Microheterogeneous Solvation for Aminolysis Reactions in AOT-Based Water-in-Oil Microemulsions

Luis García-Río,*[a] Juan Carlos Mejuto,[b] and Moisés Pérez-Lorenzo[a]

Abstract: A kinetic study was carried out on the aminolysis of *p*-nitrophenyl acetate (NPA) by *n*-decylamine (DEC), piperazine (PIP) and sarcosine (SAR) in AOT/isooctane/water (w/o) microemulsions. By using the pseudophase model both the rate constants at the interface, k_2^i, and the water microdroplet, k_2^w, can be obtained. The obtained results show that k_2^i increases together with the water content of the microemulsion, whereas k_2^w increases as the water content of the system decreases. In the aqueous microdroplet the predominant interaction $Na^+ \cdots OH_2$ causes a decrease in the strength of the hydrogen bonds and therefore facilitates the desolvation of the reagents as W decreases. This desolvation of the reagents causes the increase of k_2^w as W decreases. In the interface of the microemulsion the predominant interaction $SO_3^- \cdots HOH$ causes an increase in the electronic density on the water molecules and the consequent decrease in their efficiency in the solvation of the partial negative charge, which develops on the carbonyl oxygen atom in the transition state of the reaction. This decrease in the solvation causes k_2^i to decrease together with the water content of the system.

Keywords: aminolysis • kinetics • reaction mechanism • microemulsions • reactivity

Introduction

A microemulsion is defined as a thermodynamically stable, isotropic dispersion of two relatively immiscible liquids, consisting of microdomains of one or both liquids stabilized by an interfacial film or surface-active molecules.[1,2] In preparative organic chemistry microemulsions have been used to overcome reagent solubility problems because the ability of microemulsions to solubilize both polar and non-polar substances and to compartmentalize and concentrate reagents[3] Microemulsions are also very widely used to the design and synthesis of novel materials that requires a precise control of the shape and size of the precursor materials.[4]

In order to improve the applications of microemulsions as new reaction media it is necessary to have models, which explain the kinetic behavior of simple reactions in these media. These models should take into account the distribution of different reagents throughout the various pseudophases of the microemulsion and the possibility of the reaction-taking place simultaneously in one or many phases. It will thus be possible to design experiments in which a variation of the composition of the microemulsion causes the reaction to occur in different microenvironments of the system. An additional factor, which complicates the kinetic studies carried out on microemulsions, are the changes in their physical properties as the water content varies. The most used surfactant is sodium bis(2-ethylhexyl)sulfosuccinate, also known as AOT. The phase diagram of AOT/water/isooctane shows a very large domain of water-in-oil droplets.[5,6] As the parameter W varies, $W = [H_2O]/[AOT]$, changes occur in the microviscosity of the system, polarity, and so on. In this sense, the changes observed by various techniques[7–24] are especially important when studying the properties of the solubilized water in AOT-based microemulsions. These changes in the physical properties of the water can modify the reactivity[25] and even the mechanism by which the reactions occur.[26]

The present study intends to extend the kinetic models to the study of reactions that can occur simultaneously in vari-

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[a] Prof. L. García-Río, Dr. M. Pérez-Lorenzo
Departamento Química Física
Facultade de Química, Universidade de Santiago
15782 Santiago (Spain)
Fax: (+34) 981-595-012
E-mail: qflgr3cn@usc.es

[b] Prof. J. C. Mejuto
Departamento Química Física
Facultade de Ciencias, Universidade de Vigo
Campus de Ourense, Ourense (Spain)

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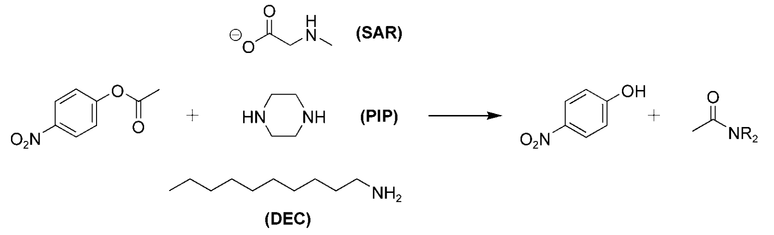
ous microenvironments of microemulsions. In order to carry out the study a reaction has been chosen which is very well known in water and in various organic solvents, namely the aminolysis of the 4-nitrophenylacetate. Three different amines have been chosen because of their different degrees of hydrophobicity: *n*-decylamine, piperazine and sarcosine (Scheme 1). The use of sarcosine and piperazine will allow us to verify whether the reactivity sequence observed in an aqueous medium is transferred to the microdroplet and the interface of the microemulsion on using amines with different pK_a values.

The results obtained show that the aminolysis of the NPA by piperazine and sarcosine takes place simultaneously in the interface and in the aqueous microdroplet. As the water content of the system decreases, there is an increase in the percentage of the reaction, which occurs in the interface of the microemulsion. Aminolysis by *n*-decylamine takes place only at the interface of AOT-based microemulsions.

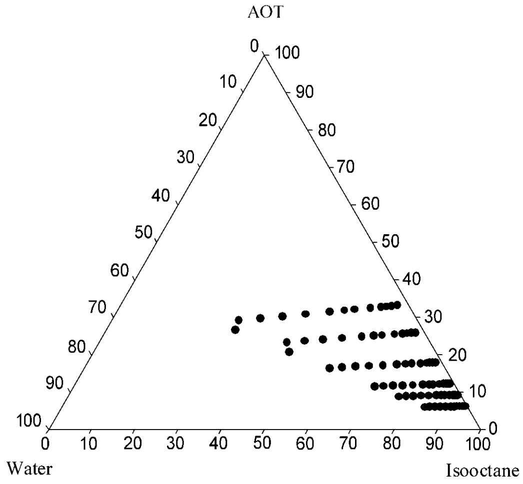


Scheme 1.

Results

A study was carried out on the influence of the composition of the microemulsion on the aminolysis rate constant of 4-nitrophenylacetate by amino acids, piperazine and *n*-decylamine. The compositions of the w/o microemulsions, which have been used to carry out this study, is shown in the phase diagram below. The compositions were selected with the purpose of covering a wide interval: the content of AOT varies between 6–30% (w/w); that of water between 0.5–43% (w/w) and that of the isooctane between 29–93% (w/w). These composition intervals allow us to vary W, $W=[H_2O]/[AOT]$, between $W=2$–40. Hence we used microemulsions which display a wide variation in properties such as polarity, viscosity, hydrogen bond donation capacity, and saline content.

In all cases it was found that the observed rate constant presents a linear dependency on the nucleophilic concentration when the reaction takes place in the microemulsion. This behavior is consistent with that found in water and in other polar solvents.[27] The different solubilities of SAR, piperazine and *n*-decylamine mean that the kinetic behavior in the microemulsions is different. Therefore, we will present separately the results in order, so that the hydrophilic character of the amine increases: aminolysis of NPA by DEC; aminolysis by PIP and finally the aminolysis of the NPA by SAR.



Aminolysis of NPA by decylamine: A study has been carried out on the influence of the microemulsion composition on k_{obs} in the aminolysis of NPA by decylamine, keeping the total amine concentration constant with regard to the total volume of the system, $[DEC] = 2.50\times10^{-2}$ M, and varying the composition of the microemulsion. Figure 1 shows by way of example the values of k_{obs} obtained for different compositions of the system. These results show that k_{obs} increases together with the AOT concentration, and then decreases.

The results shown in Figure 1 can be explained as a consequence of the DEC and NPA incorporation to the interface of the microemulsions when increasing the [AOT], which increases the local concentration of the reagents and thus the

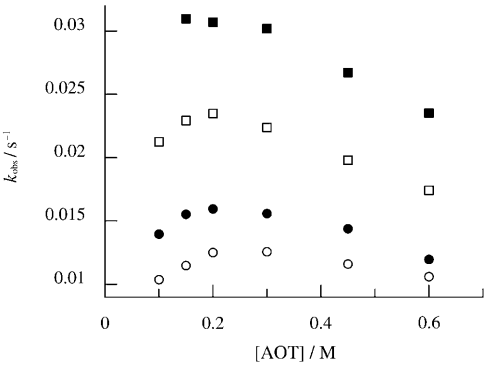


Figure 1. Influence of the microemulsion composition on k_{obs} for the aminolysis of NPA by *n*-decylamine. $[DEC]=2.50\times10^{-2}$ M referred to the total volume of the system; $T=25\,°C$; ○: W=3, ●: W=7, □: W=20, and ■: W=35.

reaction rate. Once all the NPA and DEC have been associated with the interface, as the [AOT] increases there is also an increase in the interfacial volume and therefore a dilution of the reagents in the interface with the consequent reduction of k_{obs}. When the [AOT] remains constant and W increases, there is an increase in the size of the droplets and, therefore, in the fraction of the disperse phase. This increase in the fraction of the disperse phase causes a reduction in the volume occupied by the continuous medium, so that the quantity of NPA and DEC associated with the interface increases. In this way the increase of k_{obs} together with W can be explained.

