Reactivity in Water/Oil Microemulsions. Influence of Sodium Bis(2-ethylhexyl)sulfosuccinate/Isooctane/Water Microemulsions on the Solvolysis Mechanism of Substituted Benzoyl Chlorides

Luis García-Rio,* José Ramón Leis, and José A. Moreira

*Contribution from the Dpto Química Física, Facultad de Química, Universidad de Santiago, 15706 Santiago, Spain*

Received April 27, 2000. Revised Manuscript Received August 1, 2000

Abstract: A study was carried out on the solvolysis of the following substituted benzoyl chlorides in sodium bis(2-ethylhexyl)sulfosuccinate (AOT)/isooctane/water microemulsions: 4-CH$_3$O, 3,4-(CH$_3$O)$_2$, 4-CH$_3$, 4-H, 4-Cl, 3-Cl, 4-CF$_3$, 3-CF$_3$, 3-NO$_2$, and 4-NO$_2$. The benzoyl chlorides are found distributed between the isooctane and the interface, where they react with its hydration water. From the kinetic data we have been able to obtain the true rate constant for the reaction at the interface, k_i. Two extreme types of behavior have been observed: for those processes which occur via a predominantly dissociative pathway, k_i decreases together with W ($W =$ [H$_2$O]/[AOT]), while for those processes which occur through a predominantly associative pathway, the rate constant at the interface, k_i, increases as W decreases. The decrease of k_i with W is interpreted as being due to the capacity of interfacial water for solvating the leaving Cl$^-$. For the associative process, the increase in the nucleophilic capacity of the interfacial water as W decreases is the factor responsible for the increase in k_i, so that the lesser capacity for solvation of the transition state can be compensated for as the water content of the microemulsion decreases. A comparative analysis of the reactivity of substituted benzoyl chlorides at the interface of the microemulsion shows an increase of the rate of the associative pathway and a decrease of the dissociative counterpart. Hence for $W = 50$, the change between the two reaction pathways is observed for the benzoyl chlorides with substituents 4-Cl and 3-Cl, while in bulk water this change takes place with more electron-attracting substituents. When the water content of the microemulsion decreases ($W = 2$), only the benzoyl chlorides 4-CH$_3$O and 3,4-(CH$_3$O)$_2$ will react predominantly through the dissociative pathway.

Introduction

Microemulsions are pseudohomogeneous mixtures of water-insoluble organic compounds, water, and a surfactant/cosurfactant mixture. In recent decades reactions in microemulsions have developed to constitute an emerging technology. In most instances oil-continuous microemulsions, water in oil systems (w/o) have been used and the water droplets have proven useful as "minireactors" for various types of synthesis.[1] In preparative organic synthesis microemulsions are of interest as a way of overcoming incompatibility problems between nonpolar organic compounds and inorganic salts. For this purpose, microemulsions can be regarded as an alternative to two-phase systems with added phase transfer reagents. 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: (a) the internal aqueous core or water pool, (b) the micellar interface formed by a monolayer of surfactant molecules with their polar headgroups oriented toward the water pool, and (c) the external organic phase.[2−5] Transition from a homogeneous solvent system to a microemulsion may also affect the regioselectivity

of organic reactions due to orientation of reactants at the oil−water interface.[1] The most intensively studied three-component w/o microemulsions have been systems of the form water/AOT/oil, where AOT is sodium bis(2-ethylhexyl)sulfosuccinate.[6] Droplet radius depends linearly on the water content of the microemulsion, as confirmed by several experimental techniques.[7] An important property of these systems is the highly structured nature of the water at the interface when the [H$_2$O]/[AOT] ratio W is small.
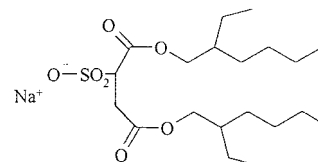
AOT, Sodium bis(2-ethylhexyl)sulfosuccinate

Dynamical measurements have been used to characterize the intramicellar water in w/o microemulsions. These studies all find that the water inside the micelles moves differently from bulk water. Using viscosity sensitive probes, Hasegawa et al.[8]

(1) Holmberg, K. *Adv. Colloid Interface Sci.* **1994**, *51*, 137.
(2) Pileni, M. P. *Structure and Reactivity in Reverse Micelles*; Elsevier: Amsterdam, 1989.
(3) *Reverse Micelles*; Luisi, P. L., Straub, B. E., Eds.; Plenum Press: New York, 1984.
(4) Degiorgio, V. *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*; North-Holland: Amsterdam, 1985.

(5) (a) Dvolaitzkay, M.; Guyot, M.; Lagues, M.; Le Pesant, J. P.; Ober, R.; Taupin, C. *J. Phys. Chem.* **1978**, *69*, 3279. (b) Drifford, M.; Tabony, J.; De Geyer, A. *Chem. Phys. Lett.* **1983**, *96*, 119.
(6) De, T. K.; Maitra, A. *Adv. Colloid Interface Sci.* **1995**, *59*, 95.
(7) Zulauf, M.; Eicke, H. F. *J. Phys. Chem.* **1979**, *83*, 480.
(8) Hasegawa, M.; Sugimura, T.; Shindo, Y.; Kitahara, A. *Colloids Surf. A* **1996**, *109*, 305.

10326   *J. Am. Chem. Soc., Vol. 122, No. 42, 2000*

García-Rio et al.

have measured the microviscosity inside reverse micelles of varying size. Their results indicate that the water inside micelles with $W < 10$ has a higher viscosity than that of the bulk, a fact that they ascribe to water bound to the AOT polar headgroups. For microemulsions larger than $W = 10$, the viscosity decreases slowly as the size of the microemulsions increases. Solvent relaxation with fluorescence probes[9,10] reveals two different solvation rates inside the microemulsions that authors attribute to water bound to the polar headgroups of AOT and bulklike water. The results from these and other studies[11] indicate that water in AOT microemulsions moves more slowly than bulk water. While ordinary water molecules relax in the subpico-second time scale, inside microemulsions the solvation dynamics becomes several thousand times slower and occurs in the nanosecond time scale.[11a,12] Water motion in the low water content microemulsions was essentially frozen while in higher ones additional bulklike relaxation components developed.

The study of the chemical reactivity in microemulsions requires knowledge of the concentrations of the reagents in the different pseudophases, and the true rate constants in each pseudophase also need to be determined. On these premises, the prediction and/or interpretation of the kinetic influence of these media is relatively easy when both reagents congregate in the aqueous microdroplets, which act as variable-size nanoreactors concentrating the reagents.[13-15] Less attention has been paid to reactions in which the reagents are distributed in the aqueous and apolar phases and at their interface.[16,17] From the viewpoint of chemical reactivity, owing to the existence of large internal interfaces and to the unusual state of water in the droplets, the w/o microemulsions have attracted great interest because they can be used as substitutive novel media capable of significantly altering the rates of chemical and biochemical reactions compared with their rates in the bulk water. Although variations in the observed kinetics of reactions in microemulsions have previously been attributed to changes in the structuredness of the interfacial water,[14,18] no attempt has been made to model this behavior. A thorough knowledge of these properties is of major importance for the understanding of studies on reactivity, because reactivity in any reaction medium depends not only on the chemical nature but also on its structure.

In this study we will examine the solvolysis of substituted benzoyl chlorides in AOT/isooctane/water microemulsions for the purpose of evaluating the effect of changes in the structure of the water on reaction kinetics that take place through different mechanisms.
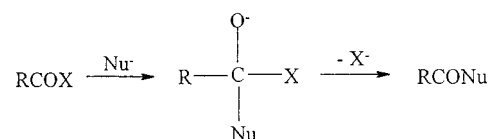
Acyl transfer reactions are commonly classified into three groups:[19] (a) dissociative mechanism, with an acylium ion intermediate,

$$RCOX \longrightarrow \overset{+}{R}C{=}O \overset{Nu^-}{\longrightarrow} RCONu$$
$$\underset{X^-}{}$$
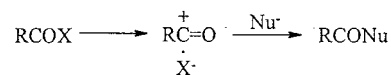
(b) concerted displacement, which can have an associative or dissociative character,

$$RCOX \overset{Nu^-}{\longrightarrow} [TS]^{\neq} \overset{-X^-}{\longrightarrow} RCONu$$
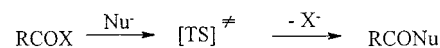
(c) associative, or addition−elimination, with a tetrahedral addition intermediate.

$$RCOX \overset{Nu^-}{\longrightarrow} R{-}\underset{Nu}{\overset{O^-}{\underset{|}{\overset{|}{C}}}}{-}X \overset{-X^-}{\longrightarrow} RCONu$$

The aim of this study is to investigate the repercussion that the changes in the water properties of the microemulsions have on reactions that are highly sensitive to the properties of the reaction medium. Likewise, the comparison of the reactivity of the different benzoyl chlorides in microemulsions with different water contents allows us to study the possibility that the changes in the structural properties of the water give rise to a change in the solvolysis mechanism of benzoyl chlorides.

Experimental Section

Materials. AOT (Aldrich) was dried in a vacuum desiccator for 2 days and then used without further purification. Substituted benzoyl chlorides (all from Aldrich) were of the highest available purity and were used as supplied; all of them were dissolved in isooctane (Aldrich). Aldrich provided D_2O for the study of kinetic solvent isotope effects.

