Reactivity in w/o microemulsions. Activation parameters for solvolysis in AOT/isooctane/water systems

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A kinetic study was carried out on the solvolysis of different benzoyl halides in microemulsions of AOT/isooctane/water: 4-methoxybenzoyl chloride (4-CH_3O), 3-methoxybenzoyl chloride (3-CH_3O), benzoyl fluoride (BzF) and 4-trifluoromethylbenzoyl chloride (4-CF_3). The application of the formalism of the pseudophase allows us to obtain the true rate constants for the solvolysis in the interface, k_i, which decreases 350 times on going from $W = 50$ to $W = 2$ ($W = [H_2O]/[AOT]$) for 4-CH_3O; 35 times for 3-CH_3O and 3 times for BzF. In the solvolysis of 4-CF_3 k_i decreases 3.5 times on going from $W = 2$ to $W = 50$. This behavior has been interpreted as a consequence of a decrease of the electrophilic character of water when W decreases, whereas the nucleophilic character increases. As a consequence the rate constant for the dissociative processes decreases as W decreases, due to a reduction in the water's ability to solvate the leaving group, and the rate of the associative processes increases due to the greater nucleophilicity of the water. The obtained results are compatible with the activation parameters determined in the microemulsion: for the solvolysis of BzF and 4-CF_3, $\Delta S^{\neq}$ takes values which are close to $\Delta S^{\neq} \approx -180$ J mol^{-1} K^{-1} and $\Delta S^{\neq} \approx -150$ J mol^{-1} K^{-1} respectively. These values are lower than those observed in pure water and compatible with a greater degree of structuring of the interfacial water than that of bulk water. For the solvolysis of 4-CH_3O it is observed that $\Delta S^{\neq}$ decreases from $\Delta S^{\neq} \approx -40$ J mol^{-1} K^{-1} for $W = 50$ to $\Delta S^{\neq} \approx -150$ J mol^{-1} K^{-1} for $W = 2$. This behavior is consistent with a change from a dissociative mechanism to an associative one which also is shown when studying a Hammett correlation using Taft σ values.

Introduction

Water in oil microemulsions (w/o) are a type of colloidal system formed by water, an alkane and a tensioactive agent. Microscopically speaking these systems are made up of three very different microenvironments: a continuous medium formed by the alkane, a disperse phase formed by aqueous microdrops and a tensioactive film which separates the aqueous phase from the alkane and allows the solubilization to occur.[1–3] The existence of these three microenvironments gives these systems a particular ability to modulate chemical reactivity due to the compartmentalization of the reactants in different microenvironments. At the same time we can discover their important applications in the field of organic synthesis allowing the solubilization of, and contact between, reactants with very different hydrophobic properties. This property allows these systems to be used as an alternative to phase transfer catalysts.[4]

Much research has been carried out on the hydration of the surfactants with the solubilized water in the microemulsions, which enables us to understand the dynamics of the physical and chemical processes involved and to find applications in chemical and biological reactions.[5,6] Generally, the existence of three types of water has been considered:[7] *free water*, *bonded water* and *trapped water*. However, the most recent studies involve four water types considering the different effects of the polar head groups of the surfactant and of the counterion.[8] This interaction between the water molecules and the surfactant is so strong that the hydration of the surfactants has been considered to be the driving force for the water solubilization process in microemulsions. The existing studies in the bibliography show that the properties of the water are modified as the water content of the microemulsion varies. For example the vibration frequency of the O–H bond of the water is displaced from 3493 cm^{-1} to 3416 cm^{-1} when W (W being the molar relationship $W = [H_2O]/[AOT]$) increases from $W = 1$ until $W = 20$, reaching a value near to that obtained in pure water for high W-values in microemulsions of AOT/heptane/water (AOT is the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate). When ^{1}H-NMR techniques were used to investigate the properties of the water, it was found that the chemical shift of the water protons increases from $\delta = 4.030$ ppm for $W = 4$ to $\delta = 4.430$ ppm for $W = 50$ in microemulsions of AOT/isooctane/water. This behavior is compatible with a model which considers the existence of three/four types of water in the microemulsions.[8] The local interactions of the water molecules with the counterions and with the head groups of the surfactants have opposite effects on the water structure. The hydration of the anionic head groups of the surfactants increases the electronic density on the hydrogen atoms in the water molecules, with a consequent breakage of the hydrogen bonds of the normal water. The strength of the O–H bonds increases, and this factor means that the chemical shift of the protons of the bonded water to the head groups takes place to higher field than in the case of normal water and the vibration frequency of the O–H bond is centered on higher frequencies. On the other hand, the counterions accumulated in the interior of the aqueous microdroplets can polarize the water molecules giving rise to a lower electronic density in the vicinity of the protons, and consequently a reduction in the strength of the O–H bond of the water. This effect shifts the ^{1}H-NMR resonance signals of the water protons to lower fields and also displaces the vibration frequency of the O–H bond to lower frequencies. The anomalous properties of the water of

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microemulsions can, therefore, be modulated as the water content of the system varies.

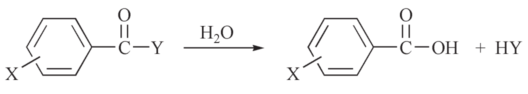
These changes in the water properties of microemulsions have very important consequences from the point of view of the chemical reactivity which accelerates or decelerates the processes in question. More precisely, we have found that the rate of chemical processes in microemulsions[9] (in particular the solvolysis of diphenylmethyl chloride) can vary by approximately 500 times as the water content of the microemulsion varies. It is important to point out that not only does the reaction rate vary, but also the mechanism by which it occurs can be modified.[10] For the solvolysis of benzoyl chlorides we have found that many processes take place by means of dissociative or associative mechanisms depending on the composition of the microemulsion. These results have allowed us to propose the use of microemulsions as an alternative to solvent mixtures in the research on reaction mechanisms.

A series of changes in reaction conditions (*e.g.*, changing the electronegativity of substituents on the substrate or the ionizing ability of the solvent) will, of course, almost always cause a series of changes in the rate of a chemical reaction or the position of a chemical equilibrium. If the same series of changes in conditions affects the rate or equilibrium of a second reaction in exactly the same way as it affected the first except when attenuated by an amount that depends on the second substrate, there exists a linear free-energy relationship between the two sets of effects. Where such relationships exist they can be very useful in helping to elucidate mechanisms, in predicting reaction rates and the extent of reaction at equilibrium, and in discovering under what conditions a change in mechanism occurs. Another tool widely used in researching reaction mechanisms is the analysis of the activation parameters. In this article we present the determination of activation parameters for the solvolysis of benzoyl halides in microemulsions of AOT/isooctane/water. The reactions used, namely solvolysis of 4-methoxybenzoyl chloride (4-CH_3O), solvolysis of 3-methoxybenzoyl chloride (3-CH_3O), benzoyl fluoride (BzF) and 4-trifluoromethylbenzoyl chloride (4-CF_3), show a gradual variation from an associative mechanism to a dissociative one[11] as the substituents on the aromatic ring vary or as the nature of the leaving group varies (Scheme 1).