Reaction of piperazine with NPA: To investigate the influence of the composition of the microemulsion on the aminolysis of the NPA by piperazine experiments were carried out varying the composition of the microemulsion using as an aqueous medium a 0.10 M solution of piperazine. Therefore, on varying the composition of the microemulsion, the amine concentration also varies, so that in order to analyze the results obtained it is more convenient to use a second order rate pseudoconstant, k_2^{app}, which includes the piperazine concentration: $k_{obs} = k_2^{app}[PIP]_T$. The term $[PIP]_T$ corresponds to the total concentration of piperazine in the microemulsion referred to the total volume of the system. The results are shown in Figure 2. The rate constant k_2^{app} decreases as the surfactant concentration increases and as the water content of the system increases.

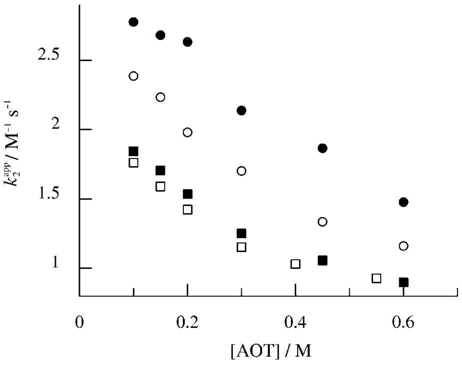


Figure 2. Influence of the microemulsion composition on k_2^{app} in the aminolysis of NPA by PIP. $[PIP]_T$ = 0.10 M referred to the aqueous phase of the system; T = 25 °C; ●: W = 7, ○: W = 15, ■: W = 30, and □: W = 40.

This behavior is contrary to that observed in the aminolysis of the NPA by DEC (see Figure 1) and must be a consequence of the different distribution of the reagents and to an increase of the volume of the interface on increasing [AOT]. It is important to note that in all cases the rate constant k_2^{app} is lower than the aminolysis rate constant of NPA by piperazine in bulk water, $k_2^{H_2O}$ = 6.09 M^{-1}s^{-1}. This decrease of the rate constant is due to the distribution of the reagents throughout the different pseudophases of the system.

Reaction of SAR with NPA: A kinetic study has been carried out in which we have varied the concentration of amino acid, SAR, as well as the composition of the microemulsion. In all cases the concentration of nitrophenyl acetate, [NPA] = (2–4) × 10^{-5} M, was much lower than the concentration of amino acid. On varying the concentration of amino acid while keeping the composition of the microemulsion constant, the observed rate constant, k_{obs}, presents a linear dependency on the amino acid concentration (not shown). In other experiments the composition of the microemulsion and the concentration of amino acid have been varied simultaneously, while keeping constant the concentration of amino acid referred to the aqueous volume of the microemulsion,[28] $[SAR]_w^w$ = 5.00 × 10^{-2} M. In all cases a quantity of sodium hydroxide was added to the amino acid solution, sufficient to guarantee that the amino acid would take an anionic form. Given that on varying the microemulsion composition also varies the amino acid concentration, it is more simple to carry out an analysis of the results in terms of a second order rate pseudoconstant, k_2^{app}, which includes the concentration of amino acid: $k_{obs} = k_2^{app}[SAR]_T$. The term $[SAR]_T$ corresponds to the total concentration of sarcosine in the microemulsion referred to the total volume of the system. The value of k_2^{app} is always lower than that which is found in pure water, $k_2^{H_2O}$ = 2.01 M^{-1}s^{-1}.

Figure 3 shows that k_2^{app} decreases as the surfactant concentration and the water content of the system increase as was observed in the aminolysis by piperazine.

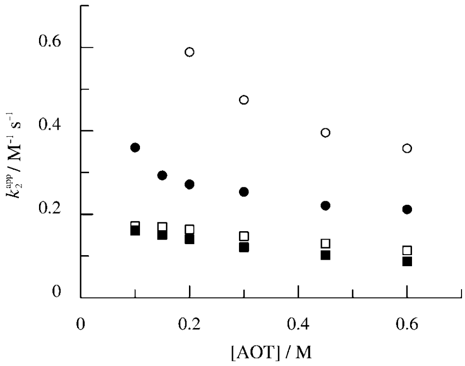


Figure 3. Influence of the microemulsion composition on k_2^{app} for the aminolysis of NPA by SAR [SAR] = 5.00 × 10^{-2} M referred to the aqueous phase of the system; T = 25 °C; ○: W = 4, ●: W = 7, □: W = 15, and ■: W = 30.

Discussion

Kinetic studies of reactions in water in oil (w/o) microemulsions can be interpreted in terms of reactivity, only if local reagent concentrations and intrinsic rate constants in the various microphases of these organized media can be obtained from the overall, apparent rate data. In our research group a kinetic model has been developed, based on the formalism of the pseudophase which can be applied to interpret quantitatively the influence of the composition of the microemulsion on the chemical reactivity.[29,30] As is usual on studying reactivity in colloidal systems (micelles, vesicles and microemulsions) the activity coefficients of the components in these systems are independent of their concentrations. To apply this formalism to the aminolysis of the NPA we must consider the microemulsion formed by three strongly differentiated pseudophases:[31] an aqueous pseudophase (w), a continuous medium formed fundamentally by the isooctane (o) and an interface formed fundamentally by the surfactant (i). The different kinetic behavior makes it necessary for us to propose different kinetic models for aminolysis by *n*-decylamine, piperazine and sarcosine.

NPA aminolysis by *n*-decylamine: The experimental results obtained in the aminolysis of NPA by decylamine can be interpreted from Figure 4. The NPA is found distributed between the three pseudophases of the system. The low solubility of the *n*-decylamine in water allows us to exclude the possibility of it being distributed throughout the three pseudophases of the microemulsion. In this way the NPA and the decylamine will only be able to contact the continuous medium and the interface of the microemulsion.

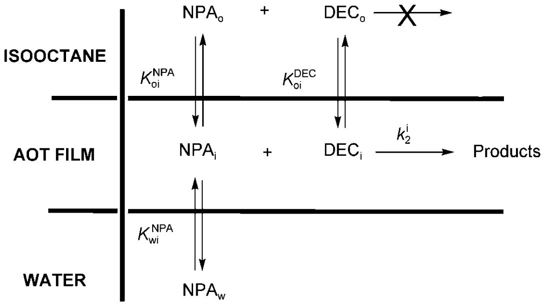


Figure 4.

The distribution of the NPA throughout the different pseudophases of the microemulsion (Figure 4) is governed by the following equilibrium constants:

$$K_{wi}^{NPA} = \frac{[NPA]_i}{[NPA]_w} W \qquad K_{oi}^{NPA} = \frac{[NPA]_i}{[NPA]_o} Z \tag{1}$$

where $[NPA]_w$, $[NPA]_i$ and $[NPA]_o$ correspond to the NPA concentrations in the aqueous microdroplet, the interface and the continuous medium in the microemulsion, referred to the total volume of the system. The parameter Z has been defined as the molar relationship Z = [isoooctane]/[AOT], by analogy with the parameter W. We can evaluate the concentrations of NPA in the aqueous microdroplet, $[NPA]_w$, and in the interface of the microemulsion, $[NPA]_i$, considering that the total concentration of NPA will be the sum of the concentration in each of the three pseudophases of the system:

$$[NPA]_w = \frac{K_{oi}^{NPA} W [NPA]_T}{K_{oi}^{NPA} K_{wi}^{NPA} + K_{wi}^{NPA} Z + K_{oi}^{NPA} W} \tag{2}$$

$$[NPA]_i = \frac{K_{oi}^{NPA} K_{wi}^{NPA} [NPA]_T}{K_{oi}^{NPA} K_{wi}^{NPA} + K_{wi}^{NPA} Z + K_{oi}^{NPA} W} \tag{3}$$

where the concentrations are referred to the total volume of the system.

The possibility of the reaction taking place in the continuous medium can be discarded due to the second order dependency which exists between k_{obs} and the amine concentration in isooctane (data not shown). Likewise, the value of k_{obs} obtained for the aminolysis of the NPA by *n*-decylamine in pure isooctane, $k_{obs} \cong 4.5 \times 10^{-5} s^{-1}$ for $[DEC] = 2.50 \times 10^{-2}$ M, is approximately 250 times lower than the value obtained in AOT-based microemulsions for the same amine concentration. Therefore, the reaction will take place solely in the interface of the microemulsion.

