Modification of reactivity by changing microemulsion composition. Basic hydrolysis of nitrophenyl acetate in AOT/isooctane/water systems

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A study was carried out on the basic hydrolysis of p-nitrophenyl acetate (NPA) in AOT/isooctane/water microemulsions keeping constant the hydroxide ion concentration referred to the droplet water. The obtained results show that the pseudofirst order rate constant, k_{obs}, is approximately 100 times lower than the corresponding value in bulk water and increases together with the [AOT], keeping constant the molar ratio W, $W = [H_2O]/[AOT]$. On experiments varying W, keeping constant [AOT], it can be observed that k_{obs} decreases from $W = 2$ to $W = 10$ as W increases, reaching a minimum value for $W \cong 10$, and then increasing again. The observed behavior is a consequence of two factors: the variation of hydroxide ion concentration referred to the total volume of the system, and the association of the NPA to the interface of the microemulsion. The experimental results can be explained quantitatively considering that the NPA is distributed throughout the three pseudophases of the system and that the reaction takes place solely in the aqueous microdroplet. The second order rate constant in the aqueous microdroplet of the microemulsion, k_2^w, increase as W decreases, showing a parallelism with the behavior observed in aqueous DMSO. The values of k_2^w increase approximately 35 times from $W = 40$ to $W = 2$ due fundamentally to the partial desolvation of the hydroxide ions as the water content of the microemulsion decreases.

Introduction

Microemulsions are pseudohomogeneous mixtures of water-insoluble organic compounds, water and a surfactant. They are often good solvents for both inorganic salts and nonpolar organic molecules, and therefore are excellent media for reactions between compounds with widely differing solubility characteristics.[1,2] In anhydrous media, surfactants form small polydisperse aggregates.[3] Added water is solubilized in the polar cores of the micelles, which grow accordingly. In dilute systems, the structure of microemulsions is accounted for by the "droplet model",[4] which considers the disperse phase to be formed by monodisperse spherical droplets, each one surrounded by a layer of surfactant molecules.[5] Amongst the tensioactive agents most widely used for the formation of microemulsions we can cite the sodium salt of bis (2-ethyhexyl)-sulfosuccinate, (AOT), which has the peculiarity of not needing the addition of a co-surfactant in order for it to form microemulsions.

Microemulsions are more and more frequently used as microreactors, taking advantage of the reagent compartmentalization and of the particular properties of the encased water. The hydration of the tensioactives with the solubilized water in the microemulsions has been the subject of a large body of research,[6] given that an understanding of this process is very useful for understanding physicochemical processes and for finding applications in chemical and biological reactions.[7] Generally, three types of water are considered to exist:[8] *free water, bound water and trapped water*. However, the most recent studies broaden this range to include four types, considering the different effects of the polar head groups of the tensioactive and of the counterion. This interaction between the water molecules and the surfactant is so strong that it has been considered that the hydration of the tensioactives is the driving force of the solubilization process of water in the microemulsions.

In spite of these peculiarities, the influence of this type of aggregate on chemical reactivity has not undergone much research. Certain organic reactions are faster in water than in less polar solvents[9] and therefore they should benefit from the hydrophobic–hydrophilic equilibrium in microemulsions. However, the changes in reactivity of the encased water compared to that in network-organized bulk water, are far from being well known and are even less well controlled. Recent studies carried out in our laboratory show that the changes in the properties of the interfacial water can alter not just the reaction rate,[10] but also the mechanism[11] as the relationship W varies, $W = [water]/[surfactant]$. These results are a consequence of the modification of the electrophilic and nucleophilic character of the interfacial water. As W decreases the interfacial water molecules are fundamentally implicated in the solvation of the head group of the tensioactive. Consequently, a decrease in the electrophilic character of the water occurs, which in turns makes the solvation of anionic salient groups more difficult. An increase in the nucleophilic character also takes place. The equilibrium between these two factors is responsible for the associative mechanisms being favored[12] as the W value decreases.

Previous studies on solvolytic reactions show that changes in the properties of the interfacial water have repercussions on the chemical reactivity. However existing mechanistic studies do not reflect the changes in the properties of the water in the water pool. In fact, a number of researchers consider that for those reactions to take place in the water pool, the rate constant must be equal to that which exists in conventional aqueous media. This extrapolation is a consequence of a

simplified vision of the structure of the microemulsions, where the existence of only three types of water is considered: *bulk water*, *bound water* and *trapped water*. In this simplified version it is considered that the properties of the *bulk water* are equal to those of conventional water, insofar as the difference between the properties of the water of the microemulsions and the conventional water is due to the different proportions of *bound* and *trapped water*.