The results obtained show a variation from a dissociative mechanism for the solvolysis of benzoyl chlorides with electron-donating groups to an associative mechanism as the water content of the microemulsion varies. An analysis of the variation of $\Delta S^{\neq}$ with the water content of the microemulsion indicates that the latter becomes more negative as W decreases for 4-CH_3O, whereas it remains invariable for BzF and 4-CF_3. These results are compatible with the existence of a good correlation between the rate constants at the interface and the Taft σ parameter, indicating that for $W = 2$ the reaction takes place solely by means of an associative mechanism.

Experimental

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



4-MeO: X = 4-CH_3O; Y = Cl
3-MeO: X = 3-CH_3O; Y = Cl
BzF: X = H; Y = F
4-CF$_3$: X = 4-CF_3; Y = Cl

Scheme 1

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 Varian Cary 500 Scan UV–Vis–NIR spectrophotometer fitted with thermostated cell holders (experiments were carried out at temperatures ranging from 15 °C to 45 °C). The wavelengths used for the kinetic studies fell between $\lambda = 290–300$ nm. The kinetic absorbance *vs.* time data always fit the first-order integrated rate equation satisfactorily ($r > 0.999$) and 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 we verified 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 microemulsion composition on the solvolysis rate constants

Figs. 1 and 2 show the variation of k_{obs} with the surfactant concentration for solvolysis of 4-CH_3O and BzF at different temperatures for series of experiments carried out on $W = 18$. As we can observe, k_{obs} increases along with [AOT] and temperature. This increase of k_{obs} as the concentration of AOT increases is due to the incorporation of benzoyl halide at the interface of the microemulsion.

In order 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 nitroso group transfer[12,13] and solvolytic processes.[9] We will consider that the system is made up of three pseudophases (Scheme 2), where the substrate is distributed between the continuous medium and the interface of the microemulsion[14] with a distribution constant K_{oi}.

The reaction will take place only in the interface of the microemulsion, as this will be the area where the benzoyl halide and the water molecules will come into contact.

$$r = k_i[\text{Substrate}]_i \qquad (1)$$

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

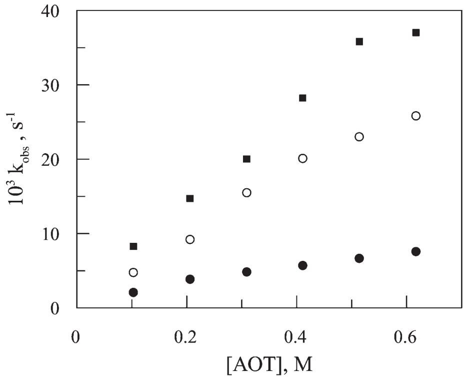


Fig. 1 Influence of [AOT] on k_{obs} for solvolysis of 4-MeO in AOT/isooctane/water microemulsions for $W = 18$. (●) $T = 15$ °C; (○) $T = 25$ °C and (■) $T = 30$ °C.

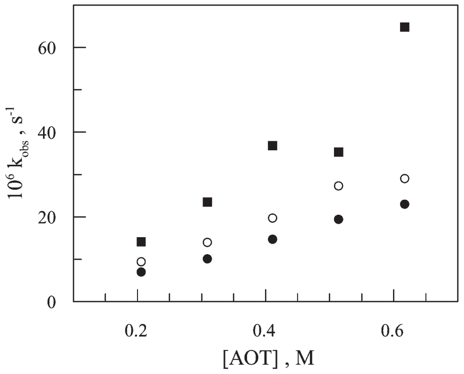


Fig. 2 Influence of [AOT] on k_{obs} for solvolysis of BzF in AOT/isooctane/water microemulsions for $W = 18$. (●) $T = 35\,°C$; (○) $T = 40\,°C$ and (■) $T = 45\,°C$.

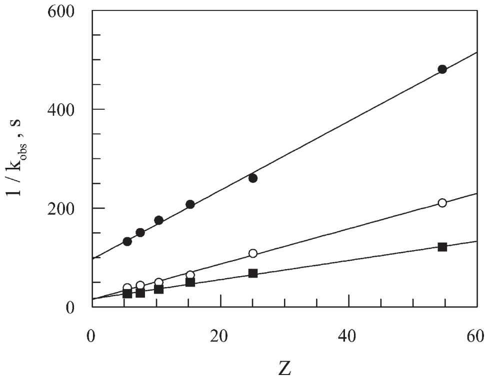


Fig. 3 Plot of data of Fig. 1 according to $1/k_{obs}$ *vs.* Z [eqn. (4)] for the solvolysis of 4-MeO in AOT/isooctane/water microemulsions for $W = 18$. (●) $T = 15\,°C$; (○) $T = 25\,°C$ and (■) $T = 30\,°C$.

as eqn. (2):

$$K_{oi} = \frac{[\text{Substrate}]_i}{[\text{Substrate}]_o} Z \qquad (2)$$

where the concentrations refer to the total volume of the microemulsion and where Z is defined as $Z = [\text{Isooctane}]/[\text{AOT}]$ by analogy with the parameter W. Given that the total concentration of the substrate will be the sum of the concentrations in the three pseudophases, we can obtain eqn. (3):

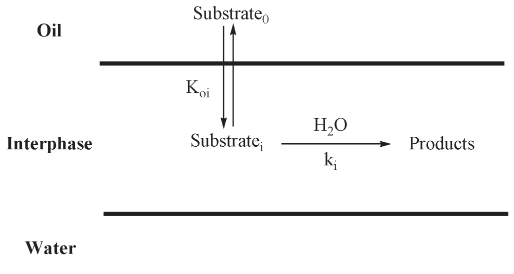
$$k_{obs} = \frac{k_i K_{oi}}{K_{oi} + Z} \qquad (3)$$

which predicts the existence of a linear dependence between $1/k_{obs}$ *vs.* Z [eqn. (4)]:

$$\frac{1}{k_{obs}} = \frac{1}{k_i} + \frac{Z}{k_i K_{oi}} \qquad (4)$$

Figs. 3 and 4 show the linearized plots of $1/k_{obs}$ *vs.* Z for the solvolysis of 4-CH_3O and BzF at different temperatures for $W = 18$. On the basis of the relationship between the intercept/slope the values of K_{oi} at different temperatures can be obtained. Table 1 shows K_{oi} values obtained for different benzoyl halides at different temperatures and for $W = 18$.