Equation (3) can be simplified taking into account the values previously obtained[32] for K_{oi}^{NPA} and K_{wi}^{NPA} ($K_{oi}^{NPA} = 25.9$ and $K_{wi}^{NPA} = 996$):

$$[NPA]_i \cong \frac{K_{oi}^{NPA} [NPA]_T}{K_{oi}^{NPA} + Z} \tag{4}$$

The following expression for the observed rate constant, k_{obs}, can be obtained:

$$k_{obs} = k'_i \frac{K_{oi}^{NPA}}{K_{oi}^{NPA} + Z} \tag{5}$$

where k'_i is the first order rate pseudoconstant referred to the interface. This rate constant can be expressed as a bimolecular rate constant in the interface, k_2^i, thus:

$$k'_i = k_2^i [DEC]_i^i = k_2^i \frac{V_{tot}}{V_i} [DEC]_i = k_2^i \frac{[DEC]_i}{\bar{V}_{AOT} [AOT]} \tag{6}$$

where $[DEC]_i^i$ refers to the *n*-decylamine concentration in the interface of the microemulsion referred to the volume of the interface, whereas $[DEC]_i$ corresponds to the amine concentration in the interface of the microemulsion referred to the total volume of the system. As is usual in microemulsions and direct micelles, the interface has been considered to be consisting solely of the surfactant, in such a way that the volume of the interface is given by the volume occupied by the AOT. In this way $V_{tot}/V_i = 1/\bar{V}_{AOT}[AOT]$ where $\bar{V}_{AOT}$ represents the molar volume of the surfactant, $\bar{V}_{AOT} = 0.34\,M^{-1}$ and [AOT] represents the total concentration of AOT referred to the total volume of the microemulsion.

On the basis of the distribution equilibrium of the *n*-decylamine between the continuous medium and the interface of the microemulsion, we can obtain:

$$[\mathrm{DEC}]_\mathrm{i} = \frac{K_\mathrm{oi}^\mathrm{DEC}}{K_\mathrm{oi}^\mathrm{DEC} + \mathrm{Z}}[\mathrm{DEC}]_\mathrm{T} \tag{7}$$

By combining Equations (5)–(7) we obtain:

$$k_\mathrm{obs} = \frac{k_2^\mathrm{i}}{V_\mathrm{AOT}[\mathrm{AOT}]}\frac{K_\mathrm{oi}^\mathrm{NPA}}{(K_\mathrm{oi}^\mathrm{NPA} + \mathrm{Z})}\frac{K_\mathrm{oi}^\mathrm{DEC}[\mathrm{DEC}]_\mathrm{T}}{(K_\mathrm{oi}^\mathrm{DEC} + \mathrm{Z})} \tag{8}$$

The rate equation can be reordered thus:

$$\frac{[\mathrm{DEC}]_\mathrm{T}}{k_\mathrm{obs}\bar{V}_\mathrm{AOT}[\mathrm{AOT}]} = \frac{(K_\mathrm{oi}^\mathrm{NPA} + \mathrm{Z})(K_\mathrm{oi}^\mathrm{DEC} + \mathrm{Z})}{k_2^\mathrm{i} K_\mathrm{oi}^\mathrm{NPA} K_\mathrm{oi}^\mathrm{DEC}} \tag{9}$$

which predicts the existence of a linear and quadratic dependency of $[\mathrm{DEC}]_\mathrm{T}/k_\mathrm{obs}\bar{V}_\mathrm{AOT}[\mathrm{AOT}]$ on the parameter Z of microemulsion composition. Figure 5 shows by way of example the good fit of previous equation to the experimental results.

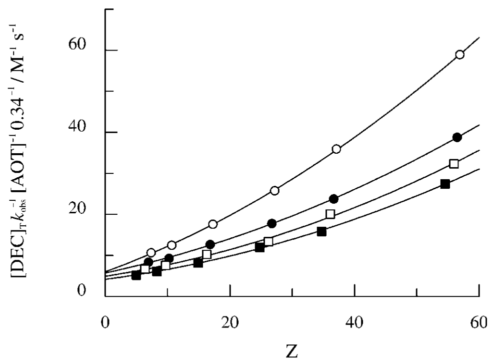


Figure 5. Experimental results obtained for the aminolysis of NPA by *n*-decylamine in AOT-based microemulsions according to Equation (9). $[\mathrm{DEC}]_\mathrm{T} = 2.50 \times 10^{-2}\,\mathrm{M}$; $T = 25\,°\mathrm{C}$; ○: W=3, ●: W=7, □: W=12, and ■: W=25.

From representations such as those of Figure 5, and using the value of $K_\mathrm{oi}^\mathrm{NPA} = 25.9$, we can obtain the values of the distribution constant of the *n*-decylamine between the continuous medium and the interface, $K_\mathrm{oi}^\mathrm{DEC}$, and the aminolysis rate constant at the interface, k_2^i. The obtained values for $K_\mathrm{oi}^\mathrm{DEC}$ are independent of W, allowing us to calculate a mean value for $K_\mathrm{oi}^\mathrm{DEC} = 48.4$. However, the values obtained for k_2^i present a clear variation with W, as shown in Figure 6. As the water content of the system increases, there is also an increase in the aminolysis rate constant at the interface. This behavior is consistent with the decrease in the nitroso group transfer rate constant in the interface of AOT-based microemulsions, as the water content of the system decreases.[29] This decrease has generally been attributed to an insufficient hydration of the interface of the microemulsion as the water content of the system decreases.

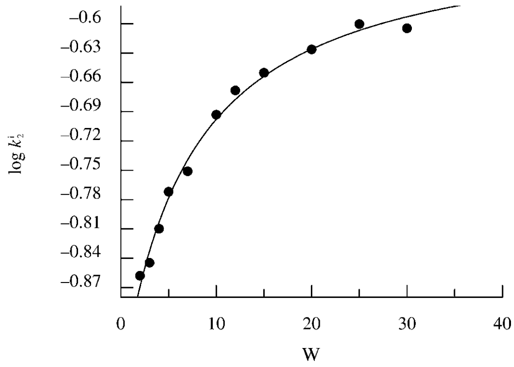


Figure 6. Influence of W on $\log k_2^\mathrm{i}$ for the aminolysis of NPA by *n*-decylamine in AOT/isooctane/water microemulsions at 25 °C; $[\mathrm{DEC}] = 2.50 \times 10^{-2}\,\mathrm{M}$ referred to the total volume of the system.

NPA aminolysis by piperazine: The piperazine is a hydrophilic species, insoluble in isooctane, which is found between the aqueous microdroplet and the interface of the microemulsion. To explain the kinetic behavior that we observed in the aminolysis of the NPA by piperazine we must consider the reactive scheme showed in Figure 7, where the aminolysis reaction can take place simultaneously in the interface and in the microdroplet of the microemulsion.

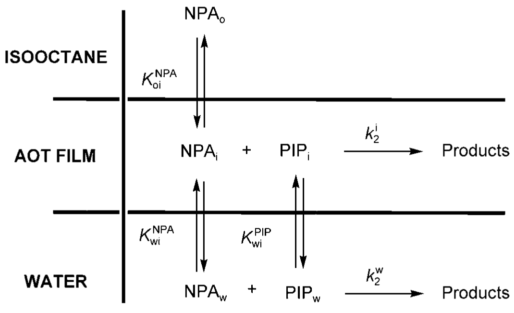


Figure 7.

Using the same procedure as we used to obtain the NPA concentration in the different microenvironments of the microemulsion, we can obtain the concentrations of piperazine:

$$[\mathrm{PIP}]_\mathrm{i} = \frac{K_\mathrm{wi}^\mathrm{PIP}[\mathrm{PIP}]_\mathrm{T}}{K_\mathrm{wi}^\mathrm{PIP} + \mathrm{W}} \qquad [\mathrm{PIP}]_\mathrm{w} = \frac{\mathrm{W}[\mathrm{PIP}]_\mathrm{T}}{K_\mathrm{wi}^\mathrm{PIP} + \mathrm{W}} \tag{10}$$