In order to clarify this, we have carried out a kinetic study on the basic hydrolysis of *p*-nitrophenyl acetate (NPA) (Scheme 1) in microemulsions of AOT/isooctane/water. The choice of this system is due to the fact that on account of electrostatic considerations the basic hydrolysis of the NPA can only occur in the water pool of the microemulsion. Likewise, the rate constant of this reaction in an aqueous medium increases along with the percentage of DMSO.[13] The obtained results will show that the reaction rate in microemulsions is sensitive to the water content, and increases as the W parameter decreases. In this sense it is possible to establish a correlation between the values of W and the percentage of DMSO in the reaction medium, so that the reaction rate in microemulsions of $W = 2$ will be equivalent to aqueous media with 75% (v/v) of DMSO.

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 (Aldrich) was of the highest available purity and was used as supplied.

The hydrolysis reactions were followed by monitoring the UV-Vis absorbance of the products of the reaction at $\lambda = 400$ nm, using a HP 8453 spectrophotometer fitted with thermostated cell holders. In all experiments the NPA concentration, typically [NPA] $= 5.00 \times 10^{-5}$ M, was much smaller than that of NaOH, and temperature was keep constant at 25 °C. For the kinetic experiments the microemulsions were prepared using an aqueous solution of NaOH, [OH$^-$] $= 5.00 \times 10^{-2}$ M. Thus, in all the experiments, unless stated to the contrary, the concentration of hydroxide ions referred to the aqueous phase is 5.00×10^{-2} M. The kinetic absorbance *vs.* 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 ±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.

The NPA distribution coefficient between water and isooctane has been determined mixing equal volumes of both solvents to which a constant amount of NPA was added. When this had been vigorously shaken the mixture was separated into phases at constant temperature (25 °C) and a spectrophotometric analysis of the NPA content in the aqueous and isooctane phase was carried out. A mean value of $K_o^w = 2.60 \times 10^{-2}$ was obtained, indicating that the solubility of the NPA in isooctane is much greater than in bulk water. Because salts may affect solubilities of organic compounds in water, we have determined the distribution coefficient between

water and isooctane, K_o^w, by using different salt (NaClO$_4$) concentrations in the water phase. The obtained results show that K_o^w is independent of the salt concentration: $K_o^w = 2.60 \times 10^{-2}$; 2.70×10^{-2}; 2.94×10^{-2}; 2.70×10^{-2}; 2.67×10^{-2} and 2.89×10^{-2} for [NaClO$_4$] $= 0$; 1.00; 2.00; 3.25; 5.00 and 6.00 M. The absence of dependence of the distribution coefficient on the salt concentration allows us to use K_o^w as a distribution coefficient between the oil and water pseudophases of the microemulsion irrespective of W values.

Results

A kinetic study was carried out in which the hydroxide ions concentration, as well as the microemulsion composition was varied. In all experiments the nitrophenyl acetate concentration, [NPA] $\cong 5.00 \times 10^{-5}$ M, was much lower than that of the hydroxide ions. Fundamentally two types of experiment were carried out, in which the concentration of the hydroxide ions was varied while keeping constant the microemulsion composition, and studies in which the microemulsion composition and the hydroxide ion concentration were varied simultaneously. In the latter case the OH$^-$ concentration was kept constant, referred to the aqueous volume of the system.

Fig. 1 shows the influence of the concentration of OH$^-$ on k_{obs} for the basic hydrolysis of the NPA in AOT-based microemulsions of $W = 2$, [AOT] $= 0.40$ M and [AOT] $= 0.70$ M, and $W = 50$ and [AOT] $= 0.40$ M. In all cases we observe a clear linear dependence between the pseudo-first-order rate constant and the [OH$^-$]$_w^w$ (eqn. (1)), where the [OH$^-$]$_w^w$ corresponds with the concentration of hydroxide ions in the aqueous phase, referred to the volume of the aqueous microdroplet of the microemulsion.

$$k_{\text{obs}} = (k_2^{\text{app}})_w^w [\text{OH}^-]_w^w \tag{1}$$

As can be observed in Fig. 1 the slope of the representation corresponds with the apparent second order rate constant, $(k_2^{\text{app}})_w^w$. This rate constant should not be confused with the true second order rate constants, since $(k_2^{\text{app}})_w^w$ depends on the composition of the microemulsion.