There are several discrepancies between the values of K_{oi} obtained at different temperatures. K_{oi} values for 4-CH_3O are (13 ± 4); (7 ± 2); (4 ± 1) and (9 ± 2) for $T = 15$; 20; 25 and 30 °C respectively. As we can see there is no clear tendency for K_{oi} values on increasing the temperature. Such behavior can be a consequence of the fact that as the temperature increases there is also an increase in the solubility of the substrate in the continuous medium as well as in the interface of the microemulsion. We found a similar behavior for solvolysis of 4-CF_3 with K_{oi} values of (1.8 ± 0.3); (4 ± 1); (1.1 ± 0.2); (1.4 ± 0.4) and (2.2 ± 0.6) for $T = 20$; 25; 30; 35 and 40 °C and also for solvolysis of BzF (see Table 1). The discrepancies which can prevail between the different values of K_{oi} are due to the uncertainty in the determination of the intercept in Figs. 3–4 [eqn. (4)].



Scheme 2

Influence of W on the true rate constants at the interface

Once the value of K_{oi} is known, we can obtain the true rate constant for the solvolysis process in the interface making use of eqn. (3). To avoid the values of k_i being altered by the uncertainty regarding K_{oi} at different temperatures, it has been decided to use a mean value of K_{oi}. The mean values of K_{oi} are $K_{oi} = 8.25$; $K_{oi} = 4$; $K_{oi} = 2.1$ and $K_{oi} = 4.8$ for solvolysis of 4-CH_3O; 3-CH_3O; 4-CF_3 and BzF respectively (Table 1).

k_i values vary as much in accordance with the nature of the substrate as with the water content of the microemulsion[9,17] as a consequence of the variation in the water properties.[15] By way of example in Figs. 5 and 6 we show the variation $\log k_i$ with W at three temperatures for 4-CH_3O and 4-CF_3. In Table 2 we present by way of example the values obtained for k_i in the solvolysis of 4-CH_3O, 3-CH_3O and BzF at different W values.

As we can observe, k_i increases as does the water content of the microemulsion for 4-CH_3O (see Fig. 5 and Table 2) from a value of $k_i = 4.85 \times 10^{-4}$ s^{-1} for $W = 2$ to $k_i = 0.158$ s^{-1} for $W = 50$ at 25 °C. The results obtained show that k_i increases approximately 325 times as the water content of the microemulsion increases and that the value of k_i obtained for high water contents, $W = 50$, is still about 370 times less than in pure water. With 3-CH_3O and at 25 °C we observe similar behavior where k_i increases from $k_i = 7.2 \times 10^{-5}$ s^{-1} for $W = 2$ to $k_i = 2.43 \times 10^{-3}$ s^{-1} for $W = 50$ (see Table 2). In this case k_i increases approximately 35 times as the water content of the microemulsion increases and the limit value reached for high water contents is approximately 225 times lower than the value obtained in an aqueous medium. Using a benzoyl halide with a weaker leaving group, BzF, we observe analogous behavior but in this case the decrease of k_i as W decreases

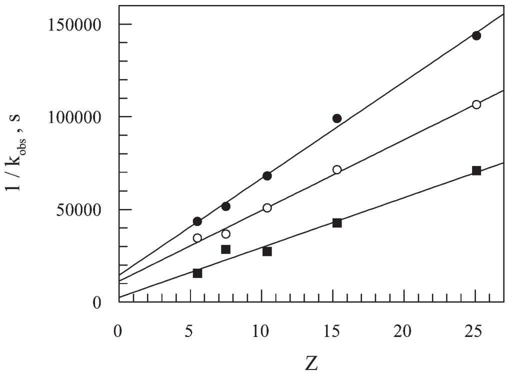


Fig. 4 Plot of data of Fig. 2 according to $1/k_{obs}$ *vs.* Z [eqn. (4)] for the solvolysis of BzF in AOT/isooctane/water microemulsions for $W = 18$. (●) $T = 35\,°C$; (○) $T = 40\,°C$ and (■) $T = 45\,°C$.

Table 1 Values of K_{oi} for distribution of benzoyl halides between the continuous media and the interface of AOT/isooctane/water microemulsions at different temperatures

	K_{oi}			
$T/°C$	4-MeO	3-MeO	4-CF_3	BzF
15	13 ± 4			
20	7 ± 2		1.84 ± 0.3	
25	4 ± 1	4 ± 1	4 ± 1	$(5.0 \pm 0.7)^a$
30	9 ± 2		1.1 ± 0.2	
35			1.4 ± 0.4	2.7 ± 0.6
40			2.2 ± 0.6	5.5 ± 0.9
45				6 ± 1
Mean value	8.25	4	2.1	4.8

[a] Obtained by initial rates method.

is very small (see Table 2), so that k_i barely increases 3 times when passing from $W = 2$ to $W = 50$ and the value of k_i for $W = 50$ is approximately 75 times lower that the value obtained in an aqueous medium.

When we study benzoyl chlorides with electron-attracting groups, 4-CF_3, we observe the opposite behavior and k_i decreases as the water content of the microemulsion increases (see Fig. 6). The values obtained show that k_i decreases from $k_i = 1.02 \times 10^{-2}$ s^{-1} for $W = 2$ up to $k_i = 2.23 \times 10^{-3}$ s^{-1} for $W = 50$. Besides, the maximum value of k_i obtained for $W = 2$ is approximately 3.5 times lower that the value obtained in highly aqueous media.

Establishing the activation parameters

Once we have the values of k_i we can determine the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ making use of Eyring's equation [eqn (5)]:

$$\ln\frac{k_i}{T} = \ln\frac{k_B}{h} + \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT} \qquad (5)$$

where k_i is the rate constant in the interface for the corresponding benzoyl halide, k_B is the Boltzmann constant, h is Planck's constant, and $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are the corresponding activation parameters.