In accordance with the mechanism of Figure 7, the reaction will take place simultaneously in the interface and in the aqueous microdroplet of the microemulsion. Therefore, on the basis of Equations (2) and (3), we can propose the following expression for the observed rate constant, k_{obs}:

$$k_{obs} = \frac{k'_w K_{oi}^{NPA} W + k'_i K_{oi}^{NPA} K_{wi}^{NPA}}{K_{oi}^{NPA} K_{wi}^{NPA} + K_{wi}^{NPA} Z + K_{oi}^{NPA} W} \tag{11}$$

where k'_i and k'_w are the rate pseudoconstants of the first order referred to the interface and the aqueous microdroplet, respectively. These rate constants can be expressed as bimolecular rate constants in the interface, k_2^i (see previous discussion of the aminolysis of the NPA by *n*-decylamine), and in the aqueous microdroplet, k_2^w, thus:

$$k'_i = k_2^i[\mathrm{PIP}]_i^i = k_2^i \frac{V_{tot}}{V_i}[\mathrm{PIP}]_i = \frac{k_2^i}{\bar{V}_{AOT}[\mathrm{AOT}]} \frac{K_{wi}^{PIP}[\mathrm{PIP}]_T}{(K_{wi}^{PIP} + W)} \tag{12}$$

$$k'_w = k_2^w[\mathrm{PIP}]_w^w = k_2^w \frac{V_{tot}}{V_{H_2O}}[\mathrm{PIP}]_w = \frac{k_2^w}{\bar{V}_{H_2O}[\mathrm{AOT}]} \frac{[\mathrm{PIP}]_T}{(K_{wi}^{PIP} + W)} \tag{13}$$

where $[\mathrm{PIP}]_i^i$ and $[\mathrm{PIP}]_w^w$ correspond to the concentrations of PIP in the interface and in the aqueous microdroplet, referred to the volumes of these pseudophases. These concentrations are transformed into concentrations referred to the total volume of the system by taking into account just the phase volumes. By combining Equations (11)–(13) we can obtain the following rate Equation (14):

$$k_{obs} = \frac{k_2^i \frac{K_{oi}^{NPA} K_{wi}^{NPA} K_{wi}^{PIP}}{\bar{V}_{AOT}[AOT]} + k_2^w \frac{K_{oi}^{NPA} W}{\bar{V}_{H_2O}[\mathrm{AOT}]}}{K_{oi}^{NPA} K_{wi}^{NPA} + K_{wi}^{NPA} Z + K_{oi}^{NPA} W} \frac{[\mathrm{PIP}]_T}{(K_{wi}^{PIP} + W)} \tag{14}$$

This Equation can be rewritten:

$$\frac{[\mathrm{PIP}]_T}{k_{obs}[\mathrm{AOT}]\bar{V}_{H_2O}\bar{V}_{AOT}} = \frac{(K_{wi}^{PIP} + W)[K_{oi}^{NPA} K_{wi}^{NPA} + K_{oi}^{NPA} W + K_{wi}^{NPA} Z]}{k_2^i K_{oi}^{NPA} K_{wi}^{NPA} K_{wi}^{PIP} \bar{V}_{H_2O} + k_2^w K_{oi}^{NPA} \bar{V}_{AOT} W} \tag{15}$$

and predicts the existence of a linear dependency between $[\mathrm{PIP}]_T/(k_{obs}[\mathrm{AOT}]\bar{V}_{H_2O}\bar{V}_{AOT})$ and the Z parameter of microemulsion composition. Figure 8 shows the good fit of Equation (15) to the experimental results.

The ordinates and slopes of Figure 8 show a clear dependency on W, as predicted by Equation (15). To carry out a quantitative analysis it is fitting to use the slopes, since they can be determined more accurately. Figure 9 shows the dependency of 1/slope (from Figure 8) on W for the aminolysis of the NPA by piperazine. As can be observed, the term 1/slope increases as the water content of the system (W) decreases, until a maximum value for W is reached, W ≅ 10. A subsequent reduction in W causes a reduction in 1/slope.

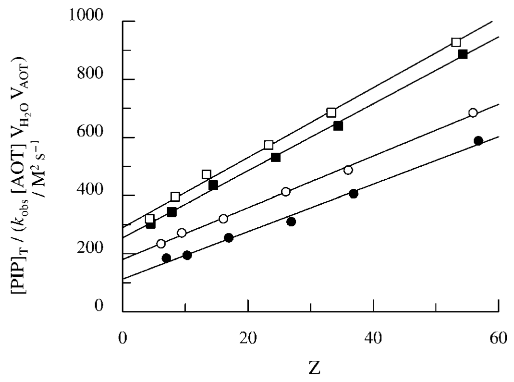


Figure 8. Fit of Equation (15) for the aminolysis of the NPA by PIP. $[\mathrm{PIP}] = 0.10\,\mathrm{M}$ referred to the aqueous phase of the system; $T = 25\,°C$; ●: W = 7, ○: W = 15, ■: W = 30, and □: W = 40.

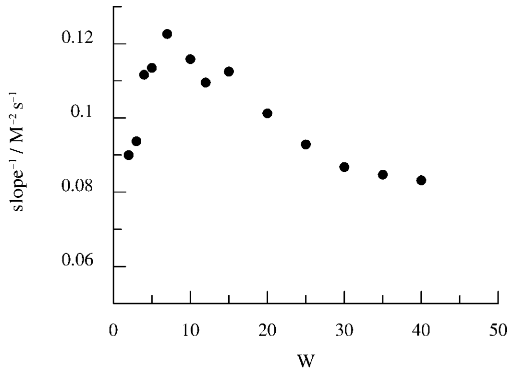


Figure 9. Influence of W on 1/slope (from plots like those of Figure 8) for the aminolysis of NPA by piperazine in AOT/isooctane/water microemulsions at 25 °C; $[\mathrm{PIP}] = 0.10\,\mathrm{M}$, referred to the aqueous phase of the system.

The results can be interpreted considering the following Equation (16) that relates 1/slope with the water content of the microemulsion.

$$\frac{1}{\mathrm{slope}} = \frac{k_2^i K_{oi}^{NPA} \bar{V}_{H_2O} + \frac{k_2^w K_{oi}^{NPA} \bar{V}_{AOT}}{K_{wi}^{NPA} K_{wi}^{PIP}} W}{1 + \frac{1}{K_{wi}^{PIP}} W} \tag{16}$$

Previous studies[29] have allowed us to determine the value of the distribution constant of the piperazine between the continuous medium and the interface of AOT-based microemulsions $K_{wi}^{PIP} = 9.5$ at 25 °C. Using this value, we can rewrite Equation (16) as:

$$\frac{1 + 0.105\,W}{\mathrm{slope}} = k_2^i K_{oi}^{NPA} \bar{V}_{H_2O} + \frac{k_2^w K_{oi}^{NPA} \bar{V}_{AOT}}{K_{wi}^{NPA} K_{wi}^{PIP}} W \tag{17}$$

which predicts the existence of a linear dependency between (1+0.105 W)/slope and the W parameter of microemulsion composition. Figure 10 shows the observed behavior in the aminolysis of NPA by piperazine.

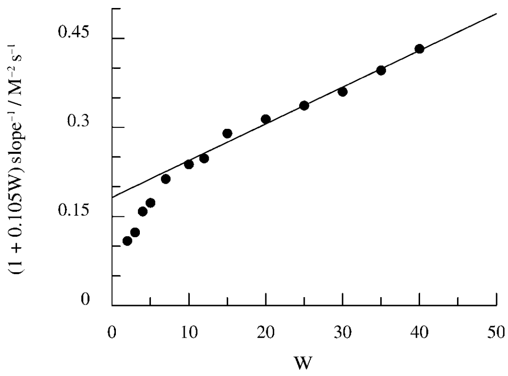


Figure 10. Influence of W on (1+0.105 W)/slope [Eq. (17)] for the aminolysis of NPA by piperazine in AOT/isooctane/water microemulsions at 25 °C; [PIP] = 0.10 M, referred to the aqueous phase of the system. The line represents the fit of Equation (17) to the experimental results; for the fit only the values obtained for W > 10 have been considered.

As can be observed there exists a clear linear dependency for values of W > 10, while there is a negative deviation from the linearity for W < 10. From the linear adjustment, and considering the values of $K_{oi}^{NPA}=25.9$ and $K_{wi}^{NPA}=996$ obtained previously we can obtain the rate constants $k_2^w = 6.64\,\text{M}^{-1}\text{s}^{-1}$ and $k_2^i = 0.39\,\text{M}^{-1}\text{s}^{-1}$. The value of k_2^w obtained for W > 10 is perfectly compatible with that which is determined in bulk water, $k_2^{H_2O} = 6.09\,\text{M}^{-1}\text{s}^{-1}$. Likewise the value of k_2^i obtained for W > 10 shows a 17-fold decrease in the rate constant when passing from bulk water to the interface of the microemulsion. This reduction of the rate constant is a consequence of the lower polarity of the interface of the microemulsion by comparison with the aqueous microdroplet, and it is compatible with the decrease in the rate constant in other processes such as nitroso group transfer.[29] It is important to point out that the ordinate of Figure 10 corresponds to the reaction in the interface. As can be observed, in all cases the reaction in the interface is significant against the total reaction percentage, due fundamentally to the high value of K_{wi}^{PIP}.

On the basis of Equation (17) and the results in Figure 10 we can calculate the reaction percentage which takes place in the interface and in the aqueous microdroplet for each value of W. For high W values, W = 40, approximately 55 % of the reaction takes place in the aqueous microdroplet. This percentage decreases sharply as the water content of the system decreases, in such a way that for W = 10 this percentage has been reduced to 22 %. These results show that for values of W < 10 more than 80 % of the reaction must take place in the interface of the AOT-based microemulsion.