Methods. Microemulsions were prepared by mixing isooctane, water, and 1.00 M AOT/isooctane solution in appropiate proportions. The solvolysis reactions were followed by monitoring the UV absorbance of substrate solutions (concentration range $(1-2) \times 10^{-4}$ M) using a Varian Cary 500 Scan UV−vis−NIR spectrophotometer fitted with thermostated cell holders (all experiments were carried out at 25 °C). The wavelengths used for the kinetic studies fell between $\lambda = 280$ and 290 nm for 4-CH₃O, 3,4-(CH₃O)₂, 4-CH₃, 4-H, 4-Cl, 3-Cl, 4-CF₃, 3-CF₃ and $\lambda = 295$ nm for 3-NO₂ and $\lambda = 305$ nm for 4-NO₂. The kinetic data always fitted the first-order integrated rate equation satisfactorily ($r > 0.999$); in what follows, k_{obs} denotes the pseudo-first-order rate constant. We were able to reproduce the rate constants with an error margin of ±5%. In all cases it was checked that the final spectrum of the product of the reaction coincided with another obtained in pure water, guaranteeing that the presence of the microemulsions did not alter the product of the reaction.

Results

Influence of the Composition of the Microemulsion. A study was carried out on the influence of the microemulsion composition on the rate of solvolysis of substituted benzoyl chlorides by varying the surfactant concentration, typically $[AOT] = (0.05-0.60)M$, and maintaining the molar relation W constant. Figure 1 shows the variation of k_{obs} with the surfactant concentration in the solvolysis of 3-CF₃ for series of experiments carried out on $W = 18$ and $W = 40$. As we can observe, k_{obs} increases along with [AOT] and decreases as the water content

(9) Zhang, J.; Bright, F. V. *J. Phys. Chem.* **1991**, *95*, 7900.

(10) Cho, C. H.; Chung, M.; Lee, J.; Nguyen, T.; Singh, S.; Vedamuthu, M.; Yao, S. H.; Zhu, J. B.; Robinson, G. W. *J. Phys. Chem.* **1995**, *99*, 7806.

(11) (a) Sarkar, N.; Das, K.; Datta, A.; Das, S.; Bhattacharyya, K. *J. Phys. Chem.* **1996**, *100*, 10523. (b) Riter, R. E.; Willard, D. M.; Levinger, N. E. *J. Phys. Chem. B* **1998**, *102*, 2705. (c) Riter, R. E.; Undiks, E. P.; Levinger, N. E. *J. Am. Chem. Soc.* **1998**, *120*, 6062. (d) Mittleman, D. M.; Nuss, M. C.; Colvin, V. L. *Chem. Phys. Lett.* **1997**, *275*, 332.

(12) Das, S.; Datta, A.; Bhattachatyya, K. *J. Phys. Chem. A* **1997**, *101*, 3299.

(13) Valiente, M.; Rodenas, E. *J. Phys. Chem.* **1991**, *95*, 3368.

(14) Moyá, M. L.; Izquierdo, C.; Casado, J. *J. Phys. Chem.* **1991**, *95*, 6001.

(15) Gómez-Herrera, C.; Graciana, M. M.; Muñoz, E.; Moyá, M. L.; Sánchez, F. *J. Colloid Interface Sci.* **1991**, *141*, 454.

(16) (a) García-Rio, L.; Leis, J. R.; Peña, M. E.; Iglesias, E. *J. Phys. Chem.* **1993**, *97*, 3437. (b)García-Rio, L.; Leis, J. R.; Mejuto, J. C. *J. Phys. Chem.* **1996**, *100*, 10981.

(17) See, for example (a) Casavino, F. P.; Sbriziolo, C.; Turco Liveri, M. L. *J. Phys. Chem. B* **1998**, *102*, 3143. (b) Casavino, F. P.; Sbriziolo, C.; Turco Liveri, M. L. *J. Phys. Chem. B* **1998**, *102*, 5050, and references therein. (c) Durantini, E. N.; Borsarelly, C. D. *J. Chem. Soc., Perkin Trans 2* **1996**, 719. (d) Correa, N. M.; Durantini, E. N.; Silber, J. J. *J. Org. Chem.* **1999**, *64*, 5757.

(18) (a) O'Connor, C. J.; Fendler, E. J.; Fendler, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 600. (b) El-Seoud, O. A.; Da Silva, M. J.; Barbur, L. P.; Martine, A. *J. Chem. Soc., Perkin Trans 2* **1978**, 331. (c) López, P.; Rodriguez, A.; Gómez-Herrera, C.; Sánchez, F.; Moyá, M. L. *J. Chem. Soc., Faraday Trans 1* **1992**, *88*, 2701.

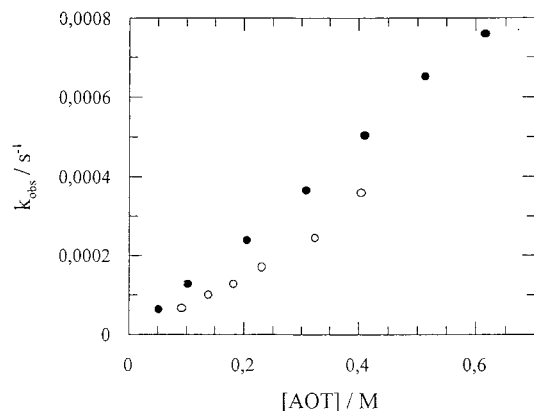(19) Song, B. D.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8470.

Reactivity in Water/Oil Microemulsions

J. Am. Chem. Soc., Vol. 122, No. 42, 2000 10327

Figure 1. Influence of AOT concentration on k_{obs} for the solvolysis of 3-CF$_3$ at (●) $W = 18$ and (○) $W = 40$ in AOT/isooctane/water microemulsions at 25 °C.
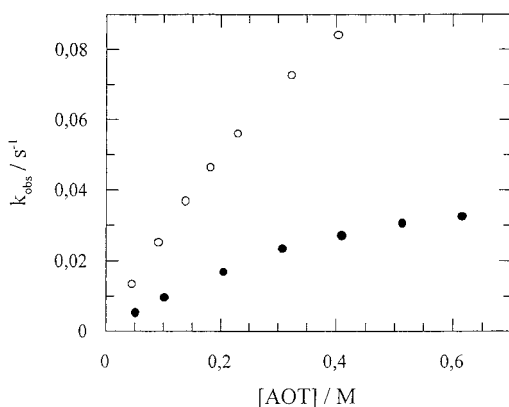

Figure 2. Influence of AOT concentration on k_{obs} for the solvolysis of 3,4-(CH$_3$O)$_2$ at (●) $W = 18$ and (○) $W = 40$ in AOT/isooctane/water microemulsions at 25 °C.

of the microemulsion increases, that is, as W increases. The values of k_{obs} in the microemulsion are much lower than those observed in pure water,[19] $k_{H_2O} = 0.034$ s^{-1},and greater (especially when high concentrations of AOT are involved) than the values obtained for the solvolysis of 3-CF$_3$ in 90% trifluoroethanol:10% water[20] ($k_{90\%TFE} \cong 7.99 \times 10^{-5}$ s^{-1}) and in 97% trifluoroethanol:3% water[21] ($k_{97\%TFE} \cong 5.86 \times 10^{-5}$ s^{-1}).

During the study of the solvolysis of a benzoyl chloride with electron-donating substituents, a different behavior pattern can be observed. Figure 2 shows the variation of k_{obs} with [AOT] in the solvolysis of the 3,4-(CH$_3$O)$_2$ for a series of experiments on $W = 18$ and 40. In this case the observed rate constant increases along with the water content of the microemulsion and with the surfactant concentration. The values of the pseudo-first-order rate constant, k_{obs}, in the microemulsion are much lower than the value observed in pure water, [22] $k_{H_2O} = 161$s^{-1}. Unlike with the solvolysis of the 3-CF$_3$, in the solvolysis of the 3,4-(CH$_3$O)$_2$ the values of k_{obs} in the microemulsion are always lower than the values obtained in 90% trifluoroethanol:10% water[20] ($k_{90\%TFE} \cong 0.62$ s^{-1}) and in 97% trifluoroethanol: 3% water[21] ($k_{97\%TFE} \cong 0.47$ s^{-1}).

To interpret the experimental results correctly, it is necessary to obtain the true rate constants for the solvolysis process. The kinetic results obtained can be quantitatively explained by

(20) Volume percent: Song, B. D.; Jencks, *W. P. J. Am. Chem. Soc.* **1989**, *111*, 8470.
(21) Weight percent: Bentley, T. *W.*; Harris, H. C. *J. Chem. Soc., Perkin Trans 2* **1986**, 619.
(22) Values extrapolated from Hammett plots and data in ref 19.

Scheme 1
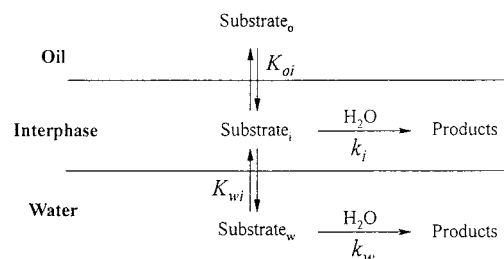
applying the pseudophase[16,23] model generally used for reactions in micellar systems.[24] The microemulsions are assumed to be divided into three regions corresponding to the oil-rich domain, o; the central aqueous core, w; and the surfactant interfacial region, i. The reagents are distributed between the three pseudophases according to their solubilities, and the global rate of the reaction will be the sum of the rates in the different pseudophases.