Figs. 7–8 show how the previous equation is confirmed for the solvolysis of 4-CH_3O at different W values ($W = 7$; 28 and 45) and for the solvolysis of 4-CF_3 also at different values of W ($W = 6$; 28 and 50). On the basis of the slopes and intercepts of representations like those shown in Figs. 7–8, and the application of eqn. 5, we can obtain the values of the activation enthalpy, $\Delta H^{\neq}$, and the activation entropy, $\Delta S^{\neq}$, for different W values (Table 3). The obtained results for the solvolysis of 4-CF_3 show that $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are independent of the water content of the microemulsion, with values of $\Delta S^{\neq}$ near to -150 J mol^{-1} K^{-1}. The behavior obtained for the solvolysis of BzF is similar, in that both $\Delta S^{\neq}$ and $\Delta H^{\neq}$ prove to be independent of the water content of the system and a value of $\Delta S^{\neq}$ near to -175 J mol^{-1} K^{-1} is obtained.

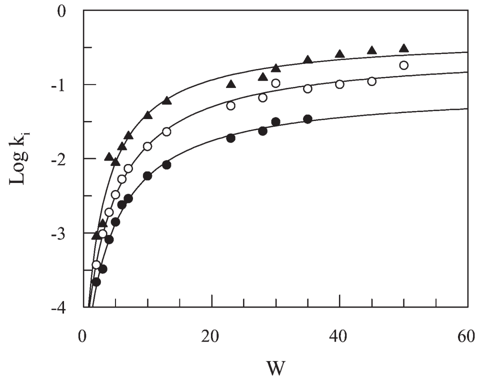


Fig. 5 Plot of log k_i *vs.* W for solvolysis of 4-CH_3O in AOT/isooctane/water microemulsions for (●) $T = 15\,°C$; (○) $T = 25\,°C$ and (▲) $T = 35\,°C$.

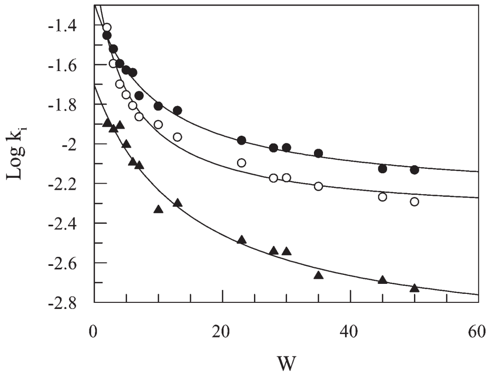


Fig. 6 Plot of log k_i *vs.* W for solvolysis of 4-CF_3 in AOT/isooctane/water microemulsions for (●) $T = 40\,°C$; (○) $T = 35\,°C$ and (▲) $T = 20\,°C$.

The solvolysis of 4-CH_3O shows a clearly different behavior. In this case the activation entropy shows a clear dependence on the water content of the system. In this way $\Delta S^{\neq}$ decreases from $\Delta S^{\neq} \approx -40$ J mol^{-1} K^{-1} to $\Delta S^{\neq} \approx -150$ J mol^{-1} K^{-1}. This behavior must be closely bound up with the effect of the composition of the microemulsion altering the mechanism of the reaction, in such a way that as the water content of the microemulsion decreases, an associative mechanism is favored over a dissociative one.

Electric percolation is a well-documented phenomenon which occurs as the volume fraction of the disperse phase of the microemulsion increases, or as the temperature increases.[18] When we study the influence of the temperature on the rate of reaction, varying the temperature between 15 °C and 45 °C, we are comparing microemulsions in situations which are prior and subsequent to the appearance of the phenomenon of electric percolation. Since electrical percolation has a marked effect on the transport of solubilized species, it would be expected to

Table 2 Influence of W on k_i values for solvolysis of 4-CH_3O and 3-CH_3O benzoyl chlorides in AOT/isooctane/water microemulsions at 25 °C and for the solvolysis of BzF in microemulsions of AOT/isooctane/water at 35 °C. For the purpose of comparison the values obtained for the solvolysis of the said benzoyl halides are also shown, k_{H_2O}, in 3% CH_3CN–97% H_2O (v/v) at 25 °C

	k_i/s^{-1}		
W	4-MeO	3-MeO	BzF
2	4.85×10^{-4}	7.20×10^{-5}	2.08×10^{-5}
3	1.30×10^{-3}	1.11×10^{-4}	2.54×10^{-5}
4	2.58×10^{-3}	1.44×10^{-4}	2.49×10^{-5}
5	4.48×10^{-3}	1.92×10^{-4}	3.03×10^{-5}
6	7.11×10^{-3}	2.15×10^{-4}	3.04×10^{-5}
7	9.88×10^{-3}	2.42×10^{-4}	3.12×10^{-5}
10	1.99×10^{-2}	3.49×10^{-4}	3.16×10^{-5}
13	3.18×10^{-2}	4.18×10^{-4}	3.48×10^{-5}
18	4.87×10^{-2}	7.51×10^{-4}	4.53×10^{-5}
23	7.76×10^{-2}	9.71×10^{-4}	4.84×10^{-5}
28	9.64×10^{-2}	1.11×10^{-3}	4.87×10^{-5}
30	0.104	1.35×10^{-3}	5.28×10^{-5}
35	0.119	1.62×10^{-3}	7.22×10^{-5}
40	0.140	1.92×10^{-3}	8.39×10^{-5}
45	0.156	2.13×10^{-3}	7.19×10^{-5}
50	0.158	2.43×10^{-3}	9.29×10^{-5}
k_{H_2O}	58.2	0.54	1.80×10^{-3}

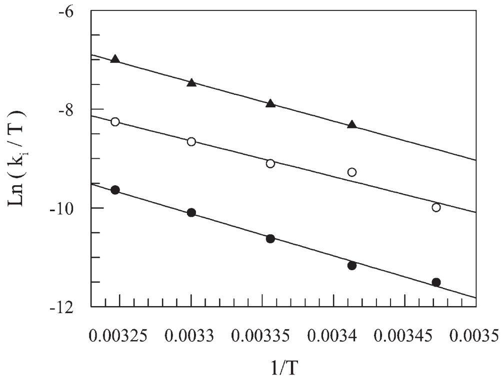


Fig. 7 Eyring plot according to eqn. (5) for solvolysis of 4-CH_3O in AOT/isooctane/water microemulsions for (●) $W = 7$; (○) $W = 28$ and (▲) $W = 45$.