A second type of experiment was carried out by studying the influence of the composition of the microemulsion on the rate of hydrolysis of the NPA. To this end, experiments were performed in which the surfactant concentration was varied, [AOT] $= (0.10-0.60)$ M, while keeping constant the ratio W. Experiments were carried out for W values between 2 and 40. In all cases the hydroxide ion concentration was kept constant, referred to the aqueous medium of the microemulsion,
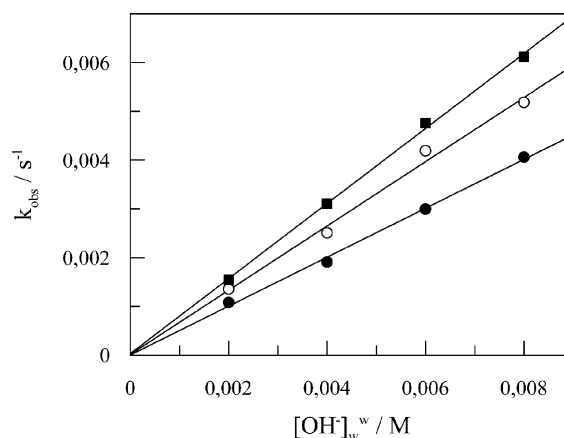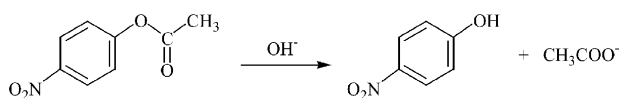

Fig. 1 Influence of the hydroxide ions concentration on k_{obs} for the basic hydrolysis of the NPA in AOT/isooctane/water microemulsions at 25 °C. (○) $W = 20$; [AOT] $= 0.40$ M; (●) $W = 20$; [AOT] $= 0.70$ M and (■) $W = 50$; [AOT] $= 0.40$ M. The concentrations of hydroxide ions are referred to the volume of the aqueous microphase.

Scheme 1

$[OH^-]_w^w = 5.00 \times 10^{-2}$ M. Fig. 2 shows the obtained results by studying the influence of the surfactant concentration on k_{obs} for values of $W = 10$; 20 and 40.

As can be observed k_{obs} increases together with the surfactant concentration. When surfactant concentration increases keeping constant the ratio W, the volume of the aqueous phase should increase too. Therefore, the OH^- concentration referred to the total volume of the microemulsion will increase. Moreover because the basic hydrolysis reaction should take place in the aqueous microdroplet (the only domain of the microemulsion which is accesible for the hydroxide ions), when the surfactant concentration increases so does the NPA incorporated into the interface. Consequently the NPA concentration in the aqueous medium will decrease. So the experimental results showed in Fig. 2 should be a result of the balance between the increase of OH^- concentration and decrease of NPA concentration in the aqueous microdroplet.

The reagent concentrations ($[NPA] = 5.00 \times 10^{-5}$ M and $[OH^-]_w^w = 5.00 \times 10^{-2}$ M) guarantees that $[OH^-]_w^w$ keeps constant during the reaction time and allow us to neglect the possibility of changes in the dynamical properties of the microemulsion due to the reaction products. Moreover the basic hydrolysis of AOT[14] is a well known process that can affect the kinetic behavior of basic hydrolysis process carried out in microemulsions, as we have shown for the basic hydrolysis of crystal violet.[14a] Recently we have studied the basic hydrolysis of AOT by using sodium nitroprusside as a chemical probe[14b] yielding a value for the second order rate constant of $k = 4.4 \times 10^{-4}$ M^{-1} s^{-1}. The most unfavorable conditions for AOT hydrolysis competition would be the higher AOT concentration microemulsion. By using $[AOT] = 0.60$ M we can obtain an AOT half life time of 43.6 min. At this AOT concentration the lowest NPA hydrolysis rate constant is 3.75×10^{-3} s^{-1}. This rate constant corresponds to a NPA half life time of 3.1 min. As can be seen the rate for the basic hydrolysis of AOT is at least 15 times lower that the NPA one.

Fig. 3 shows the experimental results obtained on studying the influence of W on the pseudo-first-order rate constant, k_{obs}, for the basic hydrolysis of the NPA. The experiments have been carried out while keeping the surfactant concentration constant, $[AOT] = 0.45$ M. As can be observed, k_{obs} decreases as W increases, reaching a minimum value for $W \cong 10$, and, subsequently, it increases once again when W increases. The increase in k_{obs} as W changes is due fundamentally to an increase in the volume of the aqueous microphase, with the consequent increase of hydroxide ions referred to the total volume of the microemulsion.
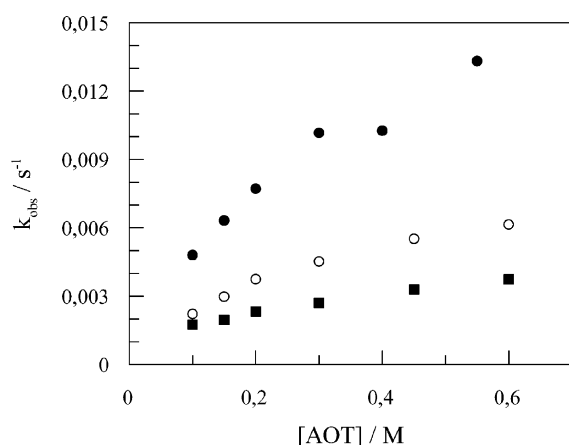