Under the conditions of this study, the solvolysis reactions can take place in the aqueous pseudophase and at the interface, depending on the distribution of the reagents. The benzoyl chlorides used are hydrophobic substrates, but there is a chance that a small quantity could have access to the aqueous pseudophase, where the reaction rate would be probably greater than at the interface. Therefore, it is important to determine the possible localization/distribution of the reagents and the reaction position or positions.

Identification of the Reaction Position. The application of the pseudophase formalism allows us to evaluate the distribution of the substrates through the microemulsion.

(a) Simultaneous Reaction at the Interface and in the Aqueous Pseudophase. In a first approximation, we can suppose that substrate is distributed between the three pseudophases of the microemulsion (Scheme 1), so that the solvolysis process can take place simultaneously at the interface and the aqueous pseudophase.

The global reaction rate will be the sum of the rates in both pseudophases.

$$r = k_i[S]_i + k_w[S]_w \tag{1}$$

The distribution equilibria of the substrate between the pseudophases can be defined in terms of molar relation such as

$$K_{wi} = \frac{[S]_i}{[S]_w}W \qquad K_{oi} = \frac{[S]_i}{[S]_o}Z \tag{2}$$

where the concentrations refer to the total volume of the microemulsion and where Z is defined as $Z = $ [isooctane]/[AOT]

(23) (a) Fletcher, P. D. I.; Robinson, B. H. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2417. (b) Schomäcker, R.; Stickdorn, K.; Knoche, *W. J. Chem. Soc., Faraday Trans 1* **1991**, *87*, 847. (c) Miyake, Y.; Owari, T.; Ishiga, F.; Teramoto, M. *J. Chem. Soc., Faraday Trans* **1994**, *90*, 979. (d) López, P.; Rodríguez, A.; Gómez-Herrera, C.; Sánchez, F.; Moyá, M. L. *Int. J. Chem. Kinet.* **1995**, *27*, 525. (e) Cavasino, F. P.; Sbriziolo, C.; Turco Liveri, M. L. *J. Chem. Soc., Faraday Trans* **1988**, *94*, 395. (f) Mackay, R. A. *J. Phys. Chem.* **1982**, *86*, 4756. (g) Athanassakis, V.; Bunton, C. A.; McKenzie, D. C. *J. Phys. Chem.* **1986**, *90*, 5858. (h) Da Rocha Pereira, R.; Zanette, D.; Nome, F. *J. Phys. Chem.* **1990**, *94*, 356. (i) Cavasino, F. P.; Sbriziolo, C.; Cusumano, M.; Giannetto, A. *J. Chem. Soc., Faraday Trans* **1996**, *92*, 2263. (j) Cusumano, M.; Giannetto, A.; Cavasino, F. P.; Sbriziolo, C. *Inorg. Chim. Acta* **1992**, *201*, 49. (k) Berezin, I. V.; Martinek, K.; Yatsimirsckii, A. K. *Russ. Chem. Rev.* **1973**, *42*, 787. (l) Fletcher, P. D. I. *J. Chem. Soc., Faraday Trans 1* **1986**, *82*, 2651.
(24) (a) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975. (b) Bunton, C. A.; Savelli, G. *Adv. Phys. Org. Chem.* **1986**, *22*, 213.

Table 1. Influence of W on the Ratio Intercept/Slope According to Eq 4 or Eq 7 for Solvolysis of Benzoyl Chloride (4-H), 4-Methoxybenzoyl Chloride (4-CH$_3$O), and Diphenylmethyl Chloride (DPhMeCl) in AOT/Isooctane/Water Microemulsions at 25 °C[a]

W	Slope/Intercept		
	4-H	4-CH$_3$O	DPhMeCl
2	2.2	12.6	
3	1.8	10.4	
4	2.5	17.8	3.2
5	2.5	13.3	3.3
6	4.0	10.2	2.6
7	4.2	10.7	2.2
10	6.5	8.9	3.3
13	3.4	9.1	3.1
18	4.1	8.6	2.5
23	5.5	8.8	1.9
30	3.3		1.5
40	4.0		2.1
50	3.7		2.2
55	4.2		

[a] Data from ref 25.

by analogy with the parameter W. Considering that the total concentration of the substrate will be the sum of the concentrations in the three pseudophases, we can obtain

$$k_{obs} = \frac{k_i K_{oi} K_{wi} + k_w K_{oi} W}{K_{wi} K_{oi} + K_{oi} W + K_{wi} Z} \quad (3)$$

This equation can be transformed as

$$\frac{1}{k_{obs}} = \frac{K_{oi} K_{wi} + K_{oi} W}{k_i K_{oi} K_{wi} + k_w K_{oi} W} + \frac{K_{wi}}{k_i K_{oi} K_{wi} + k_w K_{oi} W} Z \quad (4)$$
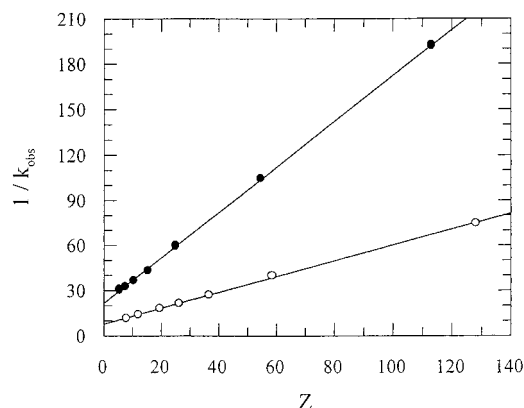
As has been shown previously[25] for the solvolysis of hydrophobic substrates, notably the 4-methoxybenzoyl chloride (4-CH$_3$O), benzoyl chloride (4-H), and diphenylmethyl chloride (DPhMeCl), there exists a linear dependence between the inverse of k_{obs} and the Z parameter. On the basis of eq 4, the following equation is obtained for the quotient intercept/slope:

$$\frac{intercept}{slope} = K_{oi} + \frac{K_{oi}}{K_{wi}} W \quad (5)$$

This relationship predicts that the intercept/slope of the representations of $1/k_{obs}$ vs Z should vary with W. Table 1 displays the results of this relationship previously obtained for the solvolysis of the 4-CH$_3$O, 4-H, and DPhMeCl in microemulsions of AOT/isooctane/water. As we can see, the intercept/slope remains independent[26] 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 referred to in the bibliography[17c] 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.

(25) García-Rio, L.; Leis, J. R.; Iglesias, E. *J. Phys. Chem.* **1995**, *99*, 12318.

(26) In the case of the 4-CH$_3$O there exists a slight dependence of the quotient intercept/slope on W. However, the variation found is contrary to that expected, given the eq 5. In fact, the value of the quotient intercept/slope decreases, instead of increasing, as W increases. This behavior is considered to be fundamentally due to the errors existing in the determination of the quotient intercept/slope.

Scheme 2
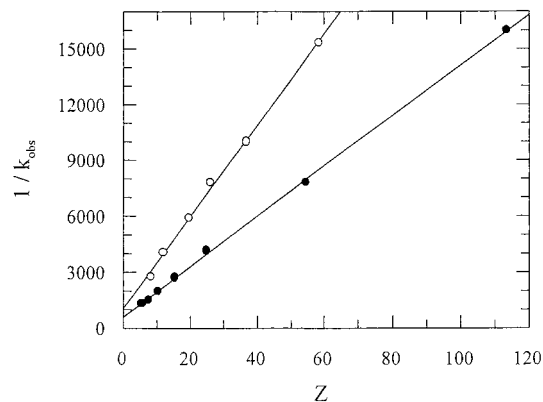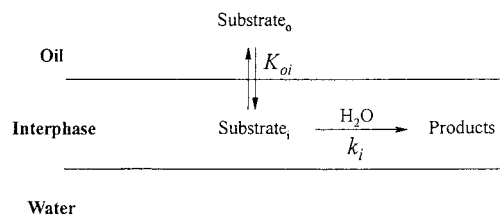
Figure 3. Linearization of the results of Figure 1 of the formula $1/k_{obs}$ vs Z (eq 7) for the solvolysis of 3-CF$_3$ at (●) $W = 18$ and (○) $W = 40$ in AOT/isooctane/water microemulsions at 25 °C.

Figure 4. Linearization of the results of Figure 1 of the formula $1/k_{obs}$ vs Z (eq 7) for the solvolysis of 3,4-(CH$_3$O)$_2$ at (●) $W = 18$ and (○) $W = 40$ in AOT/isooctane/water microemulsions at 25 °C.

(b) Reaction at the Interface Alone. The results shown previously indicate that the substrates are distributed solely between the isooctane pseudophase and the interface. Therefore, the mechanistic scheme shown in diagram 1 can be simplified to Scheme 2.