The results of Figure 10 show a deviation from the behavior predicted by Equation (17) for values of W < 10. Moreover the behavior observed for the aminolysis of the NPA by piperazine at the interface must be similar to that observed for the aminolysis by *n*-decylamine. Figure 6 shows how k_2^i decreases for the aminolysis of NPA by DEC, as W decreases, especially for values of W < 10. It is important to point out that in the case of the DEC the reaction occurs solely in the interface of the microemulsion. For the aminolysis reaction of NPA by piperazine we expect to find an analogous behavior, that is, we expect that k_2^i will decrease along with W. This decrease in k_2^i could explain the negative deviation observed in Figure 8 when plotting (1+0.105 W)/slope against W. In this interpretation we are assuming that the negative deviation of Figure 10 is due to the decrease of k_2^i with W, and we ignore the influence of W on k_2^w. The validity of this approximation lies in the fact that for W < 10 more than 80 % of the reaction takes place in the interface of the microemulsion in such a way that the possible effects on k_2^w must be of less importance. It is important to note that the percentage of reaction in the interface increases as W decreases.

From a quantitative point of view the negative deviation observed in the representation of Figure 10 is compatible with the decrease of k_2^i with W. The deviation between the value predicted by Equation (17) and the value shown in Figure 10 is 78 %; this indicates that k_2^i has decreased in value by approximately 78 %. If we compare this extrapolation with the results of Figure 6 we observe that the rate constant of aminolysis of the NPA by decylamine in the interface of AOT-based microemulsions, k_2^i, decreases by 79 % on passing from high values of W to W = 2.

NPA aminolysis by sarcosine: To analyze the kinetic behavior that is observed in the aminolysis of NPA by amino acids it is necessary to consider a distribution model for these reagents. The amino acids in their ionic form are highly hydrophilic species, which guarantees their presence in the aqueous microdroplet of the microemulsion. The size of the sarcosine also allows us to consider the possibility of its incorporation into the interface. Judging by the structures shown in Scheme 1 it would be possible to consider the penetration of the amino group of the sarcosine in the interface of the microemulsions, while the carboxylate group can remain in the aqueous medium. Therefore, to explain the kinetic behavior observed in the aminolysis of the NPA by sarcosine we need to consider an analogous behavior to that proposed previously for piperazine (Figure 7), where the aminolysis reaction can take place simultaneously in the interface and in the microdroplet of the microemulsion.

In the same way as previously, we can obtain the SAR concentrations in the different microenvironments of the microemulsion:

$$[\text{SAR}]_i = \frac{K_{wi}^{SAR}\,[\text{SAR}]_T}{K_{wi}^{SAR} + \text{W}} \qquad [\text{SAR}]_w = \frac{\text{W}[\text{SAR}]_T}{K_{wi}^{SAR} + \text{W}} \tag{18}$$

In accordance with the mechanism of Figure 7 and with the methodology devised previously for the aminolysis of the

NPA by piperazine, we can obtain a rate equation analogous to Equation (15), which predicts the existence of a linear dependency between $[SAR]_T/(k_{obs}[AOT]\bar{V}_{H_2O}\bar{V}_{AOT})$ and Z parameter of microemulsions composition. Figure 11 shows the good fit of Equation (15) to the experimental results.

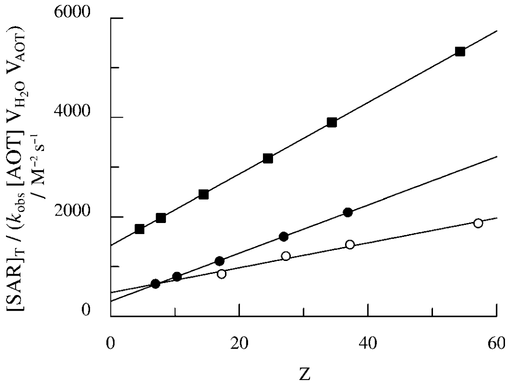


Figure 11. Fit of Equation (15) for the aminolysis of the NPA by SAR; $[SAR] = 5.00\times10^{-2}$ M referred to the aqueous phase of the system; $T = 25$ °C; ○: W = 4, ●: W = 7, and ■: W = 30.

Figure 12 shows the influence of W on 1/slope. As we can observe the term 1/slope decreases as the water content of the system increases, tending to reach a limiting value for W > 10. This tendency to reach a limiting value is the main qualitative difference between the behavior observed for the aminolysis of the NPA by piperazine (Figure 9) and by sarcosine (Figure 12).

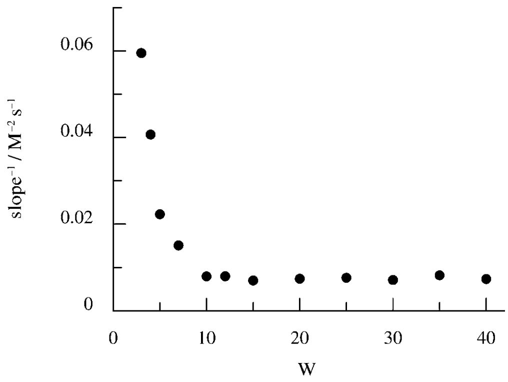


Figure 12. Influence of W on 1/slope for the aminolysis of NPA by sarcosine in AOT/isooctane/water microemulsions at 25 °C; $[SAR] = 5.00\times10^{-2}$ M referred to the aqueous phase of the system.

The existence of this limit value for W > 10 can be explained by using Equation (16) and considering that

$$k_2^i K_{oi}^{NPA}\bar{V}_{H_2O} \ll \frac{k_2^w K_{oi}^{NPA} V_{AOT}}{K_{wi}^{NPA} K_{wi}^{SAR}} W \text{ and } 1 \ll \frac{1}{K_{wi}^{SAR}} W.$$

In this way it can be shown that $\frac{1}{\text{slope}} \cong \frac{k_2^w K_{oi}^{NPA}\bar{V}_{AOT}}{K_{wi}^{NPA}}$. If we use the known values of $K_{oi}^{NPA} = 25.9$ and $K_{wi}^{NPA} = 996$, we can obtain 1/slope $\cong 8.84\times10^{-3} k_2^w$. By using the limiting value of Figure 10 for the aminolysis of the NPA by sarcosine, 1/slope $= 7.50\times10^{-3}$, we can obtain the value of $k_2^w = 0.85\,M^{-1}s^{-1}$; the obtained value is slightly lower than that obtained in bulk water, $k_2^{H_2O} = 1.73\,M^{-1}s^{-1}$. This difference in reactivity may be a consequence of the high ionic concentration inside the aqueous microdroplet. For a microemulsion of W = 15, the saline concentration in the microdroplet would be 3.7 M if the surfactant were completely dissociated. This decrease in the aminolysis rate constant with the saline concentration is consistent with the experimental results obtained in bulk water, where the addition of $NaClO_4$ causes a decrease in the reaction rate.

The existence of the limit value in the representation of Figure 12 allows us to obtain a maximum value of K_{wi}^{SAR}. In order to be able to observe the limit value it is necessary to verify the inequality: $1 \ll W/K_{wi}^{SAR}$. Given that this inequality is verified for values of W > 10, it is necessary for $K_{wi}^{SAR} \leq 1$. Henceforth we will use the value of $K_{wi}^{SAR} = 1$, which will allow us to obtain the corresponding minimum values of k_2^i. Using this maximum value of K_{wi}^{SAR} we can write an equation that is analogous to Equation (17) for the aminolysis of the NPA by SAR.

$$\frac{1 + W}{\text{slope}} = k_2^i K_{oi}^{NPA}\bar{V}_{H_2O} + \frac{k_2^w K_{oi}^{NPA}\bar{V}_{AOT}}{K_{wi}^{NPA} K_{wi}^{SAR}} W \qquad (19)$$

Figure 13 shows the representation of (1 + W)/slope for the aminolysis NPA by SAR. As in the case of the aminolysis of NPA by piperazine, a good fit of Equation (19) can be observed for values of W > 10. On the basis of the linear adjustment and considering the values of $K_{oi}^{NPA} = 25.9$, $K_{wi}^{NPA} = 996$, and $K_{wi}^{SAR} = 1$) obtained previously we can obtain the rate constants $k_2^w = 0.823\,M^{-1}s^{-1}$ and $k_2^i = 2.59\times10^{-2}\,M^{-1}s^{-1}$. Once again it can be seen that the rate constant in the interface of the AOT-based microemulsion is approximately 30 times lower that in the aqueous microdroplet. This difference is greater than in the aminolysis by piperazine and can be due in part to the statistical advantage that the piperazine has, through possessing two equivalent nitrogen atoms. It is to be expected that this statistical advantage will increase in the interface of the microemulsion, a region of restricted mobility.