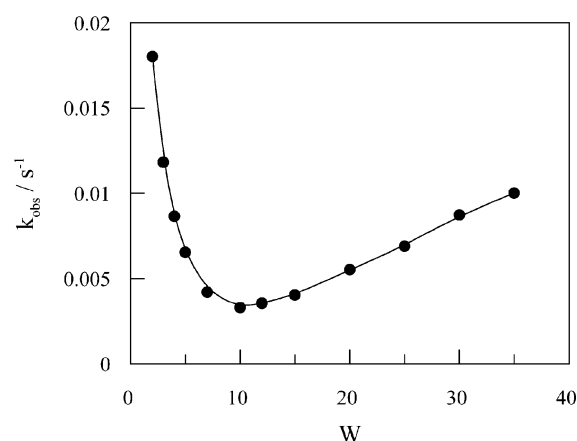**Fig. 3** Influence of W on k_{obs} for the basic hydrolysis of the NPA in AOT/isooctane/water microemulsions at 25 °C, $[AOT] = 0.45$ M and $[OH^-]_w^w = 5.00 \times 10^{-2}$ M referred to the aqueous medium.

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. Our research group has devised a kinetic model based on the formalism of the pseudophase which can be applied to carry out a quantitative interpretation of the influence of the composition of the microemulsion on the chemical reactivity.[15,16] In order to apply this formalism to the basic hydrolysis of the NPA we need to consider the microemulsion formed by three strongly differentiated pseudophases: an aqueous pseudophase (w), a continuous medium formed fundamentally by the isooctane (o) and an interface formed fundamentally by the surfactant (i). For electrostatic reasons, the hydroxide ions are to be found solely within the aqueous pseudophase, while the NPA is distributed throughout the three pseudophases of the system (Scheme 2). The only convergence point of the reactants will be, therefore, the aqueous pseudophase of the microemulsion.

1. Determination of the true rate constants

The distribution of the NPA through the different pseudophases is characterized by distribution constants from the aqueous medium to the interface, K_{wi}^{NPA}, and from the continuous medium to the interface, K_{oi}^{NPA}, given by eqn. (2):

$$K_{wi}^{NPA} = \frac{[NPA]_i}{[NPA]_w} W \quad K_{oi}^{NPA} = \frac{[NPA]_i}{[NPA]_o} Z \quad (2)$$

where the parameter Z is defined as the molar ratio $Z = [Isooctane]/[AOT]$, by analogy with parameter W.
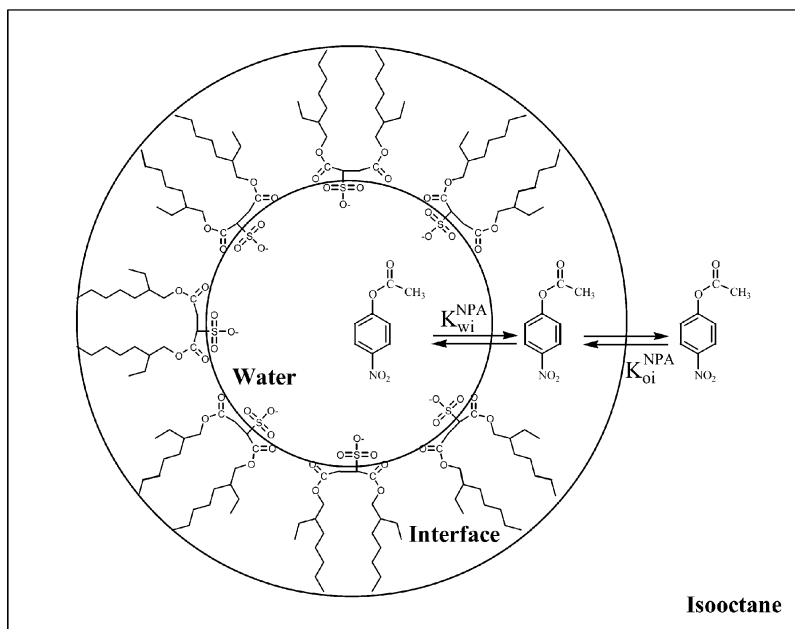
Considering that the total NPA concentration will be the sum of the concentrations in each of the three pseudophases of the microemulsion, we can evaluate the concentration of the NPA in the aqueous phase, $[NPA]_w$, thus:

$$[NPA]_w = \frac{K_{oi}^{NPA} W [NPA]_T}{K_{oi}^{NPA} K_{wi}^{NPA} + K_{wi}^{NPA} Z + K_{oi}^{NPA} W} \quad (3)$$