On the basis of this diagram, the following expression for k_{obs} can easily be formulated

$$k_{obs} = \frac{k_i K_{oi}}{K_{oi} + Z} \quad (6)$$

which predicts the existence of a linear dependence between $1/k_{obs}$ vs Z.

$$\frac{1}{k_{obs}} = \frac{1}{k_i} + \frac{Z}{k_i K_{oi}} \quad (7)$$

Figures 3 and 4 show the linearized representation of $1/k_{obs}$ vs Z for the solvolysis of 3-CF$_3$ and 3,4-(CH$_3$O)$_2$ at $W = 18$ and 40. On the basis of the relationship between the intercept/

Table 2. K_{oi} Values for Incorporation of Substituted Benzoyl Chlorides at the Interface of AOT/Isooctane/Water Microemulsions at 25 °C and $W = 18$

4-CH$_3$O	3,4-(CH$_3$O)$_2$	4-CH$_3$	4-H	4-Cl	3-Cl	4-CF$_3$	3-CF$_3$	3-NO$_2$	4-NO$_2$
5.9 ± 0.9	14.3 ± 0.3	2.7 ± 0.4	4.6 ± 1.1	2.5 ± 0.1	6.3 ± 0.4	3.2 ± 0.6	4.4 ± 0.5	121 ± 9	164 ± 20

Table 3. Influence of W on k_i Values for Solvolysis of Substituted Benzoyl Chlorides in AOT/Isooctane/Water Microemulsions at 25 °C

| W	4-CH$_3$O	3,4-(CH$_3$O)$_2$	4-CH$_3$	4-H	4-Cl	3-Cl	3-CF$_3$	4-CF$_3$	3-NO$_2$	4-NO$_2$
2	4.85×10^{-4}	3.07×10^{-4}	2.08×10^{-4}	3.97×10^{-4}	3.23×10^{-3}	1.95×10^{-3}	5.40×10^{-3}	1.02×10^{-2}	4.65×10^{-3}	8.32×10^{-3}
3	1.30×10^{-3}	1.12×10^{-3}	2.41×10^{-4}	3.69×10^{-4}	3.17×10^{-3}	1.86×10^{-3}	5.04×10^{-3}	1.07×10^{-2}	3.86×10^{-3}	8.23×10^{-3}
4	2.58×10^{-3}	2.37×10^{-3}	2.92×10^{-4}	3.54×10^{-4}	2.79×10^{-3}	1.61×10^{-3}	4.27×10^{-3}	9.19×10^{-3}	3.70×10^{-3}	7.40×10^{-3}
5	4.48×10^{-3}	4.12×10^{-3}	3.86×10^{-4}	3.64×10^{-4}	2.51×10^{-3}	1.43×10^{-3}	3.43×10^{-3}	8.10×10^{-3}	3.47×10^{-3}	7.58×10^{-3}
6	7.11×10^{-3}	6.26×10^{-3}	5.60×10^{-4}	4.11×10^{-4}	2.18×10^{-3}	1.31×10^{-3}	3.24×10^{-3}	7.32×10^{-3}	3.32×10^{-3}	6.85×10^{-3}
7	9.88×10^{-3}	8.81×10^{-3}	8.40×10^{-4}	4.86×10^{-4}	2.02×10^{-3}	1.18×10^{-3}	2.63×10^{-3}	6.53×10^{-3}	3.17×10^{-3}	6.30×10^{-3}
10	1.99×10^{-2}	1.75×10^{-2}	1.39×10^{-3}	6.44×10^{-4}	1.58×10^{-3}	1.09×10^{-3}	2.37×10^{-3}	6.24×10^{-3}	2.89×10^{-3}	6.65×10^{-3}
13	3.18×10^{-2}	2.71×10^{-2}	2.27×10^{-3}	9.00×10^{-4}	1.47×10^{-3}	8.85×10^{-4}	1.98×10^{-3}	5.42×10^{-3}	2.66×10^{-3}	5.79×10^{-3}
18	4.87×10^{-2}	4.60×10^{-2}	3.02×10^{-3}	1.31×10^{-3}	1.43×10^{-3}	8.44×10^{-4}	1.70×10^{-3}	4.27×10^{-3}	2.20×10^{-3}	4.33×10^{-3}
23	7.76×10^{-2}	5.98×10^{-2}	4.50×10^{-3}	1.73×10^{-3}	1.16×10^{-3}	6.97×10^{-4}	1.40×10^{-3}	4.11×10^{-3}	2.11×10^{-3}	5.35×10^{-3}
28	9.64×10^{-2}	8.39×10^{-2}	5.97×10^{-3}	2.19×10^{-3}	9.61×10^{-4}	5.58×10^{-4}	1.08×10^{-3}	3.32×10^{-3}	1.87×10^{-3}	5.47×10^{-3}
30	0.104	7.73×10^{-2}	6.17×10^{-3}	2.31×10^{-3}	1.01×10^{-3}	5.78×10^{-4}	1.18×10^{-3}	3.45×10^{-3}	1.84×10^{-3}	4.69×10^{-3}
35	0.119	0.101	7.22×10^{-3}	2.86×10^{-3}	9.55×10^{-4}	5.37×10^{-4}	1.06×10^{-3}	3.02×10^{-3}	1.81×10^{-3}	4.27×10^{-3}
40	0.140	0.128	7.96×10^{-3}	3.29×10^{-3}	9.57×10^{-4}	4.26×10^{-4}	9.09×10^{-4}	2.52×10^{-3}	1.60×10^{-3}	3.66×10^{-3}
45	0.156	0.131	1.01×10^{-2}	3.64×10^{-3}	8.48×10^{-4}	4.17×10^{-4}	7.94×10^{-4}	2.40×10^{-3}	1.65×10^{-3}	3.16×10^{-3}
50	0.158	0.149	1.15×10^{-2}	4.14×10^{-3}	8.57×10^{-4}	3.97×10^{-4}	7.27×10^{-4}	2.23×10^{-3}	1.55×10^{-3}	2.84×10^{-3}

slope (Figure 3) the values of K_{oi} for the solvolysis of the 3-CF$_3$, $K_{oi} = 4.43 \pm 0.5$ and 4.40 ± 0.7 for $W = 18$ and 40, respectively, can be obtained. Likewise, we obtain $K_{oi} = 14.3 \pm 0.3$ and 14.9 ± 0.6 for $W = 18$ and 40, respectively, for the solvolysis of the 3,4-(CH$_3$O)$_2$ (Figure 4). Constant K_{oi} values obtained at $W = 18$ and 40 is a good reflection of the fulfilment of the mechanistic model proposed in Scheme 2.

Table 2 shows the values of K_{oi} obtained for the different substrates at $W = 18$. As we can observe in all cases, the association constant at the interface, K_{oi}, is similar and is independent of the substituents in the benzoyl chloride. Only the substrates substituted with the nitro group present a clear deviation form this behavior pattern. For the 3-NO$_2$ and 4-NO$_2$, K_{oi} values are approximately 50 times greater than those presented by the other benzoyl chlorides. This behavior pattern could be due to the greater hydrophilicity of the nitro group, which gives rise to a greater association constant at the interface of the microemulsion.

On the basis of eq 6, the values of the true solvolysis rate constant at the interface, k_i, can be calculated from the values of K_{oi} obtained for $W = 18$ and the values of k_{obs} for different compositions of the microemulsion. Table 3 shows the values of k_i obtained for the solvolysis of the different benzoyl chlorides according to the water content of the microemulsion.

Discussion

As mentioned in the Introduction, the acyl-transfer reaction mechanisms should be classed as dissociative, with an acylium ion intermediate; as concerted displacement, which can have associative or dissociative character; and as associative or addition−elimination , with a tetrahedral addition intermediate.[19] These mechanisms are well-defined, with a clear borderline between them. The term borderline is meaningful in this context: it refers to a reaction series in which a small change in the structure of one of the reactants, or in the reaction conditions, causes a change from a concerted to a stepwise mechanism, or vice versa. Therefore, the existence of at least two predominant reaction pathways (associative and dissociative) means that the discussion of the results previously presented must be dealt with separately. To begin with we will analyze the behavior of the 4-CH$_3$O, which reacts fundamentally
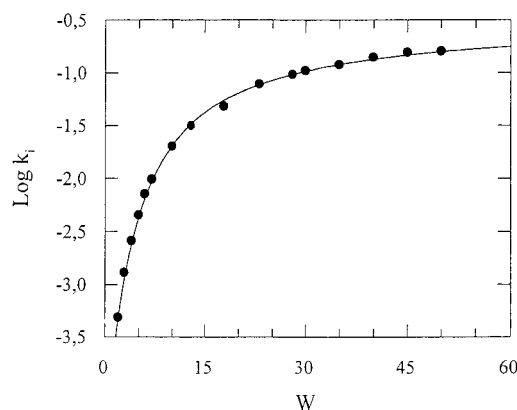

Figure 5. Plot of log k_i vs W for solvolysis of 4-CH$_3$O in AOT/isooctane/water microemulsions at 25 °C.

by means of a dissociative reaction. Second we will analyze the behavior presented by the 4-CF$_3$, a benzoyl chloride that reacts by means of a fundamentally associative pathway, and finally, we will study the behavior presented by the unsubstituted benzoyl chloride. The solvolysis mechanism of the unsubstituted benzoyl chloride shows that this substance reacts simultaneously by both associative and dissociative reaction pathways, which produces a different behavior pattern. The results obtained will show that the effect that the microemulsions have on the rate of the reactions is closely tied up with the mechanisms whereby these reactions take place.

1. Solvolysis of 4-CH$_3$O. Figure 5 (data in Table 3) shows the variation of log k_i with the water content of the microemulsion. As we can observe, log k_i decreases together with W. This behavior pattern is analogous to that observed for the 3,4-(CH$_3$O)$_2$ (see Table 3). The rate constant at the interface increases with W, tending to reach a limit value. This limit value of $k_i \cong 0.18$ s^{-1} is much lower than that obtained in pure water,[22] $k_{H_2O} = 223$ s^{-1}, and slightly higher than the values of the rate constants in mixtures of 90% trifluoroethanol:10% water,[20] $k_{90\% TFE} = 0.62$ s^{-1}, and 97% trifluoroethanol:3% water,[21] $k_{97\% TFE} \cong 0.57$ s^{-1}. These results show that the solvolysis of 4-CH$_3$O is very sensitive to solvent-ionizing power. Likewise, it can be observed that the solvolysis at the interface decreases from $k_i \cong 0.16$ s^{-1} for $W = 50$ to $k_i \cong 4.8 \times 10^{-4}$ s^{-1} for $W =$

2, resulting in a reduction of approximately 300 times in the rate constant of the reaction.