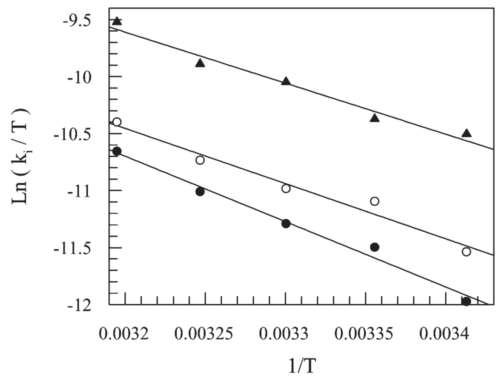


Fig. 8 Eyring plot according to eqn. (5) for solvolysis of 4-CF_3 in AOT/isooctane/water microemulsions for (●) $W = 50$; (○) $W = 28$ and (▲) $W = 6$.

affect the reaction rate. However, the results of this study could be adjusted to the same model whether or not such percolation phenomena were in evidence. Only when the rate of solvolysis is faster than the rate of transport of reactants into the interface, *e.g.* when it is determined by diffusion of the reactants within the microemulsion, will the presence or absence of percolation phenomena impinge on the reaction rate. The results obtained in this study show that Eyring's equation is applicable to situations prior and subsequent to the appearance of the phenomenon of electric percolation, which can be taken as evidence that the process which is being studied, solvolysis of benzoyl halides, is subject to chemical control, with its rate being far greater than the rate of exchange of material between droplets.

Discussion

Solvolysis mechanism of benzoyl halides

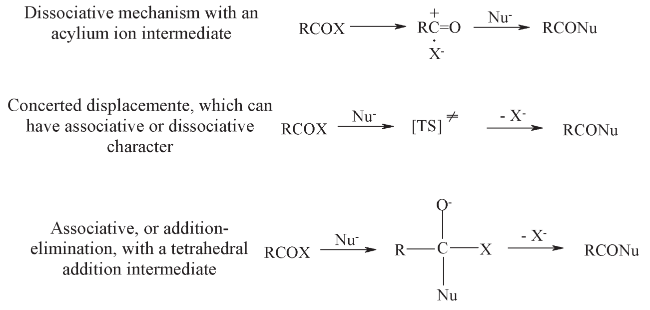
The solvolysis of benzoyl chlorides is a well known process in water and in different solvents,[11] in such a way that acyl group transfer can occur by means of three mechanisms: dissociative, associative, and concerted displacement, such as shown in Scheme 3. These mechanisms are well-defined, with 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*.

In order to avoid extrapolations or interpolations we have determined the rate constants of solvolysis of benzoyl chlorides with different substituents in highly aqueous media[19] (3% CH_3CN (v/v)). The obtained results show the existence of a double correlation with σ^+ (data not shown). For benzoyl chlorides with electron-donating groups or with a low electron-attracting capacity (4-CH_3O; 3-CH_3O; 3-CH_3; 4-CH_3; 4-H; 4-Cl and 3-Cl) we can observe a good correlation with a slope of $\rho^+ = -(2.7 \pm 0.3)$, whereas for benzoyl chlorides with electron-attracting groups (3-CF_3; 4-CF_3; 3-NO_2 and 4-NO_2) we obtain a correlation with a value of $\rho^+ = (1.5 \pm 0.5)$. This change in slope is consistent with a change in mechanism from a dissociative path for the benzoyl chlorides with electron-donating groups to an associative path for the benzoyl chlorides with electron-attracting groups.

The change from a dissociative to an associative path as the electron-attracting character of the substituents increases occurs much later in the case of benzoyl chlorides than in that of the fluorides, because the rate of the associative path is independent of the leaving group, while in the dissociative mechanism the reaction rate is heavily dependent on the nature of the leaving group. The situation can be represented schematically by a More O'Ferrall–Jencks diagram[20] (Scheme 4). 4-CH_3O reacts by means of a dissociative transition state giving rise to an acylium ion intermediate, which reacts rapidly with the solvent (path *a*). With benzoyl chlorides with electron-attracting substituents there is no barrier for reaction of the acylium ion and the potential well no longer exists, although

Table 3 Influence of W on $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values for solvolysis of substituted benzoyl halides in AOT/isooctane/water microemulsions

	4-CF_3	BzF	4-CH_3O			
W	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}
2	34 ± 2	–(164 ± 25)	49 ± 4	–(174 ± 29)	47 ± 4	–(153 ± 23)
3	36 ± 3	–(159 ± 23)	35 ± 3	–(219 ± 37)	45 ± 4	–(153 ± 22)
4	39 ± 3	–(151 ± 23)	52 ± 4	–(165 ± 20)	53 ± 4	–(120 ± 19)
5	43 ± 3	–(137 ± 19)	23 ± 2	–(257 ± 46)	66 ± 5	–(80 ± 11)
6	45 ± 4	–(132 ± 20)	50 ± 4	–(178 ± 27)	66 ± 5	–(69 ± 10)
7	44 ± 4	–(137 ± 21)	47 ± 4	–(177 ± 25)	71 ± 6	–(46 ± 7)
10	44 ± 4	–(137 ± 20)	57 ± 5	–(144 ± 22)	64 ± 5	–(51 ± 8)
13	40 ± 3	–(152 ± 23)	46 ± 4	–(182 ± 28)	71 ± 6	–(39 ± 6)
18			43 ± 3	–(188 ± 27)	69 ± 6	–(40 ± 6)
23	43 ± 4	–(144 ± 23)	46 ± 4	–(182 ± 27)	69 ± 6	–(39 ± 6)
28	40 ± 3	–(156 ± 23)	56 ± 5	–(146 ± 22)	65 ± 6	–(44 ± 7)
30	40 ± 3	–(156 ± 24)	42 ± 3	–(190 ± 26)	67 ± 6	–(42 ± 6)
35	51 ± 4	–(122 ± 19)	59 ± 4	–(133 ± 16)	65 ± 6	–(44 ± 7)
40	49 ± 4	–(129 ± 19)	39 ± 3	–(196 ± 39)	67 ± 5	–(39 ± 6)
45	43 ± 4	–(147 ± 23)	42 ± 3	–(187 ± 32)	66 ± 5	–(41 ± 6)
50			34 ± 3	–(213 ± 43)	61 ± 6	–(48 ± 8)



Scheme 3

the rate limiting transition state is essentially the same. Therefore the reaction will follow the path indicated by *b*.