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

The reaction can only take place in the aqueous pseudophase, since this is the only zone of the microemulsion where the reactants can come into contact with each other.[18] We can obtain the following expression for the pseudo-first-order rate constant

$$k_{obs} = k' \frac{K_{oi}^{NPA} W}{K_{oi}^{NPA} K_{wi}^{NPA} + K_{wi}^{NPA} Z + K_{oi}^{NPA} W} \quad (4)$$

Fig. 2 Influence of surfactant concentration on k_{obs} for the basic hydrolysis of the NPA in AOT/isooctane/Water microemulsions at (●) $W = 40$; (○) $W = 20$ and (■) $W = 10$. $T = 25$ °C. $[OH^-]_w^w = 5.00 \times 10^{-2}$ M referred to the aqueous phase of the microemulsion.

Scheme 2

where k' is the pseudo-first-order rate constant referred to the aqueous medium. This rate constant can be expressed as a second order rate constant in the aqueous microdroplet, k_2^{w}, as

$$k' = k_2^{\mathrm{w}}[\mathrm{OH}^-]_{\mathrm{w}}^{\mathrm{w}} \qquad (5)$$

where $[\mathrm{OH}^-]_{\mathrm{w}}^{\mathrm{w}}$ refers to the concentration of hydroxide ions in the aqueous microdroplet referred to the volume of the aqueous pseudophase of the microemulsion. We can write the following expressions for k_{obs} and $(k_2^{\mathrm{app}})_{\mathrm{w}}^{\mathrm{w}} = k_{\mathrm{obs}}/[\mathrm{OH}^-]_{\mathrm{w}}^{\mathrm{w}}$:

$$k_{\mathrm{obs}} = k_2^{\mathrm{w}}[\mathrm{OH}^-]_{\mathrm{w}}^{\mathrm{w}}\frac{W K_{\mathrm{oi}}^{\mathrm{NPA}}}{K_{\mathrm{oi}}^{\mathrm{NPA}} K_{\mathrm{wi}}^{\mathrm{NPA}} + K_{\mathrm{wi}}^{\mathrm{NPA}} Z + K_{\mathrm{oi}}^{\mathrm{NPA}} W} \qquad (6)$$

$$\frac{W}{(k_2^{\mathrm{app}})_{\mathrm{w}}^{\mathrm{w}}} = \frac{K_{\mathrm{wi}}^{\mathrm{NPA}} + W}{k_2^{\mathrm{w}}} + \frac{K_{\mathrm{wi}}^{\mathrm{NPA}}}{k_2^{\mathrm{w}} K_{\mathrm{oi}}^{\mathrm{NPA}}} Z \qquad (7)$$

Fig. 4 shows the good fit of eqn. (7) for series of experiments carried out keeping constant the ratio W. Table 1 shows the obtained values for the intercepts and slopes according to W.

As we can observe from the data in Table 1, both the slope and the intercept increase along with W, tending to reach a limiting value for W values higher than 15. In order to analyze the dependence on W of the intercept and slope we should consider the distribution constants of the NPA to be independent

of the water content of the microemulsion. In this way, $K_{\mathrm{wi}}^{\mathrm{NPA}}$ and $K_{\mathrm{oi}}^{\mathrm{NPA}}$ should remain constant in spite of the changes in the properties of the interfacial water and the aqueous microdroplet.[17] The only term which can justify the variation of the intercept and slope of eqn. (7) with W is the rate constant for NPA hydrolysis in the aqueous microdroplet, k_2^{w}. If this rate constant increases as W decreases,[19] it would be possible to justify the increase in the intercept and slope as W increases.

It would be simpler to evaluate the dependency on W of the quotient between the intercepts and slopes of Fig. 4, eqn. (7). Given that the values of the distribution constants of NPA, K_{wi}^{NPA} and K_{oi}^{NPA}, are independent of W, we should obtain a linear dependency of the type:

$$\frac{\text{Intercept}}{\text{Slope}} = K_{\mathrm{oi}}^{\mathrm{NPA}} + \frac{K_{\mathrm{oi}}^{\mathrm{NPA}}}{K_{\mathrm{wi}}^{\mathrm{NPA}}} W \qquad (8)$$