The value of $\rho^+ = -3.0$ for the solvolysis of some substituted benzoyl chlorides in water is the same as in 90% trifluoroethanol, although the rates are 200–500 times faster.[19] The relationships k_{Cl}/k_F for the solvolysis of the 4-CH$_3$ and 4-(NCH$_3$)$_2$ benzoyl chlorides and of the analogous benzoyl fluorides are greater than 10^5. These differences are in marked contrast to the ratios $k_{Cl}/k_F = 1.2$ for the associative reactions of the 4-NO$_2$ benzoyl halides and confirm the strongly dissociative nature of the transition state. The relatively small negative value of ρ^+ for the benzoyl halides may reflect electron movement from oxygen toward the central carbon atom by polarization or resonance and/or nucleophilic interaction of these relatively unhindered molecules with solvent in the transition state.

$$Ar-^+C{=}O \leftrightarrow Ar-C{\equiv}O^+$$
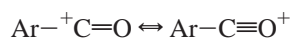
Substituted benzoyl chlorides react in water through a dissociative reaction pathway even when the acylium ion does not have a significant lifetime in the presence of solvent. The rate constant for solvolysis of the *p*-anisoyl acylium ion corresponds to a small but significant lifetime for this intermediate in water, although not enough to allow diffusion through the solvent or reaction with dilute solutes.[19] The much larger "rate constans" for the toluoyl and benzoyl acylium ions suggest that there is little or no chemical barrier for the reaction of these ions with solvent. More electron-withdrawing substituents cause a shift to the associative reaction channel; this occurs sooner for benzoyl fluorides than for chlorides because the relatively poor leaving ability of fluoride ion decreases the rate constant for the dissociative pathway. The rate of the dissociative reaction is strongly dependent on the leaving group.

As the water content of the microemulsions decreases (reduction of W), a gradual change in its properties takes place. More precisely, there is a significant alteration in the water properties. The structure of water in microemulsions is of interest due to its possible effects on the reactivity of dissolved molecules.[24a] Studies on the structure of water in microemulsions have used numerous techniques (electron solvation measurements,[28] NMR and ESR spectroscopy,[29] UV–vis spectrophotometry,[30] small-angle neutron, X-ray, and light scattering,[7,31] fluorescence decay,[32] microcalorimetry,[33] and IR and Raman spectroscopy[34]), and two or even three water types have been identified. Water added to a nonaqueous solution ($W \ll 2$) of AOT initially hydrates the anionic headgroups, with the first three water molecules strongly binding to the anionic member of the ion pair and the next three molecules hydrating the sodium cation. Under these conditions ($W \ll 2$) the AOT molecules form compact, polymorphic assemblies with low aggregation numbers. Adding more water but maintaining $W < 2$ leads to micellization, and the added water forms a droplet which is trapped within the micellar core. A further increase in the amount of water leads to destruction of the ion pairs of the aggregated AOT molecules and further hydration of the individual anions and cations by the interfacial water. Simultaneously, structural changes squeeze out water molecules trapped in the hydrophobic network of isooctane molecules and AOT tail groups. Any further water added ($W > 11$) is incorporated into the aqueous droplet, which swells as W increased. The water at the center of this droplet has physical properties which are essentially those of water in a continuous aqueous phase, while the water at its periphery has greater structure and properties which differ from those of ordinary water, especially in terms of viscosity, polarity, and other properties affected by ionic strength.[7,29,34c,35]

In the solvolysis of 4-CH$_3$O, the steady decrease seen in the value of k_i with decreasing W must be related to the predominantly dissociative character of the solvolysis mechanism of this compound. This being the case, the reaction rate will be affected by changes in the physical properties of the interface, particularly its polarity. Wong et al.[35a] have studied microemulsions comprising AOT, water, and heptane or decane and concluded that the water trapped in microemulsions is less polar than water in a continuous aqueous phase, the former having Kosower Z values[36] between 65 and 80 when the percent of water is increased from 3%. In addition, dielectric constant values of the interface[37] range from $\epsilon = 31$ (for $W = 1$) to $\epsilon = 47$ (for $W = 45.2$). Notably, the limit value observed for $k_i \cong 0.18$ s^{-1} (see Figure 5) is much lower than the value obtained in pure water,[22] $k_{H2O} \cong 223$ s^{-1}. This reduction in the reactivity by approximately 1000 times is due to the fact that in the microemulsion the reaction is occurring at the interface. This zone will not provide a complete hydration for the expulsion of the leaving group, Cl$^-$, which will explain the difference between this behavior and that observed in pure water.

As W decreases, so will the polarity of the interface and, consequently, its capacity to solvate the Cl$^-$ leaving group. This change in the properties of the interfacial water is presumably the cause of the decrease in k_i from $k_i \cong 0.16$ s^{-1} for $W = 50$ to $k_i \cong 4.8 \times 10^{-4}$ s^{-1} for $W = 2$. There are only a few systematic studies of the physical properties of the microemulsion as a function of W, mainly covering properties such as polarity of the interface, viscosity, and water penetration. In the bibliography two studies are included on the variation of λ_{max} of the dye ET(30)[38] in microemulsions.[37,39] We have used the values of λ_{max} ET(30) of Grieser[37] to calculate the E_T parameter according to W. Figure 6 shows a good correlation between log k_i and the polarity parameter for the interface of

(27) Bentley, T. W.; Koo, I. S. *J. Chem. Soc., Chem. Commun.* **1988**, 41.

(28) Bakale, G.; Beck, G.; Thomas, J. K. *J. Phys. Chem.* **1981**, *85*, 1062.

(29) (a) Wong, M.; Thomas, J. K.; Nowak, T. *J. Am. Chem. Soc.* **1977**, *99*, 9, 4730. (b) Llor, A.; Rigny, P. *J. Am. Chem. Soc.* **1986**, *108*, 7533.

(30) Nishimoto, J.; Iwamoto, E.; Fujiwara, T.; Kumamaru, T. *J. Chem. Soc., Faraday Trans 1* **1993**, *89*, 535.

(31) (a) Robinson, B. H.; Toprakcioglu, C.; Dore, J. C.; Chieux, P. *J. Chem. Soc., Faraday Trans 1* **1984**, *80*, 13. (b) Howe, A. M.; Toprakcioglu, C.; Dore, J. C.; Robinson, B. H. *J. Chem. Soc., Faraday Trans 1* **1986**, *82*, 2411. (c) Fletcher, P. D. I.; Robinson, B. H.; Tabony, J. *J. Chem. Soc., Faraday Trans 1* **1986**, *82*, 2311. (d) Fulton, J. L. *J. Phys. Chem.* **1991**, *95*, 458. (e) Fulton, J. L. *J. Phys. Chem.* **1991**, *95*, 1445. (f) Chen, S. H.; Chang, S. L. *J. Phys. Chem.* **1990**, *94*, 1907.

(32) (a) Howe, A. M.; McDonald, J. A.; Robinson, B. H. *J. Chem. Soc., Faraday Trans 1* **1987**, *83*, 1007. (b) Lang, J.; Jada, A.; Mallians, A. *J. Phys. Chem.* **1988**, *92*, 1946. (c) Belletete, M.; Durocher, G. *J. Colloid Interface Sci.* **1990**, *134*, 289. (d) Belletete, M.; Durocher, G. *J. Phys. Chem.* **1990**, *94*, 5337. (e) Gaudel, Y.; Pammeret, S.; Yamada, N.; Migus, A.; Antonetti, A. *J. Am. Chem. Soc.* **1989**, *111*, 4974.

(33) Goto, A.; Harada, S.; Fujita, T.; Miwa, Y.; Yoshioka, H.; Kishimoto, H. *Langmuir* **1993**, *9*, 86.

(34) (a) Giammona, G.; Goffredi, F.; Turco Liveri, V.; Vassollo, G. *J. Colloid Interface Sci.* **1990**, *154*, 139. (b) Alliotta, F.; Vasi, C.; Migliardo, P.; D'Aprano, A.; Lizzio, A.; Livei, V. T. *J. Phys. Chem.* **1988**, *92*, 4436. (c) Jain, T. K.; Varshney, M.; Maitra, A. *J. Phys. Chem.* **1989**, *93*, 7409.

(35) (a) Wong, M.; Grätzel, M.; Thomas, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 2391. (b) Keh, E.; Valeur, B. *J. Colloid Interface Sci.* **1981**, *79*, 465. (c) Zinsli, P. E. *J. Phys. Chem.* **1983**, *83*, 3223.

(36) (a) Kosower, E. M.; Mohammed, M. *J. Am. Chem. Soc.* **1968**, *90*, 3271. (b) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253.

(37) Lay, M. B.; Drummond, C. J.; Thistlethwaite, P. J.; Grieser, F. *J. Colloid Interface Sci.* **1989**, *128*, 602.

(38) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, 1986.