As in the case of the aminolysis of the NPA by piperazine, the ordinate of Figure 13 corresponds to the reaction in the interface. As it was possible to observe, its value is very small with regard to (1 + W)/slope, indicating that the reaction takes place primarily in the aqueous microdroplet. In this case the low percentage of the reaction in the interface is due to the low value of K_{wi}^{SAR}. On the basis of the values of the ordinate and the slope of Figure 13 we can calculate the percentage of the reaction which takes place in the interface and in the aqueous microdroplet of the microemulsion. The percentage of the reaction which takes place in the aqueous microdroplet for W = 40 is 96 %, and this value decreases to 86 % for microemulsions of W = 10. Therefore, unlike what happened in the aminolysis of the NPA by piperazine, the main part of the reaction takes place in the

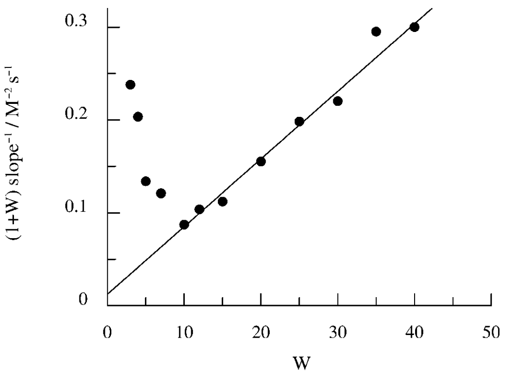


Figure 13. Influence of W on (1+W)/slope [Eq. (19)] for the aminolysis of NPA by sarcosine in AOT/isooctane/water microemulsions at 25°C; [SAR] = 5.00×10^{-2} M, referred to the aqueous phase of the system; the line represents the fit of Equation (19) to the experimental results. For the fit only the values obtained for W > 10 have been considered.

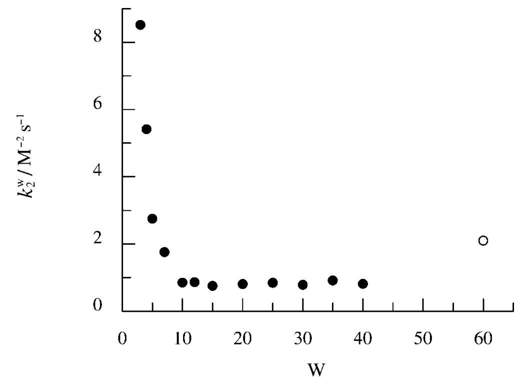
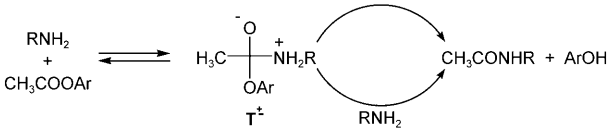


Figure 14. Influence of W on k_2^w for the aminolysis of NPA by sarcosine in AOT/isooctane/water microemulsions at 25°C (●); [SAR] = 5.00×10^{-2} M referred to the volume of the aqueous microdroplet. Bimolecular rate constant obtained in bulk water (○).

aqueous microdroplet. Likewise it is important to note that for values of W < 10 there is no observable negative deviation in the representation of Figure 13, as occurred for the aminolysis of the NPA by PIP (see Figure 10), but that a positive deviation occurred. This positive deviation is a consequence of the variations of the rate constants k_2^i and k_2^w with W. In the first place it is important to note that these rate constants are independent of W for values of W > 10. This behavior is a consequence of the fact that the greater changes undergone by the physical properties of the interface and the aqueous microdroplet are observed for small values of W, and that the aminolysis reaction of the NPA is not particularly sensitive to the polarity of the medium if it is compared with other processes such as the solvolysis reactions.

Previous studies on the aminolysis of the NPA by DEC and PIP show that k_2^i decreases together with the water content of the system as a consequence of an inadequate hydration in the interface. Therefore the positive deviation observed in Figure 13 can only be attributed to a variation of the rate constant k_2^w with W. Contrary to what occurs with k_2^i, our results show that the rate constant k_2^w must increase as the water content of the system decreases. On the basis of the results in Figure 13, and assuming a maximum value of $k_2^i = 2.59\times10^{-2}\,\text{M}^{-1}\text{s}^{-1}$, we can calculate the values of k_2^w for different values of W. In this approximation we consider a maximum value of k_2^i. From the results obtained in the aminolysis of the NPA by DEC and PIP it is to be expected that k_2^i will decrease together with W. If we use a maximum value of k_2^i we underestimate the value of k_2^w. However this discrepancy must be small given that the greater percentage of the reaction takes place in the aqueous microdroplet of the microemulsion. The results obtained are shown in Figure 14. It can be seen that the value of k_2^w increases as the water content of the system decreases. It is important to point out that this variation cannot be justified as a consequence of the reaction in the interface of the microemulsion, since the reaction constitutes just 5% of the rate observed for W = 4. The rate constants in the aqueous microdroplet of the microemulsion, k_2^w, decrease as the value of W increases, tending to reach a limit value for values of W > 10. The limit value reached for W > 10 is lower than the value of the rate constant of aminolysis in bulk water by sarcosine $k_2^{H_2O} = 1.73\,\text{M}^{-1}\text{s}^{-1}$.

Influence of W on the rate constants in the interface and in the aqueous microdroplet: The rate limiting step for aminolysis of substituted phenyl acetates in aqueous solution is first order in amine concentrations and leads to the formation of a tetrahedral intermediate ($T^{\pm}$). As the leaving ability decreases there is a change towards a rate limiting step which is second-order in amine concentration[27,34] and the breakdown of $T^{\pm}$ is the rate limiting step (Scheme 2). Since the rate limiting step for the aminolysis of the 4-nitrophenyl acetate is formation of $T^{\pm}$ the steps subsequent to its formation would be kinetically *silent* and thus no effect of crown ether would be expected; this prediction was experimentally confirmed for butylaminolysis of 4-nitrophenyl acetate in acetonitrile.[27]



Scheme 2.

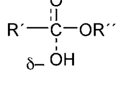
The existence of this mechanism for the aminolysis of 4-nitrophenyl acetate in water and acetonitrile suggests that this reaction mechanism must operate in the aqueous microdroplet and the interface of the microemulsion.

When studying the aminolysis of the NPA in AOT-based microemulsions we found two types of strongly differentiated behavior: the rate constant of the aminolysis in the aqueous microdroplet increases as W decreases, Figure 14, while the rate constant in the interface increases along with W, Figure 6. This change in behavior cannot be attributed to different mechanisms, since it has been shown that the aminolysis mechanism of the NPA in water and in the interface must take place through the formation of an addition intermediate, $T^{\pm}$. Therefore, this difference in behavior must be a consequence of the different properties of the water in the aqueous and interfacial microdroplet,[9,36] and of its different capacity for solvation of the reagents and transition states of the reaction.

Aminolysis of NPA by SAR in the aqueous microdroplet of AOT-based microemulsions: The results obtained on studying the aminolysis of NPA by SAR show that the aminolysis rate constant decreases until it reaches a limit value of $k_2^{w} = 0.85\,\text{M}^{-1}\text{s}^{-1}$ for $W > 10$. This value is lower than the value obtained in pure water, $k_2^{H_2O} = 1.73\,\text{M}^{-1}\text{s}^{-1}$. This deviation of the value of the rate constant obtained in the aqueous microdroplet of the AOT-based microemulsions with regard to bulk water can be explained as a consequence of the high saline content of the microdroplet of the microemulsion. Experiments carried out in bulk water show that the rate constants of aminolysis of NPA by SAR decrease approximately by 30 % when the ionic strength ($NaClO_4$) increases to 3 M.

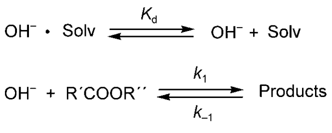
More important is the decrease in the rate constant of the reaction as W increases. The results obtained in our laboratory on studying the influence of the percentage of DMSO on the aminolysis rate of the NPA by SAR show that the rate constant of the reaction increases approximately eight times, when the percentage of DMSO increases, up to 80 %. In certain reactions S_N2 and S_NAr it has been shown that[37] the effect caused by the aprotic dipolar solvents is a combination of the solvation of the transition state and the desolvation of the nucleophile, especially in the case of the most basic nucleophiles. A correlation has been observed between k_2^{w} for the aminolysis of NPA by SAR and k_2^{w} for the basic hydrolysis[32] of the NPA by OH^- (see supplementary material). In both cases the rate constant in the aqueous microdroplet of AOT-based microemulsions increases as the water content of the system decreases.