However, the data in Table 1 show that the relationship *Intercept/Slope* remains practically constant and independent of W, with a mean value *Intercept/Slope* = 25.9. To explain the absence of this linear dependency we have recourse to the previously determined distribution coefficient of the NPA between bulk water and isooctane, $K_{\mathrm{o}}^{\mathrm{w}}$. This coefficient can be written as follows:

$$K_{\mathrm{o}}^{\mathrm{w}} = \frac{X_{\mathrm{NPA}}^{\mathrm{w}}}{X_{\mathrm{NPA}}^{\mathrm{o}}} \cong \frac{[\mathrm{NPA}]_{\mathrm{w}}^{\mathrm{w}}}{[\mathrm{NPA}]_{\mathrm{o}}^{\mathrm{o}}} \cong \frac{n_{\mathrm{NPA}}^{\mathrm{w}}/n_{\mathrm{H_2O}}}{n_{\mathrm{NPA}}^{\mathrm{o}}/n_{\mathrm{oil}}} \cong \frac{[\mathrm{NPA}]_{\mathrm{w}}}{[\mathrm{NPA}]_{\mathrm{w}}}\frac{Z}{W} \qquad (9)$$
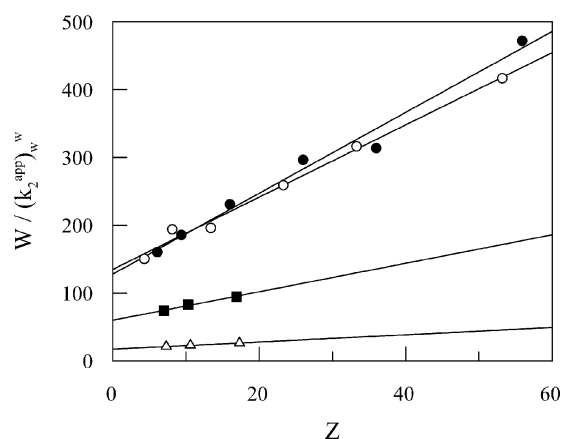
Fig. 4 Plot of the experimental data in the form $W/(k_2^{\mathrm{app}})_{\mathrm{w}}^{\mathrm{w}}$ *vs.* Z in accordance with eqn. (7). (○) $W = 40$; (●) $W = 15$; (■) $W = 7$ and (△) $W = 4$.

Table 1 Values of the intercepts and the slopes of the representations of Fig. 4 in accordance with eqn. (7)

W	Intercept	Slope	Intercept/Slope
3	8.98 ± 0.02	0.345 ± 0.002	26.03
4	17.3 ± 0.2	0.54 ± 0.02	32.04
5	28.9 ± 0.8	0.92 ± 0.06	31.41
7	60 ± 3	2.1 ± 0.2	28.57
10	112 ± 5	3.9 ± 0.2	28.72
12	117 ± 6	5.3 ± 0.3	22.08
15	128 ± 12	6.0 ± 0.4	21.33
20	129 ± 4	5.7 ± 0.1	22.63
25	130 ± 3	5.7 ± 0.1	22.81
30	132 ± 2	5.49 ± 0.06	24.04
35	135 ± 2	5.15 ± 0.08	26.21
40	135 ± 7	5.3 ± 0.3	25.47

where $X_{\text{NPA}}^{\text{w}}$ and $X_{\text{NPA}}^{\text{o}}$ represent the molar fractions of NPA in the aqueous and isooctane phases respectively: $n_{\text{NPA}}^{\text{w}}$, $n_{\text{NPA}}^{\text{o}}$ are the number of NPA moles in the aqueous and isooctane phases and $n_{\text{H}_2\text{O}}$ and n_{oil} are the number of water and isooctane moles in the respective phases. The concentrations $[\text{NPA}]_{\text{w}}^{\text{w}}$ and $[\text{NPA}]_{\text{o}}^{\text{o}}$ refer to the volume of the phase, while $[\text{NPA}]_{\text{w}}$ and $[\text{NPA}]_{\text{o}}$ refer to the total volume of the system. On the basis of eqns. (2) and (9) we can write:

$$K_{\text{o}}^{\text{w}} = K_{\text{oi}}^{\text{NPA}}/K_{\text{wi}}^{\text{NPA}} \tag{10}$$

If we combine eqns. (8) and (10) we obtain

$$\frac{\text{Intercept}}{\text{Slope}} = K_{\text{o}}^{\text{w}}\left(K_{\text{wi}}^{\text{NPA}} + W\right) \tag{11}$$

which can be simplified if $K_{wi}^{\text{NPA}} \gg W$, resulting in $\text{Intercept}/\text{Slope} = K_{\text{o}}^{\text{w}}K_{\text{wi}}^{\text{NPA}}$. This relationship justifies the fact that the quotient $\text{Intercept}/\text{Slope}$ remains constant and independent of W. From the mean value of the relationship $\text{Intercept}/\text{Slope} = 25.9$ and the value of $K_{\text{o}}^{\text{w}} = 2.60 \times 10^{-2}$ we can obtain the values of $K_{\text{oi}}^{\text{NPA}} = 25.9$ and $K_{\text{wi}}^{\text{NPA}} = 996.$[20]