(39) Correa, N. M.; Biasutti, M. A.; Silber, J. J. *J. Colloid Interface Sci.* **1995**, *172*, 71.
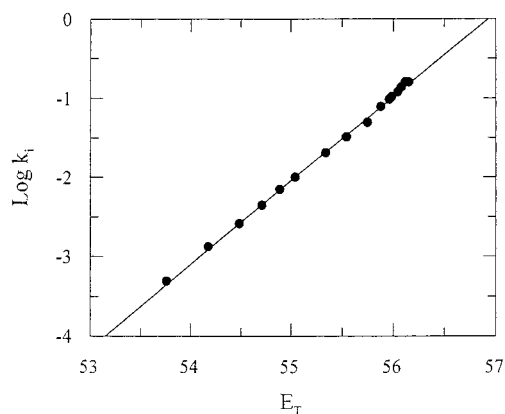
Reactivity in Water/Oil Microemulsions

J. Am. Chem. Soc., Vol. 122, No. 42, 2000 10331

Figure 6. Linear correlation between log k_i and E_T polarity parameter for solvolysis of 4-CH$_3$O in AOT/isooctane/water microemulsions at 25 °C.
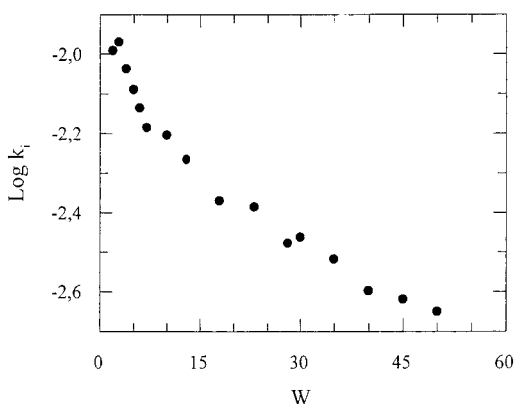

Figure 7. Plot of log k_i vs W for solvolysis of 4-CF$_3$ in AOT/isooctane/water microemulsions at 25 °C.

the microemulsion. Because of the rather localized negative charge at the phenolic oxygen atom, the standard dye ET(30) is capable of specific Lewis acid/base interactions. Therefore, in addition to the nonspecific dye/solvent interactions, the betaine dye ET(30) preferably measures the specific Lewis acidity of organic solvents. On the other hand, the positive charge of the pyridinium moiety of ET(30) is delocalized. Therefore, the solvent Lewis basicity will not be registered by the probe molecule ET(30). If this solvent property is relevant for the system under examination, other empirical measures of Lewis basicity should be used. The observed correlation between E_T and log k_i is related to the solvation of the Cl$^-$ leaving group.

2. Solvolysis of 4-CF$_3$. Figure 7 shows the variation of log k_i (data shown in Table 3) with W for the solvolysis of the 4-CF$_3$. The behavior observed is contrary to that detected in the solvolysis of the 4-CH$_3$O. In this case the rate constant decreases as W increases. The solvolysis of 4-Cl, 3-Cl, 3-CF$_3$, 3-NO$_2$, and 4-NO$_2$ shows a similar behavior pattern (see Table 3). This behavior is difficult to explain, given that the solvolysis of the 4-CF$_3$, just like that of other benzoyl chlorides with electron-attracting groups, decreases along with the polarity of the reaction medium. It is important to point out that the limit value of k_i for high values of W, $k_i = 2.0 \times 10^{-3}$ s^{-1}, as well as for small values of W, $k_i = 1 \times 10^{-2}$ s^{-1}, is lower than the value observed in an aqueous medium,[22] $k_{H_2O} = 1.50 \times 10^{-2}$ s^{-1}. The values of the rate constants at the interface, k_i, are in all cases greater than the values in mixtures of 90% trifluoroethanol: 10% water,[20] $k_{90\%TFE} \cong 4.14 \times 10^{-5}$ s^{-1}, and 97% trifluoroethanol:3% water,[21] $k_{97\%TFE} \cong 3.02 \times 10^{-5}$ s^{-1}. The values of k_i at the interface of the microemulsion are at least 100 times greater than in the mixtures 90 or 97% TFE-water. This behavior

Scheme 3
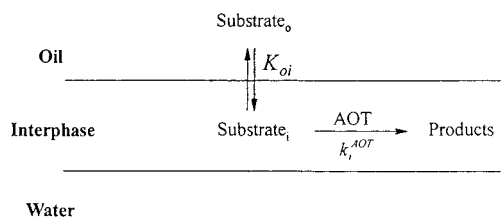
is the complete opposite to that observed previously in the solvolysis of the 4-CH$_3$O, where the values of k_i at the interface were always lower than those found in mixtures of 90% or 97% TFE-water.

The reduction of the rate constant of the reaction in the microemulsion (for high values of W) in relation to the value which is observed in an aqueous medium is probably due to the decrease in the polarity of the interface with regard to pure water. On the basis of the reduction in the rate of the reaction as the polarity of the medium decreases, it would be expected that k_i would decrease along with W. However, the experimental behavior observed is the opposite. Therefore, some additional mechanism must exist that gives rise to an increase in k_i as W decreases.

We can propose an associative transition state with rate-limiting attack of the nucleophilic reagent and little or no bond breaking in the transition state for solvolysis of 4-CF$_3$, so that the rate of the associative reaction is independent of the leaving group. Jencks and Song[19] suggest that this is the behavior expected for an addition−elimination mechanism, but they do not know whether the reaction proceeds through an addition intermediate with a significant lifetime. Fundamentally, we can propose three possible explanations for the increase in k_i as W decreases: possible nucleophile participation of the surfactant; basic catalysis by the surfactant; and alteration of the properties of the interfacial water, resulting in an increase in its nucleophile reactivity. There follows a brief description of each of these possibilities; we favor an increase in the reactivity of the water as the best explanation.

(a) Nucleophilic Catalysis by the Surfactant. An explanation of the variation of k_i with W (Figure 7) would be to consider the participation of the surfactant acting as a nucleophile catalyst according to Scheme 3. The benzoyl chloride localized at the interface could react with the surfactant, which we consider to be found totally in the interface.

The rate of the reaction will be the sum of the rate by the uncatalyzed solvolysis process, k_i, plus the process of the nucleophilic catalysis by the surfactant, k_i^{AOT}. The application of the pseudophase formalism enables us to obtain the following rate equation, where $\bar{V}_{AOT}$ represents the molar volume of the surfactant.

$$k_{obs} = \left(\frac{k_i^{AOT}}{\bar{V}_{AOT}} + k_i\right)\frac{K_{oi}}{K_{oi} + Z} \qquad (8)$$

This rate equation would be compatible with the experimental results and, therefore, would explain the decrease of k_i as W increases.

The possibility of participation of the surfactant as a nucleophilic catalyst is not consistent with other experimental evidence. We have shown that the 4-CF$_3$ is stable in solutions of AOT in isooctane (in the absence of water) for a period of some days. If some type of nucleophilic catalysis could occur, some alteration would have to have been observed in the absorption spectrum of the 4-CF$_3$ in solutions of AOT/isooctane. In

Table 4. Influence of W on the Kinetic Solvent Isotope Effects for 4-CF$_3$ Solvolysis in AOT/Isooctane/H$_2$O and AOT/Isooctane/D$_2$O Microemulsions[a]

W	$k_i^{H_2O}$	$k_i^{D_2O}$	$\dfrac{k_i^{H_2O}}{k_i^{D_2O}}$	$k_{obs}^{H_2O}$	$k_{obs}^{D_2O}$	$\dfrac{k_{obs}^{H_2O}}{k_{obs}^{D_2O}}$
2	1.02×10^{-2}	1.01×10^{-2}	1.0	3.46×10^{-3}	3.37×10^{-3}	1.0
3	1.07×10^{-2}	9.90×10^{-3}	1.1	3.29×10^{-3}	2.98×10^{-3}	1.1
4	9.19×10^{-3}	8.42×10^{-3}	1.1	3.23×10^{-3}	2.90×10^{-3}	1.1
5	8.10×10^{-3}	7.29×10^{-3}	1.1	3.05×10^{-3}	2.69×10^{-3}	1.1
6	7.32×10^{-3}	6.71×10^{-3}	1.1	2.89×10^{-3}	2.60×10^{-3}	1.1
7	6.53×10^{-3}	5.86×10^{-3}	1.1	2.61×10^{-3}	2.30×10^{-3}	1.1
10	6.24×10^{-3}	6.18×10^{-3}	1.1	1.85×10^{-3}	1.79×10^{-3}	1.0
13	5.42×10^{-3}	5.19×10^{-3}	1.0	1.95×10^{-3}	1.83×10^{-3}	1.1
18	4.27×10^{-3}	3.73×10^{-3}	1.1	1.57×10^{-3}	1.34×10^{-3}	1.2
23	4.11×10^{-3}	3.84×10^{-3}	1.1	9.82×10^{-4}	8.95×10^{-4}	1.1
28	3.32×10^{-3}	3.25×10^{-3}	1.0	6.60×10^{-4}	6.30×10^{-4}	1.0
30	3.45×10^{-3}	3.00×10^{-3}	1.1	7.94×10^{-4}	6.73×10^{-4}	1.2
35	3.02×10^{-3}	2.60×10^{-3}	1.2	7.22×10^{-4}	6.07×10^{-3}	1.2

[a] k_i was calculated using eq 6 and K_{oi} values of $(K_{oi})_{H_2O} = 3.2 \pm 0.6$ for AOT/isooctane/H$_2$O and $(K_{oi})_{D_2O} = 3.1 \pm 0.5$ for AOT/isooctane/D$_2$O microemulsions obtained at $W = 18$. The columns on the right show the isotopic effect on k_{obs}.

addition, in our laboratory,[40] as with other research groups,[13,41] we have studied the reactivity of crystal violet and malachite green in AOT microemulsions. In no case did we find any indication of a reaction between the carbocation and the AOT working with very disparate values of W. Therefore, it is not easy to understand that the AOT can act as a nucleophile in relation to benzoyl chlorides but that this behavior does not manifest itself in relation to carbocations.