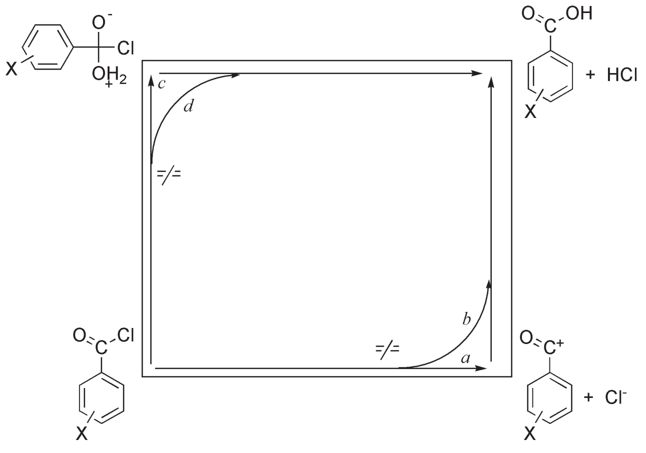
Substituents which withdraw electrons increase the energy of the acylium ion in the lower right-hand corner and of the transition state for the dissociative path, and stabilize the upper left-hand corner and the transition state for the associative mechanism, which will eventually cause a switch to an associative path. This reaction path may correspond with an addition–elimination mechanism through a tetrahedral intermediate (path *c*). However, it is possible for the reaction mechanism not to pass through this corner, if the addition intermediate does not have a significant lifetime (path *d*). A change to a less polar solvent can have exactly the same effect on the reaction mechanism.

Influence of the composition of the microemulsion

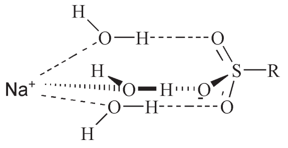
As shown in Figs. 5–6 the influence of the composition of the microemulsion on the reaction rate depends on the operating reaction mechanism. For reactions which occur by means of a dissociative mechanism a determining factor is the solvation of the leaving group. A decrease in the capacity of the reaction medium to solvate the leaving Cl^- or F^- causes a reduction in the rate.

As mentioned above, as the water content of the microemulsion varies, a gradual variation in its properties occurs.[21] The free water is found dispersed between the hydrocarbon chains of the surfactant molecules, existing as monomers or dimmers, and does not have a hydrogen bond with its surroundings. The normal water is found in the center of the aqueous microdroplet and undergoes strong interactions by means of the hydrogen bond. In addition to these two types of water, there exist other molecules of bonded water in the vicinity of the ionic surfactants.

The hydration of the anionic head groups of the surfactants increases the electronic density on the hydrogen atoms in the water molecules, with the consequent breakage of the hydrogen bonds of the normal water. This type of interaction causes a reduction in the electrophilic character of water and consequently an increase in its nucleophilic character. Scheme 5 shows a schematic representation of the hydration of the molecule of AOT.



Scheme 4



Scheme 5

Consequently the hydration of the AOT molecule gives rise to an increase in the nucleophilic character of the water and a reduction in its electrophilic character. This behavior is due to the fact that in the case of the AOT molecule the hydration of the head group of the surfactant is more important than that of the counterion, contrary to what happens with other surfactant agents such as the NaDEHP.[22] The $E_T(30)$ polarity parameter decreases together with the water content of the AOT-based microemulsions[23,24] in the same way as the electrophilic water character does.

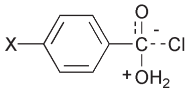
On the other hand, the increase in the degree of structuring of the interfacial water, as W decreases, increases the capacity of the water oxygen atom to participate in the formation of hydrogen bonds. More precisely, the interfacial water molecules will be involved in the solvation of the SO_3^- and carbonyl groups of the AOT. Experimental results on the variation of the AOT-based microemulsion properties show that the charge density on the AOT head group increases as the water content of the microemulsion decreases.[25] This increase in the charge density on the AOT molecule as W decreases will mean that the interactions between the head group of the surfactant and the water molecules increase as the water content decreases. Therefore a reduction occurs in the electrophilic character and an increase in the nucleophilic character of the water bonded to the head group as W decreases. This variation in the properties of the water will be responsible for the kinetic behavior observed.

The reduction of the electrophilic character of the water causes a reduction in the rate of the dissociative processes (4-CH_3O) (see Fig. 5), since the system presents a lower capacity to solvate the Cl^- leaving group. Likewise as W decreases we can observe an increase in the nucleophilic character of the water and, consequently, an increase in the solvolysis rate of 4-CF_3 (see Fig. 6), a reaction which occurs by means of an associative process. As we have already mentioned the behavior of 3-CH_3O and BzF is similar to that of 4-CH_3O but the magnitude of the decrease in k_i as W decreases is less than in 4-CH_3O. Such a difference is due to the fact that the solvolysis reaction of 3-CH_3O and of BzF occurs by means of a dissociative process but with a high percentage of associative character. The balance between the two mechanisms will be responsible for the experimental behavior.

Variation of the activation parameters with the composition of the microemulsion

In Table 3 we can see the variation of the activation parameters with the composition of the microemulsion. The activation entropy, $\Delta S^{\neq}$, is independent of W for the solvolysis of 4-CF_3 and BzF, however it decreases along with W for 4-CH_3O. This behavior is consistent with an increase in the percentage of associative character of the solvolysis mechanism as W decreases.

In an aqueous medium we observe a gradual variation of the activation parameters as the substituents in the aromatic ring vary: 4-CH_3O ($\Delta S^{\neq} = 31.9$ J mol^{-1} K^{-1}; $\Delta H^{\neq} = 72.9$



Scheme 6

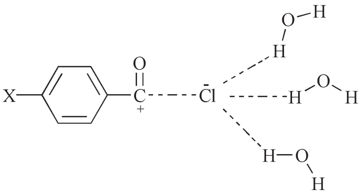
kJ mol^{-1}); 4-CH$_3$ ($\Delta S^{\neq} = 29.7$ J mol^{-1} K^{-1}; $\Delta H^{\neq} = 77.1$ kJ mol^{-1}); 4-H ($\Delta S^{\neq} = 12.6$ J mol^{-1} K^{-1}; $\Delta H^{\neq} = 76.4$ kJ mol^{-1}); 4-Cl ($\Delta S^{\neq} = 16.1$ J mol^{-1} K^{-1}; $\Delta H^{\neq} = 82.0$ kJ mol^{-1}); 4-CF$_3$ ($\Delta S^{\neq} = -24.4$ J mol^{-1} K^{-1}; $\Delta H^{\neq} = 73.8$ kJ mol^{-1}) and 4-NO$_2$ ($\Delta S^{\neq} = -53.5$ J mol^{-1} K^{-1}; $\Delta H^{\neq} = 63.5$ kJ mol^{-1}). Although the values of $\Delta H^{\neq}$ are important for determining the structure of the activated complex, in this case, where the values of $\Delta H^{\neq}$ are reasonably similar in all reactions, it is the relative value of $\Delta S^{\neq}$ which are the most important. The values of $\Delta H^{\neq}$ are reasonably similar and reasonably low (< 100 kJ mol^{-1}). This is in agreement with bimolecular reactions where the breaking of new bonds and the forming of new ones in the activated complex are highly concerted and usually synchronous. This suggests that the structures of the activated complexes in all cases are similar.