When the values of $K_{\text{oi}}^{\text{NPA}}$ and $K_{\text{wi}}^{\text{NPA}}$ are known we can obtain the values of k_2^{w} applying eqn. (7). The obtained results are shown in Fig. 5. The second order rate constant in the water droplet increases from a value of $k_2^{\text{w}} \cong 7.5 \text{ M}^{-1}\text{s}^{-1}$ for values of $W > 10$ to a value of $k_2^{\text{w}} = 257 \text{ M}^{-1}\text{s}^{-1}$ for $W = 2$. This behavior should be attributed to the changes in the water properties of the microemulsion as W varies.[21]

2. Second order rate constant dependence on W

Fig. 5 shows that the rate constant in the aqueous microdroplet increases approximately 35 times as W decreases from $W = 40$ to $W = 2$, remaining constant for values of $W > 12$. The obtained value for high water contents is slightly lower than that previously obtained in bulk water in our laboratory, $k_2^{\text{H}_2\text{O}} = 11.3 \text{ M}^{-1}\text{s}^{-1}$. This difference between $k_2^{\text{w}} \cong 7.5 \text{ M}^{-1}\text{s}^{-1}$ and $k_2^{\text{H}_2\text{O}} = 11.3 \text{ M}^{-1}\text{s}^{-1}$ can be a consequence of the effect exerted by the ionic strength on the reaction rate (see Table 2). More important is the decrease in the rate constant of the reaction as W increases. It is well known that ester saponification rates are subject to large rate accelerations on going from protic to dipolar aprotic solvents.[22] Generally two explanations have been considered for this phenomenon: the first is that the effect is a consequence of the desolvation[23] of the hydroxide ion in the dipolar aprotic solvent. An alternative theory attributes the effect to the greater capacity of the dipolar aprotic solvent to solvate the transition state.[24] The results obtained in our laboratory from studying the influence of the percentage of DMSO on the hydrolysis rate of NPA confirm
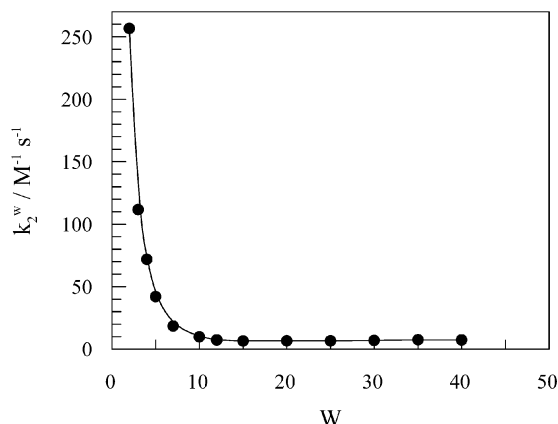

Fig. 5 Influence of W on k_2^{w} for the basic hydrolysis of the NPA in AOT/isooctane/water microemulsions at $25\,^\circ\text{C}$. $[\text{OH}^-]_{\text{w}}^{\text{w}} = 5.00 \times 10^{-2}$ M referred to the aqueous medium.

Table 2 Influence of the ionic strength (NaClO$_4$) on the observed rate constant for the hydrolysis of the NPA at $25\,^\circ\text{C}$. $[\text{NaOH}] = 5.00 \times 10^{-2}$ M

$[\text{NaClO}_4]/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$
0.05	0.554
0.50	0.422
1.00	0.344
1.50	0.285
2.25	0.234
3.00	0.199
4.00	0.169

the increase of the reaction rate as the percentage of organic co-solvent increases. In certain reactions, S$_N$2 and S$_N$Ar, it has been shown[25] that the effect caused by the dipolar aprotic solvents is a combination of the increase in the solvation of the transition state and the desolvation of the nucleophile, especially in the case of the most basic nucleophiles.

From a perusal of the previously obtained data,[26] 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 $k_{\text{DMSO}}/k_{\text{EtOH}}$ are not due to changes in the solvation of the ester molecule. The structure of the transition state for the ester hydrolysis reactions has a certain degree of negative charge on the carbonyloxygen atom (Scheme 3), which confers on this oxygen atom a good hydrogen bond acceptor capacity, in such a way that it will be solvated more efficiently 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 sink 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 $k_{\text{DMSO}}/k_{\text{EtOH}}$ value.[27]

Therefore, it seems that the greatest effect on the rate of the reaction in aqueous DMSO must be the desolvation of the hydroxide ion. The repercussion of the desolvation on the reaction rate or on reactivity–structure correlations is far-reaching. In fact, there exist numerous examples that show that the rate of certain nucleophile attacks decreases as the basicity of the nucleophile increases, entailing negative Brønsted exponents. This behavior has been found for some phosphoryl transfer reactions to amines,[28] for reactions of highly reactive carbocations with amines[29] and for reactions of thiolate ions with Fischer carbene complexes.[30] Likewise values of the Brønsted exponent near to zero have been found for reactions of diphenylketene with amines.[31] Studies carried out by Jencks[28] indicate that these anomalous Brønsted exponents are a consequence of the requirement of partial desolvation of the nucleophile prior to the reaction. Normally it is considered that the desolvation is a pre-equilibrium which occurs at a separate stage, in such a way that for a nucleophile attack a two-step model can be adopted, like that shown in Scheme 4.