(b) Basic Catalysis by the Surfactant. A second interpretation of the behavior observed could be that the surfactant acts as a basic catalyst of the nucleophilic addition of water. The studies carried out in an aqueous medium[19] indicate that the addition of water could be subject to basic catalysis. The solvent deuterium isotope effect of $k_{H_2O}/k_{D_2O} \cong 2-3$ for the associative solvolysis mechanism of benzoyl chlorides and benzoyl fluorides is consistent with a transition state such as that which is shown in the following diagram.
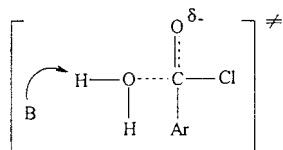
Experimental results of the variation of the properties of the microemulsions of AOT show that the charge density on the headgroup of the AOT increases as the water content of the microemulsion decreases.[42] This increase in the charge density on the headgroup of the AOT could cause its capacity to act as a basic catalyst to increase as W decreases, and therefore, it would be responsible for the increase in k_i as W decreases.

Table 4 shows the solvent deuterium isotope effects in microemulsions of AOT. As can be observed, the isotopic effect, $k_i^{H_2O}/k_i^{D_2O}$, is approximately equal to the unit and independent of W. The estimate of this isotopic effect can be affected by the determination of K_{oi} in microemulsions of AOT/isooctane/H$_2$O and AOT/isooctane/D$_2$O. A more precise estimate of the isotopic effect can be obtained by directly comparing the values of k_{obs} for both microemulsions. Table 4 shows these values,

which enable us to estimate an isotopic effect slightly greater than the unit and which remains approximately constant as W varies. This isotopic effect is much lower than that observed in processes where the addition of water presents basic catalysis, indicating, therefore, that this process is not subject to basic catalysis.

(c) Increase in the Reactivity of Water. A final explanation could be to consider that as W decreases the reactivity of water increases. As we have commented previously, the properties of the water of the microemulsions are substantially different from those of bulk water. As W decreases, the hydrogen bonds between the water molecules are destroyed, but however, a greater structuring of the water occurs, due to its strong interactions with the headgroups of the AOT and the counterions Na$^+$. More precisely, the water pool is highly viscous in the lower W region; with increasing W, η_w rapidly decreased below $W = 10$ and then gradually decreased until the micellar solution became turbid above $W = 50$. Even in the higher region, the values of η_w were considerably higher than the viscosity of the ordinary bulk water.[35b,43] The increase in the degree of structuring of the interfacial water, as the water content of the microemulsion decreases, increases the capacity of the oxygen atom of the water to participate in the formation of hydrogen bonds. More precisely, the interfacial water molecules will be involved in the solvation of the SO$_3^-$ and carbonyl groups of the AOT.
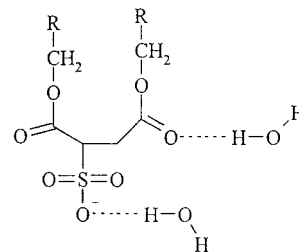
In these interactions the water molecules will act as electron acceptors, and therefore, their capacity to act as nucleophiles will increase. In this way their reactivity in relation to the benzoyl chlorides which react through an associative mechanism will increase. At the same time the values of k_i in the micoemulsion are always lower than those observed in pure water due to the smaller capacity of the interface to solvate the transition state of the reaction. The global effect observed on k_i would be the result of the combiantion of both processes.

3. Solvolysis of 4-H. Figure 8 shows the variation of log k_i with W in the hydrolysis of the unsubstituted benzoyl chloride. The rate of the reaction decreases as W does, showing a similar behavior pattern to that of the 4-CH$_3$O to $W \cong 5$. For values of $W < 5$, there is a slight increase in the rate of the reaction as the water content of the microemulsion decreases, showing an analogous behavior pattern to the 4-CF$_3$. The maximum value of the rate constant in the interface of the microemulsion, $k_i \cong 4.14 \times 10^{-3}$ s^{-1} is, once again, lower than the value observed in an aqueous medium,[19] $k_{H_2O} = 1.1$ s^{-1}, due to the lesser degree of polarity of the interface of the microemulsion, even for high values of W. The decrease in k_i with respect to the value in water ($\cong 250$ times) is similar to the behavior observed in the solvolysis of the 4-CH$_3$O. The value of k_i for $W = 50$, $k_i \cong 4.14 \times 10^{-3}$ s^{-1}, is approximately equal to the value obtained for the reaction in mixtures of 90% TFE:10% water,[20] $k_{90\% TFE}$

(40) Leis, J. R.; Mejuto, J. C.; Peña, M. E. *Langmuir* **1993**, *9*, 889.

(41) (a) Mukherjee, L.; Mitra, N.; Bhattacharya, P. K.; Moulik, S. P. *Langmuir* **1995**, *11*, 2866. (b) Valiente, M.; Rodenas, E. *J. Colloid Interface Sci.* **1989**, *127*, 522.

(42) Moran, P. D.; Bowmaker, G. A.; Cooney, R. P.; Bartlett, J. R.; Woolfrey, J. L. *J. Mater. Chem.* **1995**, *5*, 295.

(43) (a) Hasegawa, M.; Sugimura, T.; Suzaki, Y.; Shindo, Y.; Kitahara, A. *J. Phys. Chem.* **1994**, *98*, 2120. (b) Zinsli, P. E. *J. Phys. Chem.* **1979**, *83*, 3223.
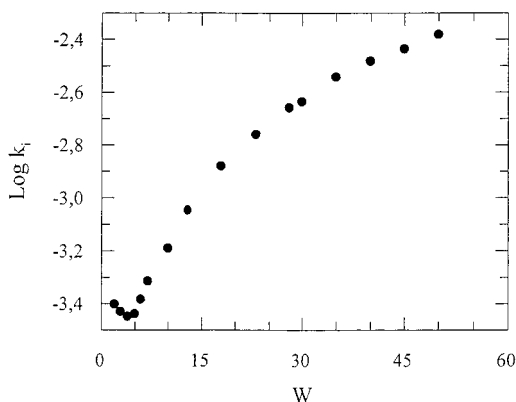
Figure 8. Plot of log k_i vs W for solvolysis of 4-H in AOT/isooctane/water microemulsions at 25 °C.

Figure 9. Correlation between log k_i and E_T polarity parameter for solvolysis of 4-H in AOT/isooctane/water microemulsions at 25 °C: (○) $W<18$; (●) $50>W>18$.

$= 5.7 \times 10^{-3}$ s^{-1}, or in mixtures of 97% TFE:3% water,[21] $k_{97\%TFE} = 3.6 \times 10^{-3}$ s^{-1}. In this way the solvolysis of the 4-H shows a similar behavior pattern to the 4-CH$_3$O. The value of k_i for $W = 2$, $k_i \cong 4 \times 10^{-4}$ s^{-1} is approximately 10 times lower than that observed in mixtures of 90 or 97% TFE-water, which contrasts with the value obtained for the solvolysis of the 4-CH$_3$O to $W = 2$, which is 800 times lower than in mixtures of 90 or 97% TFE-water.

The behavior observed for the 4-CH$_3$ is intermediate between that presented by 4-H and the 4-CH$_3$O. The solvolysis rate of the 4-CH$_3$ decreases along with the water content of the microemulsion, but for low values of W, the decrease is much less pronounced than that shown by the 4-CH$_3$O.

Two competing reaction channels have been proposed for solvolysis of benzoyl chloride.[19,44] One of these channels is predominantly dissociative in character and the rate depends sharply on the solvent polarity, whereas the competing reaction channel is much less sensitive to changes in solvent polarity. As the aqueous binary mixtures cover a wide range of solvent polarities, a mechanicistic change from one reaction channel to the other can be seen as the solvent composition is varied. Recent studies[45] showed that the mechanism of solvolysis of benzoyl chlorides is mainly dissociative in highly aqueous media.

As W decreases, the capacity of the microemulsion to solvate the Cl$^-$ leaving group also decreases, and therefore, the rate of the reaction should decrease, in the same way as the solvolysis of 4-CH$_3$O. If, as we had seen for the solvolysis of the 4-CF$_3$, the rate of the associative process increases as W decreases, probably due to the greater availability of water to react as a consequence of the destruction of its hydrogen bond structure, it would be logical to think that a change is taking place in the solvolysis mechanism of the 4-H as W decreases. Hence, for values of $W > 5$ the reaction will take place fundamentally through a dissociative pathway, whereas for values of $W < 5$ the reaction will take place fundamentally through an associative pathway.