From a perusal of the data obtained previously,[38] it is clear that the solvation of the non-electrolyte (ester molecule) is not of major importance in causing rate enhancement in aprotic solvents. Thus one can say that significant changes in the value of k_{DMSO}/k_{EtOH} are not due to changes in the solvation of the ester molecule. The structure of the transition state for the hydrolysis reactions of esters has a certain degree of negative charge on the carbonyl oxygen atom, which confers on this oxygen atom the capacity to be a good acceptor of the hydrogen bond, in such a way that it will be solvated better in protic solvents. The transition state anion in the case of an aromatic ester will be much more polarizable than that for an aliphatic ester. Further, the phenyl ring attached to the carbonyl group acts as an electron hole and thus lowers the electron density around the carbonyl group, thereby decreasing the localization of negative charge on the carbonyl oxygen atom with concurrent decrease in the hydrogen bond acceptor capacity of the transition state. This will result in an increase of the k_{DMSO}/k_{EtOH} value.[39]



$$R'-\overset{\overset{\delta-}{O}}{\underset{\underset{\delta-}{OH}}{C}}-OR''$$

Therefore, in the basic hydrolysis of the NPA it seems that the greatest effect on the reaction rate in aqueous DMSO must be the desolvation of the hydroxyl ion. The repercussion of the desolvation on the reaction or on reactivity–structure correlations is very wide. In fact, there exist numerous examples in which it has been found that the rate of certain nucleophile attacks decreases as the basicity of the nucleophile increases, leading to negative Brønsted exponents. This behavior has been found for some phosphoryl transfer reactions to amines,[40] and for reactions of highly reactive carbocations with amines[41] and for reactions of thiolate ions with Fischer carbene complexes.[42] Likewise Brønsted exponent values of around zero have been found for diphenylketene reactions with amines.[43] The studies carried out by Jencks[40] indicate that these anomalous Brønsted exponents are a consequence of the partial desolvation requirement of the nucleophile prior to the reaction. It is usually considered that the desolvation is a preequilibrium which occurs in a separate stage, in such a way as to adopt a two-step model for a nucleophilic attack like that which is shown in Scheme 3.



Scheme 3.

So that the observed effect showen in Figure 14 must be a consequence of the desolvation of the amine groups of the amino acid, with the consequent increase in reactivity, and the lower degree of solvation in the transition state, with the consequent decrease in the reaction rate. The balance of both factors will allow us to explain the behavior observed. From a quantitative point of view the desolvation of the nucleophile seems to be the greater contribution to the decrease in the activation energy of the reaction.

Aminolysis of NPA by DEC in the interface of AOT-based microemulsions: Figure 6 shows the variation of the rate constant of aminolysis of the NPA by *n*-decylamine in the interface of AOT-based microemulsions. This behavior can be explained as a consequence of the changes in the properties of the water as W varies. As mentioned previously the rate determining step of the reaction will be the formation of the intermediate $T^{\pm}$. In the transition state of the rate determining step there must be a certain degree of partial negative charge on the oxygen atom of the carbonyl group. The solvation of this partial negative charge will depend on the electrophilic character of the water molecules: as the electrophilicity decreases, so too does the reaction rate. This behavior has also been shown in the study of the solvolysis reaction of the diphenylmethyl chloride[25] in AOT-based microemulsions. The solvolysis rate constant in the interface decreases together with W due to the fact that the solvation of the salient Cl^- also decreases. A correlation have been observed between logk_2^{i} for the aminolysis of the NPA by decylamine and logk_{i} for the solvolysis of the diphenylmethyl chloride (see Supporting Information). The existence of this correlation shows that the decrease in the aminolysis rate constant of the NPA by decylamine as W decreases is a consequence of the small capacity of the interfacial water to solvate the development of the partial negative charge on the carbonylic oxygen atom in the transition state for the formation of $T^{\pm}$.

The results obtained are the first kinetic evidence of the existence of four types of water in the AOT-based microemulsions. In this study we have always used the same reaction: aminolysis of NPA but in such conditions that the reaction occurs in different microenvironments. As the water content of the system decreases the strength of the interaction $Na^+\cdots OH_2$ increases. This increase causes a decrease in the partial negative charge on the oxygen atom, and, consequently, the strength of the structure of the hydrogen bond of the water is reduced. This reduction is shown through a decrease in the solvation of the reagents (with the consequent increase in the reaction rate) and of the transition state (with the consequent reduction in the reaction rate). The obtained results show that the solvation of the reagents exerts a greater effect on the reaction rate that the decreases in the solvation of the partial negative charge on the carbonylic oxygen atom in the transition state. When the reaction takes place in the interface of the microemulsion the interaction $SO_3^-\cdots HOH$ causes an increase in the electronic density in the water molecules. This increase in the electronic density causes a decrease in the electrophilic character of the water molecules as W decreases. This decrease translates into a smaller capacity for solvation in the interface as the water content decreases and causes an increase in rate as a consequence of the solvation of the reagents and a decrease in rate by the solvation of the transition state of the reaction as W decreases. The experimental results show that the solvation of the transition state of the reaction is the predominant factor. The smaller repercussion of the solvation of the reagents is a consequence of the fact that the insufficient solvation of the interface causes the reagents to be partially desolvated even for very high W values.

Conclusion

The present study allows us to propose the following conclusions.

1) The aminolysis rate constant of NPA by *n*-decylamine in the interface of AOT-based microemulsions increases together with W. This behavior is parallel with that which is presented by the resonance signals of ^{1}H NMR of the protons of water and is similar to that which is observed for the solvolysis reaction of the diphenylmethyl chloride. This increase in the reactivity when W increases has been attributed to an increase in the solvation capacity of the partial negative charge which is generated in the transition state leading to the formation of the addition intermediate, $T^{\pm}$.
2) The aminolysis reaction of the NPA by SAR occurs predominantly in the aqueous microdroplet of the system and the rate constant increases when the water content of the system decreases. This increase is probably a consequence of the desolvation of the nucleophile as the water content of the system decreases and it is consistent with the behavior obtained on studying the reaction in mixtures of DMSO/H_2O.
3) The aminolysis of the NPA by piperazine presents an intermediate behavior: the reaction occurs simultaneously in the aqueous microdroplet and the interface, and the percentage of interfacial reaction increases as W decreases. For values of $W<10$ the reaction occurs mainly in the interface and the interfacial rate constant decreases along with W, in parallel with the behavior observed in the aminolysis of the NPA by DEC.
4) The diversity of observed behaviors is consistent with the existence of four types of water in the AOT-based microemulsions. The water present in the microdroplet is found mainly solvating the cations Na^+. This solvation, $Na^+\cdots OH_2$, causes a decrease in the negative charge on the oxygen atom and consequently weakens the hydrogen bond. This weaking in the structure of the hydrogen bonds causes a decrease in the solvation of the reagents. The interfacial water is involved fundamentally in the solvation of the head groups of the tensioactives $SO_3^-\cdots HOH$. This solvation causes an increase in the electronic density on the hydrogen atoms with the consequent decrease in their efficiency in the solvation of the partial positive charge that is developed in the transition state of the reaction.

Experimental Section

AOT (Aldrich) was dried in a vacuum desiccator for two days and then used without further purification. Microemulsions were prepared by mixing isooctane (Aldrich), water and 1.00 M AOT/isooctane solution in appropriate proportions. *p*-Nitrophenyl acetate, sarcosine, piperazine and *n*-decylamine (Aldrich) were of the highest available purity and were used as supplied.

The aminolysis reactions were followed by monitoring the UV/Vis absorbance of the products of the reaction at $\lambda = 400$ nm, using a HP8453 spectrophotometer fitted with thermostated cell holders. In all experiments the NPA concentration, typically $[\mathrm{NPA}] = (2\text{–}4)\times 10^{-5}$ M, was much smaller than that of the amine. The reaction between the NPA and SAR was studied using a concentration of amino acid of 5.0×10^{-2} M referred to the volume of the droplet. For these experiments the microemulsions were prepared using an aqueous solution of amino acid with a concentration of 5.00×10^{-2} M. An equal concentration of NaOH was added to this solution to guarantee that the carboxyl group would be deprotonated. The piperazine solutions were prepared in an aqueous medium, so that the concentration of piperazine referred to the aqueous microdroplet was 0.10 M. The solutions of DEC were prepared in isooctane and were added to the reaction mixture so that $[\mathrm{DEC}]=2.50\times10^{-2}$ M. In all the experiments the temperature remained constant at (25.0 ± 0.1) °C. The kinetic absorbance versus time data always fit 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 $\pm5\%$. 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. A compilation of the kinetic data is supplied as Supporting Information.

Acknowledgements

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[1] *Handbook of microemulsions science and technology* (Eds.: P. Kumar, K. L. Mittal), Marcel Dekker, New York, **1999**.

[2] R. Leung, M. H. Hou, C. Manohar, D. O. Shah, P. W. Chun, in *Macro- and Microemulsions* (Ed.: D. O. Shah), ACS, Washington, DC, **1985**.