The second trend is that, with the exception of 4-Cl (although it has a very similar value to that of 4-H), as the substituent is more electron-donating, so the value of $\Delta S^{\neq}$ increases. Thus as the reaction becomes more dissociative, the amount of disorder in the reaction increases. This result can be explained by examining the structures of the activated complexes. In the associative reaction we see an attack of one water molecule on the carbonyl carbon of the benzoyl chloride, forming a tetrahedral intermediate with delocalized negative charge between the oxygen and chlorine atoms (Scheme 6).

In the dissociative reaction there is partial (depending on the extent of dissociative character) bond breaking of the carbonyl carbon–chlorine bond, leading to a chlorine ion with a partial negative charge which is solvated by the surrounding water molecules (Scheme 7).

The reasons for the increase in $\Delta S^{\neq}$ from negative to positive as we pass from the associative to the dissociative mechanism are, then, two-fold. In the associative reaction we have two molecules reacting (benzoyl halide and water) to form one molecule, leading to greater order and hence a negative entropy; for the dissociative reaction there is partial breaking of the C–Cl bond giving "two" molecules, leading to an increase in disorder. The second factor is the amount of solvation by the surrounding water molecules of the negative charges on the two activated complexes. The negative charge on the tetrahedral complex in the associative reaction is delocalized, thus the amount of solvation by water is relatively low. In contrast, there is significant solvation of the partial negative charge on the chlorine atom in the dissociative reaction. Solvation by the surrounding water molecules on the complexes breaks up the water lattice; this leads to an increase in disorder and hence a more positive value of $\Delta S^{\neq}$.

It is important to point out that for solvolysis of BzF and 4-CF$_3$ in AOT-based microemulsions $\Delta S^{\neq}$ is independent of W. This behavior is consistent with a mechanism where the solvolysis of the said benzoyl halides occurs through a predominantly associative process. Likewise, it is important to point out that the value of $\Delta S^{\neq}$ is much more negative than that obtained in pure water: $\Delta S^{\neq} = -24.4$ J mol^{-1} K^{-1} for 4-CF$_3$ in pure water as opposed to the value of $\Delta S^{\neq} \approx -150$ J mol^{-1} K^{-1} obtained at the interface of the microemulsions. The most negative value obtained in the interface of the microemulsion by comparison with that obtained in pure water must be related to the greater degree of structuring which the water presents at the interface of the microemulsion in comparison with that observed in pure water. In the interface of the microemulsion the interaction of the water with the head groups of the surfactants produces a breakage in the network of hydrogen bonds, which would cause an increase in disorder, but at the same time strong interactions between the water molecules and the SO$_3^-$ group of the surfactant are established, as well as between the water molecules and the carbonyl groups of the AOT. These strong interactions cause the global result to be an increase of the order for the water molecules which solvate the head groups of the surfactant.



Scheme 7

Values of the activation entropy for solvolysis of 4-CH$_3$O show that $\Delta S^{\neq}$ decreases along with W. It should be pointed out that the obtained value for $\Delta S^{\neq}$ at high water contents ($W = 50$, $\Delta S^{\neq} \approx -40$ J mol^{-1} K^{-1}) is much lower than that obtained in pure water ($\Delta S^{\neq} = 31.9$ J mol^{-1} K^{-1}). This appreciable difference in the values of $\Delta S^{\neq}$ is considered to be due to the greater degree of structuring of the water at the interface of the microemulsion by comparison with bulk water. As the water content of the microemulsion decreases, so too does its capacity to act as an electrophile and therefore its capacity to solvate the leaving group also diminishes. At the same time an increase occurs in the nucleophilic character of the water, so that an associative mechanism is favored. The balance of both processes causes a change in the mechanism of the solvolysis of 4-CH$_3$O from a predominantly dissociative mechanism at high water contents to another predominantly associative one for small W values. This change of mechanism is responsible for the decrease of $\Delta S^{\neq}$ as W decreases, reaching a limiting value of $\Delta S^{\neq} \approx -150$ J mol^{-1} K^{-1} which is very close to that obtained for the solvolysis of 4-CF$_3$.

Compensation temperature

The existence of an isokinetic relationship can serve as an argument, but not proof, that the reactions studied share a common feature.[26,27] The meaning of the isokinetic relationship is the existence of a compensation effect between the values of enthalpy and the entropy of activation, to the extent that the Gibbs' activation energy, $\Delta G^{\neq}$, is approximately constant.[28] Fig. 9 shows the existence of a good correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the solvolysis of 4-CF$_3$ and BzF in microemulsions of AOT/isooctane/water for values of W between $W = 2$–50. The existence of such a correlation can be considered as indicative of the existence of a sole operating mechanism in these reactions. If in Fig. 9 we include the values corresponding to the solvolysis of 4-CH$_3$O, we observe an absence of correlation, which shows the existence of a change in mechanism as the water content of the microemulsion varies.

The existence of a compensation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for different reactions in microemulsions had been found previously for reactions between ionic species [Fe(CN)$_6$]$^{3-}$ and I$^-$. In this case the reaction takes place solely in the aqueous microdroplet and the rate of the reaction increases sharply as W decreases.[29] Similar isokinetic relationships have also been observed for the basic hydrolysis of crystal violet in different microemulsions.[30]

Hammett correlation

The results presented throughout this study show that as the water content in the microemulsion diminishes, there is a gradual change in the solvolysis mechanism of 4-CH$_3$O from an

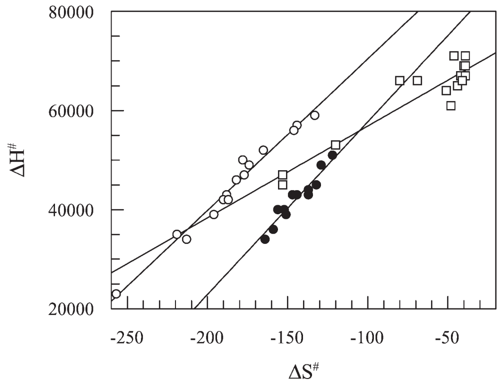


Fig. 9 Isokinetic plot for solvolysis in AOT/isooctane/water microemulsions for (●) 4-CF_3; (○) BzF and (□) 4-CH_3O.

eminently dissociative mechanism to an associative one. This change in mechanism is founded fundamentally in the variation of the activation entropy with W, which for small water contents reaches values similar to those observed for the solvolysis of 4-CF_3. This behavior should also be shown through a Hammett correlation. Fig. 10 shows a Hammett correlation for k_i values obtained at $W = 2$ with different benzoyl chlorides.