Figure 9 shows a representation of log k_i vs E_T polarity parameter. As we can observe there is a good correlation for values of $W > 18$, indicating that in the composition range of the microemulsion $W = 18-50$ the solvolysis mechanism of the 4-H takes place predominantly through a dissociative path. As W decreases, both pathways (dissociative and associative) will compete up to values of $W \cong 5$ ($E_T = 54.72$ kcal/mol).
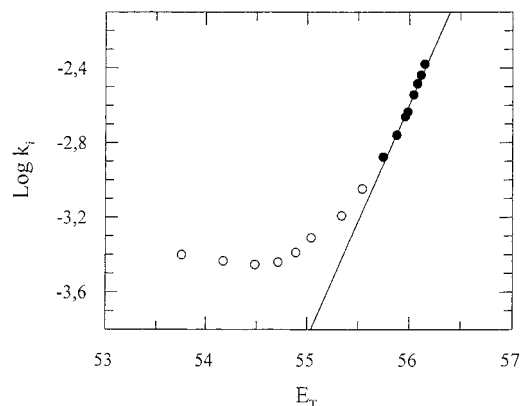
Finally for values of $W < 5$ the reaction will take place fundamentally through an associative pathway.

4. Hammett Correlations and Solvolysis Mechanism in Microemulsions. 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. The 4-CH$_3$O reacts through a dissociative transition state, bringing about an acylium ion intermediate, which reacts rapidly with the solvent. The benzoyl chlorides with electron-attracting substituents do not present an energy barrier for the breakdown of the acylium ion, although the transition state for the determining stage of the rate is essentially the same. Electron-withdrawing substituents will raise the energy of the acylium ion and of the transition state for the dissociative pathway while they will stabilize the transition state for the associative pathway. This will eventually cause a switch to the associative reaction channel. This reaction pathway could correspond to an addition−elimination mechanism through a tetrahedral intermediate. However, the reaction path may bypass this intermediate, if it does not have a significant lifetime. A change to a less polar solvent can also cause a change from the dissociative to the associative reaction channel.

A Hammett plot for reactions in 97% (v/v) trifluoroethanol shows a negative slope indicative of a dissociative mechanism ($\rho^+ = -3.1$),[27,46] as does the plot for 4-methoxy, 4-methyl, 3-chloro, and unsubstituted benzoyl chlorides in 90% (v/v) trifluoroethanol ($\rho^+ = -3.0$).[47] For the same reactions in water, the slope of the plot changes from negative ($\rho^+ = -3.0$)[47] to positive values (indicative of associative reactions) somewhere between the points corresponding to 3-CF$_3$ and 4-NO$_2$, the latter of which reacts faster than the former. Figure 10 shows that in microemulsions, as in water, there is indeed a switch from the dissociative to the associative mechanism.[48] For the microemulsion with $W = 50$ this occurs at about $\sigma^+ = 0.3$, between the points for 4-Cl and 3-Cl substituted benzoyl chlorides. For $\sigma^+ > 0.3$ there is a very good Hammett correlation with a slope of $\rho^+ = 3.5 \pm 0.3$, whereas the least-squares line through the results

(44) Bentley, T. W.; Koo, I. S. *J. Chem. Soc., Perkin Trans 2* **1989**, 1385.

(45) Bentley, T. W.; Koo, I. S.; Norman, S. J.*J. Org. Chem.* **1991**, *56*, 6, 1604.

(46) (a) Bentley, T. W.; Freeman, A. E. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1115. (b) Bentley, T. W.; Carter, G. E.; Harris, H. C. *J. Chem. Soc., Perkin Trans. 2* **1985**, 983. (c) Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6789.

(47) Bentley, T. W.; Harris, H. C. *J. Chem. Soc., Perkin Trans. 2* **1986**, 619.

(48) A preliminary account of the change in reaction mechanism has been published: García-Río, L.; Leis, J. R. *Chem. Commun.* **2000**, 455.
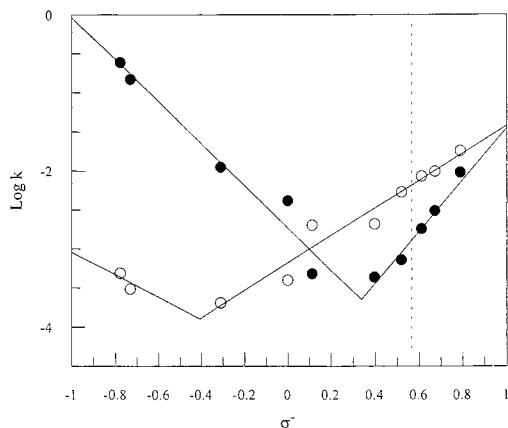
Figure 10. Hammett plots for the solvolysis of substituted benzoyl chlorides in AOT/isooctane/water microemulsions at different water content: (●) $W = 50$; (○) $W = 2$ at 25 °C. The dashed line represents the break for reaction in water (ref 19).

for substituents with $\sigma^+ < 0.3$ has a slope of $\rho^+ = -2.7 \pm 0.3$, close to the value of $\rho^+ = -3.0$ observed for reaction in pure water.

For the microemulsion with $W = 2$, the switch occurs at about $\sigma^+ = -0.4$, just below the point for 4-CH$_3$ benzoyl chloride, with a Hammett slope of $\rho^+ = 1.8 \pm 0.2$ for $\sigma^+ > -0.4$ (the number of substrates with more negative σ^+ values was too few for accurate calculation of a Hammett slope for the dissociative branch). The effect of the switch in the reaction mechanism is highlighted by comparing the observed rate constants for 4-CH$_3$O with the values that are expected if the associative mechanism held in these media at this σ^+ value: the actual rate constant exceeds the expected value by a factor of about 20 for microemulsions with $W = 2$ and by a factor of about 10^7 for those with $W = 50$.

As the water content of the medium falls, so too does the σ^+ value at which the mechanism switch occurs (see Figure 10, in which the value at which the switch occurs in bulk water is shown by a dotted line). This can be attributed to the change in the properties of micelle-borne water.[28–34,49] The change from a dissociative to an associative reaction path with increasingly electron-withdrawing substituents occurs much later in water than in AOT/isooctane/water microemulsions with $W = 50$. The rate of the associative reaction is independent of the leaving group, while the dissociative reaction is strongly dependent on the nature of the leaving group and on its solvation. For large values of W, water at the center of the aqueous micelle core is similar in nature to that of bulk water, but water in or adjacent to the interface is devoted to solvating the surfactant head groups[28–34,49] and, hence, has a limited ability to assist the leaving group; in microemulsions with $W = 2$, all water is of this latter kind. Consequently, lowering W favors the associative pathway, with the result that the change in mechanism occurs at larger σ^+ values; in the microemulsion with $W = 2$, even 4-CH$_3$ with its electron-donating substituent is hydrolyzed via the associative mechanism.

The good correlation observed between log k_i vs E_T polarity parameter for the solvolysis of the 4-CH$_3$O and 3,4-(CH$_3$O)$_2$ indicates that they react fundamentally via the dissociative pathway, even for very low values of W. An analogous correlation for the 4-CH$_3$ (not shown) shows a similar behavior pattern to that observed in Figure 9 for the 4-H. In the case of the 4-CH$_3$ the deviation of the correlation can be clearly observed for the values of k_i obtained at $W < 5$, indicating that

it is on the basis of this water content of the microemulsion that the associative reaction pathway competes clearly with the dissociative pathway. However, in this case it is not possible to observe the slight increase in k_i with W that could be seen in the solvolysis of the unsubstituted benzoyl chloride.

Conclusions

We have studied the solvolysis of substituted benzoyl chlorides in AOT/isooctane/water microemulsions. The experimental results have been interpreted by extending the formalism of the pseudophase to microemulsions, considering that the substrates are distributed between the continuous pseudophase and the interface. The reaction will take place solely at the interface. In all cases the solvolysis rate at the interface of the microemulsion is lower than in pure water.

The effect which the changes in the composition of the microemulsion (changes in W) have on k_i is closely linked to the solvolysis mechanism of the benzoyl chlorides. The benzoyl chlorides with electron-donating groups react fundamentally through a dissociative pathway. The solvation of the Cl$^-$ leaving group must be the reason why k_i decreases along with W. In these cases the existence of a good correlation between log k_i vs E_T polarity parameter has been found. When the benzoyl chloride presents electron-attracting substituents, the solvolysis mechanism takes place fundamentally through an associative pathway and the variation of the nucleophile character of the water must be the reason for the increase in k_i as W decreases. The unsubstituted benzoyl chloride reacts through both pathways simultaneously: for highly aqueous media (high W, $W > 18$) the reaction takes place fundamentally through a dissociative mechanism; as the water content of the microemulsion decreases ($5 < W < 18$), both reaction pathways, associative and dissociative, compete. Finally, for very small values of W, $W < 5$, the solvolysis of the unsubstituted benzoyl chloride takes place especially through an associative pathway.

In an aqueous medium the change from a predominantly associative to a predominantly dissociative solvolysis mechanism takes place in the presence of electron-attracting groups between the 3-CF$_3$ and the 4-CF$_3$. When the reactivities of the different benzoyl chlorides are compared for high values of W, $W = 50$, we can observe a displacement in the mechanism change point. Likewise for $W = 50$, this change takes place between the 4-Cl and the 3-Cl, which indicates that the associative mechanism is more favorable at the interface of the microemulsion than in pure water. As W decreases, this result is confirmed and for $W = 2$ only the 4-CH$_3$O and the 3,4-(CH$_3$O)$_2$ react through the dissociative mechanism. This change in mechanism is a result of the change in the properties of the interfacial water of the microemulsion as W decreases: a decrease in the capacity of the interfacial water for solvating the leaving group and an increase in its nucleophile capacity. The behavior pattern observed clearly shows the validity of the kinetic tests in obtaining structural information about the microemulsions. Likewise, 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.

(49) Tamura, K.; Nii, N. *J. Phys. Chem.* **1989**, *93*, 4825.

JA001477D