[3] a) K. Holmberg, *Adv. Colloid Interface Sci.* **1994**, 51, 137–174; b) K. Holmberg, *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 187–196; c) M. Häger, F. Currie, K. Holmberg, *Top. Curr. Chem.* **2003**, *227*, 53–74.

[4] *Nanoparticles and Nanostructured Films* (Ed: J. H. Fendler), Wiley, Weinheim, **1998**.

[5] M. P. Pileni, *J. Phys. Chem.* **1993**, *97*, 6961–6973.

[6] *Reactivity in Reverse Micelles* (Ed.: M. P. Pileni), Elsevier, **1989**.

[7] G. Onori, A. Santucci, *J. Phys. Chem.* **1993**, *97*, 5430–5434.

[8] M. B. Temsamani, M. Maeck, I. El Hassani, H. D. Hurwitz, *J. Phys. Chem. B* **1998**, *102*, 3335–3340.

[9] T. K. Jain, M. Varshney, A. Maitra, *J. Phys. Chem.* **1989**, *93*, 7409–7416.

[10] D. S. Venables, K. Huang, C. A. Schmuttenmaer, *J. Phys. Chem. B* **2001**, *105*, 9132–9138.

[11] D. M. Mittleman, M. C. Nuss, V. L. Colvin, *Chem. Phys. Lett.* **1997**, *275*, 332–338.

[12] A. Maitra, *J. Phys. Chem.* **1984**, *88*, 5122–51 225.

[13] H. Hauser, G. Haering, A. Pande, P. L. Luisi, *J. Phys. Chem.* **1989**, *93*, 7869–7876.

[14] A. D'Aprano, A. Lizzio, V. T. Liveri, F. Aliotta, C. Vasi, P. Migliardo, *J. Phys. Chem.* **1988**, *92*, 4436–4439.

[15] D. M. Willard, N. E. Levinger, *J. Phys. Chem. B* **2000**, *104*, 11 075–11 080.

[16] R. E. Riter, J. R. Kimmel, E. P. Undiks, N. E. Levinger, *J. Phys. Chem. B* **1997**, *101*, 8292–8297.

[17] R. E. Riter, D. M. Willard, N. E. Levinger, *J. Phys. Chem. B* **1998**, *102*, 2705–2714.

[18] H. Shirota, K. Horie, *J. Phys. Chem. B* **1999**, *103*, 1437–1443.

[19] J. Faeder, B. M. Ladanyi, *J. Phys. Chem. B* **2000**, *104*, 1033–1046.

[20] L. Laaksonen, J. B. Rosenholm, *Chem. Phys. Lett.* **1993**, *216*, 429–434.

[21] D. Brown, J. H. R. Clarke, *J. Phys. Chem.* **1988**, *92*, 2881–2888.

[22] D. J. Tobias, M. L. Klein, *J. Phys. Chem.* **1996**, *100*, 6637–6648.

[23] T. Simonson, *Chem. Phys. Lett.* **1996**, *250*, 450–454.

[24] a) C. González-Blanco, L. J. Rodríguez, M. M. Velázquez, *Langmuir* **1997**, *13*, 1938–1945; b) G.-W. Zhou, G.-Z. Li, W.-J. Chen, *Langmuir* **2002**, *18*, 4566–4571.

[25] L. García-Río, J. R. Leis, E. Iglesias, *J. Phys. Chem.* **1995**, *99*, 12 318–12 326.

[26] a) L. García-Río, J. R. Leis, *Chem. Commun.* **2000**, 455–456; b) L. García-Río, J. R. Leis, J. A. Moreira, *J. Am. Chem. Soc.* **2000**, *122*, 10 325–10 334; c) L. García-Río, J. R. Leis, J. C. Mejuto, *Langmuir* **2003**, *19*, 3190–3197.

[27] A. B. Maude, A. Williams, *J. Chem. Soc. Perkin Trans. 2* **1997**, 179–183.

[28] Given the microheterogeneous character of the reaction medium it is necessary to differentiate between concentrations referred to the total volume of the system and concentrations referred to the volume of the phase. We will always use a nomenclature in which $[\mathrm{S}]_{\mathrm{w}}^{\mathrm{w}}$, $[\mathrm{S}]_{\mathrm{i}}^{\mathrm{i}}$ and $[\mathrm{S}]_{\mathrm{o}}^{\mathrm{o}}$ denote the concentrations of the substrate in the aqueous microdroplet referred to the volume of the aqueous microdroplet; the substrate concentration in the interface referred to the volume of the interface and substrate concentration in the continuous medium referred to the volume of the continuous medium. The concentrations written with just a subindex will always be referred to the total volume of the system: $[S]_{\mathrm{w}}$, $[S]_{\mathrm{i}}$ and $[S]_{\mathrm{o}}$ correspond to the substrate concentrations in the aqueous microdroplet, the interface and the continuous medium respectively, referred in all cases to the total volume of the system.

[29] L. García-Río, E. Iglesias, J. R. Leis, M. E. Peña, *J. Phys. Chem.* **1993**, *97*, 3437–3442.

[30] L. García-Río, J. R. Leis, J. C. Mejuto, *J. Phys. Chem.* **1996**, *100*, 10 981–10 988.

[31] There is a large body of studies showing the validity of the droplet model as a good description of the microheterogeneous structure of the microemulsions. The existence of this microstructure guarantees the compartmentalization of the reagents and hence the validity of the kinetic model. See for example the photon correlation spectroscopy studies showing the existence of a good correlation between the Stokes radii of AOT/Isooctane/Water ternary systems with W (M. Zulauf, H. F. Eicke, *J. Phys. Chem.* **1979**, *83*, 480–486). SAXS and SANS studies also shown the existence of a linear dependence of the water pool radius with W (M. P. Pileni, *J. Phys. Chem.* **1993**, *97*, 6961–6973, and references therein). Infrared spectroscopic studies of the water structure in the microemulsion show the existence of three types of water: trapped, bound and free water. These results also shown that the fraction of bound water is as much as the half of the water content for very small W values (M. B. Temsamani, M. Maeck, I. El Hassani, H. D. Hurwitz, *J. Phys. Chem. B* **1998**, *102*, 3335–3340, and references therein).

[32] L. García-Río, J. C. Mejuto, M. Pérez-Lorenzo, *New J. Chem.* **2004**, *28*, 988–995.

[33] There is evidence of the variation of rate constants with the W parameter of the microemulsion composition. In fact, studies on the solvolysis of microemulsions of AOT/Isooctane/water show that the rate constant of the solvolysis of the diphenylmethyl chloride in the interface of AOT-based microemulsions increases together with W as a consequence of the changes in the physical properties of the water (see ref. [25]). When solvolysis reactions are investigated in the interface of AOT-based microemulsions which occur by means of an associative mechanism it is possible to observe an increase in the rate constant as W decreases (see ref. [26b]).

[34] A. C. Satterthwait, W. P. Jencks, *J. Am. Chem. Soc.* **1974**, *96*, 7018–7031.

[35] A. Williams, *Adv. Phys. Org. Chem.* **1992**, *27*, 1–55.

[36] Q. Li, S. Weng, J. Wu, N. Zhou, *J. Phys. Chem. B* **1998**, *102*, 3168–3174.

[37] a) P. Haberfield, A. Nudelman, A. Bloom, R. Romm, H. Ginsberg, P. Steinber, *J. Chem. Commun.* **1968**, 194–195; b) P. Haberfield, L. Clayman, J. S. Cooper, *J. Am. Chem. Soc.* **1969**, *91*, 787–788; c) P. Haberfield, A. Nudelman, A. Bloom, R. Romm, H. Ginsberg, *J. Org. Chem.* **1971**, *36*, 1792–1795.

[38] A. J. Parker, *Chem. Rev.* **1969**, *69*, 1–32.

[39] M. Balakrishnan, G. Venkoba Rao, N. Venkatasubramanian, *J. Chem. Soc. Perkin Trans. 2* **1974**, 6–10.

[40] W. P. Jencks, M. T. Haber, D. Herschlag, K. L. Nazaretian, *J. Am. Chem. Soc.* **1986**, *108*, 479–483.

[41] a) J. P. Richard, *J. Chem. Soc. Chem. Commun.* **1987**, 1768–1769; b) R. A. McClelland, V. M. Kanagasabapathy, N. S. Banait, S. Steenken, *J. Am. Chem. Soc.* **1992**, *114*, 1816–1823.

[42] C. F. Bernasconi, K. W. Kittredge, F. X. Flores, *J. Am. Chem. Soc.* **1999**, *121*, 6630–6639.

[43] J. Andraos, A. Kresge, *J. Am. Chem. Soc.* **1992**, *114*, 5643–5646.

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