying out mechanistic studies.

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