When the correlation is carried out using the parameter σ^+ we can observe a clear deviation of 4-CH_3O and of the 3,4-$(CH_3O)_2$. Such a deviation was explained on the bases of the existence of a dissociative mechanism for these benzoyl chlorides. However when the correlation is carried out using the σ Taft parameter[31] we observe a satisfactory correlation for all the benzoyl chlorides, including 4-CH_3O and the 3,4-$(CH_3O)_2$. This latter behavior suggests the existence of a sole associative reaction path for $W = 2$. The existence of an associative mechanism for $W = 2$ is compatible with the activation entropy of 4-CH_3O at very low water content in the microemulsion.

Conclusions

A study has been carried out on the solvolysis of benzoyl halides on microemulsions of AOT/isooctane/water. In all cases the observed rate constant in the microemulsion is smaller than in the aqueous medium. The magnitude of this inhibition depends on the nature of the substrate: 3×10^4 for 4-CH_3O; 5×10^3 for 3-CH_3O; 150 for BzF and 35 for 4-CF_3, showing that the inhibition increases together with the dissociative character of the reaction mechanism. As the dissociative mechanism is disfavored introducing a weaker leaving group (effect Cl^-/F^-) or introducing electron attracting groups (effect 4-CH_3O : 3-CH_3O : 4-CF_3) the magnitude of the inhibition decreases.

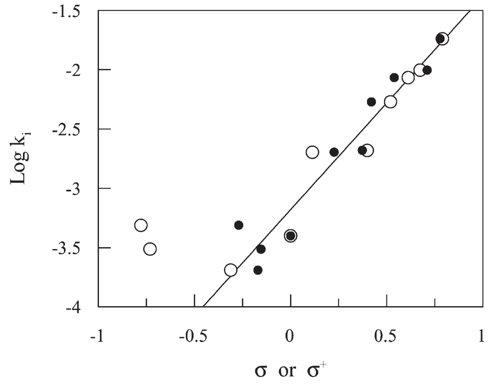


Fig. 10 Hammett plots for solvolysis of substituted benzoyl chlorides in AOT/isooctane/water microemulsions at $W = 2$ by using σ values (●) or σ^+ values (○).

The application of the formalism of the pseudophase has allowed us to obtain the rate constants at the interface of the microemulsion, k_i. We can observe two limiting behaviors: for the solvolysis of 4-CH_3O k_i increases approximately 325 times as W increases from $W = 2$ to $W = 50$; while in the solvolysis of 4-CF_3 k_i decreases approximately 5 times for the same variation of W. As W decreases there is an increase in the interaction of the water with the anionic head groups of the surfactant. This interaction produces a decrease in the electrophilic capacity of the water (consequently the rate of the dissociative processes decreases) and an increase in the nucleophilic character (with the consequent increase in k_i for the dissociative processes). The behavior observed for other benzoyl halides is qualitatively similar to that obtained for 4-CH_3O but the magnitude of the inhibition is smaller: k_i increases 35 times for 3-CH_3O and 3 times for BzF as W increases from $W = 2$ to $W = 50$. This behavior is due to the fact that the reaction takes place simultaneously by means of a dissociative and associative mechanisms on which the microemulsion exerts an opposite effect.

We have determined the activation parameters for the reaction, finding two very different types of behavior: in the solvolysis of 4-CF_3 and BzF $\Delta S^{\neq}$ is negative and independent of W, while in the solvolysis of 4-CH_3O $\Delta S^{\neq}$ decreases together with W does. These dependences are compatible with the fact that 4-CF_3 and BzF react predominantly by an associative mechanism, while for 4-CH_3O there is a gradual change in mechanism as W decreases from a dissociative to an associative one for small W values. This change in mechanism is shown when studying a Hammett correlation which predicts an associative reaction mechanism for the solvolysis of 4-CH_3O at $W = 2$ when Taft σ values are used. The results obtained show that the changes in the water properties of the microemulsions do not just alter the reaction rate but also that they can modify the mechanism by which the reactions take place.

Acknowledgements

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intercept/slope of plots like those shown in Figs. 3 and 4 are independent of W. If a small percentage of the reaction can take place at the water phase, the such ratio intercept/slope should be W-dependent as is discussed in ref. 17. Additionally there is a very good correlation between the solvolysis rate constant of 4-CH_3O and the interface polarity parameter $E_T(30)$. On the other hand if we compare the reactivity of different benzoyl chlorides we can observe that they fit a good Hammett correlation for substrates where the rate constant is very much solvent dependent and for others where the rate constant at the interface of the microemulsion is very close to the solvolysis rate constant in bulk water, as for 4-CF_3.

15 As is experimentally observed the distribution constants of the benzoyl halides between the oil and the interface, K_{oi}, are W-independent although the solvolysis rate constant at the interface varies with W. This behavior can be explained on the basis of the enthalpy of solvent transfer for the transition state of the reaction and the benzoyl chlorides. These data are not available in the literature and are difficult to obtain because of the decomposition of the benzoyl chlorides. However we can compare literature values for the hydrolysis of ethyl acetate. We can observe a difference of activation entropy of $\delta\Delta H^{\neq} = 4.0$ kcal mol^{-1} between 60% aqueous DMSO and 60% aqueous ethanol, the reaction rate being faster in aqueous DMSO. The same authors (ref. 16) found that the enthalpy of solvent transfer from 60% aqueous DMSO to 60% aqueous ethanol for ethyl acetate is $\delta\Delta H^{\mathrm{ethylacetate}}_{\mathrm{DMSO}\rightarrow\mathrm{Ethanol}} = 0.23$ kcal mol^{-1}.

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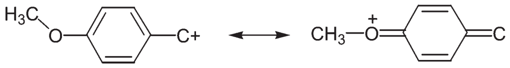
31 In Fig. 10 we can see a Hammett plot for solvolysis at $W = 2$ with both σ and σ^+. The difference between using σ and σ^+ depends on the possibility of charge stabilization by inductive effects (σ) or by resonance (σ^+). The difference between these substituent parameters is more significant for 4-CH_3O because the possibility of establishment of the resonance structures:



This kind of stabilization is important if the reaction proceeds by the lower right corner, dissociative mechanism (paths *a* or *b*), of Scheme 4, but is irrelevant if the reaction proceeds through the left upper corner, associative mechanism (paths *c* or *d*). In this way the good correlation of the solvolysis rate constants at $W = 2$ with σ Taft parameter is an indicative that reaction is taking place by the associative mechanism.