Fig. 5 shows that as the water content in the microemulsion decreases, there occurs a change in its properties which is able to alter chemical reactivity. The observed effect will be a
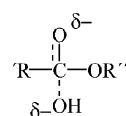
Scheme 3

consequence of the desolvation of the hydroxide ion, which entails an increase in reactivity, and the lower degree of solvation of the transition state, with a consequent decrease in the reaction rate. The balance of both factors will allow us to explain the experimental results. From a quantitative point of view the desolvation of the hydroxide ion seems to be the greatest contribution to the decrease in activation energy of the reaction.

The available studies in the bibliography[8] show that the properties of the water are modified as the water content in the microemulsion varies. For example, the frequency of the vibration of the bond O–H of the water changes from 3493 cm^{-1} to 3416 cm^{-1} when W increases from $W = 1$ to $W = 20$, reaching a value near to that obtained in pure bulk water for high values of W in microemulsions formed by NaOT/heptane/water. When the ^{1}H-NMR technique is used to investigate the properties of the water it is found that he chemical shift of the protons of the water increases from $\delta = 4.030$ ppm for $W = 4$ to $\delta = 4.430$ ppm for $W = 50$ in microemulsions of NaOT/isooctane/water.

The results obtained for the basic hydrolysis of the NPA are consistent with the existence of four types of water: *trapped water, bound water* (bound to the counterion, or bound to the headgroup of the surfactant), and *normal water*. These four types of water should coexist and interchange rapidly. The *trapped water* is found dispersed amongst the hydrocarbon chains of the surfactant molecules, existing as monomers and dimers, and does not hydrogen bond with its surroundings. The *normal water* is found in the center of the aqueous microdroplet and has strong hydrogen bond interactions. Besides these two types of water, there exist other *bound water* molecules in the vicinity of the ionic tensioactives. The local interactions of the water molecules with the counterions and the headgroups of the tensioactive (Scheme 5) cause opposite effects on the structure of the water. The hydration of the anionic head groups of the tensioactives increases the electronic density on the hydrogen atoms in the water molecules, with the consequent rupture of the hydrogen bonds of the *normal water*. The intensity of the O–H bonds increases and this factor means that the chemical displacement of the water protons bonded to the headgroups is found in higher fields than the normal water, and the vibration frequency of the O–H bond is found at 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 around the protons and consequently a decrease in the strength of the O–H bond of the water. This effect causes a displacement to lower fields of the resonance signals of ^{1}H-NMR of the protons of the water and the frequency of the vibration of the O–H bond is displaced to lower frequencies. This weakening of the strength of the hydrogen bond will contribute to the increase in thedesolvation of the hydroxide ion as the water content of the microemulsion decreases and consequently the reaction rate increases. Moreover changes in polarity, pH, viscosity and altered interfacial rigidity may concertedly act to modify the chemical reactivity in w/o microemulsions when W decreases.

3. Influence of W on the distribution constants of the NPA

Previous results show that the second order rate constant of the basic hydrolysis of the NPA decreases about 35 times as
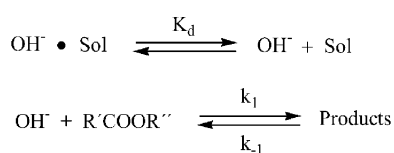
Scheme 4
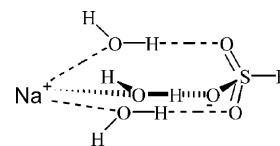
Scheme 5

the water content of the microemulsion increases, as a consequence of the variation of the physical properties of the water. However, this change in the physical properties is not reflected in the distribution constants, K_{oi}^{NPA} and K_{wi}^{NPA}, since these remain independent of W. The reason for this different sensibility must be found in the enthalpies of solvent transfer of the hydroxide ion, of the ester and of the transition state.

For the purpose of comparison, Haberfield *et al.*[22] have studied the basic hydrolysis of the ethyl acetate in 60% aqueous DMSO and 60% aqueous ethanol. The activation enthalpies for the alkaline hydrolysis are $\Delta H^{\neq} = 10.9$ kcal mol^{-1} and $\Delta H^{\neq} = 14.9$ kcal mol^{-1} for aqueous DMSO and aqueous ethanol respectively. It can be noted that a factor of $\delta\Delta H^{\neq} = 4.0$ kcal mol^{-1} favors the aqueous DMSO. This factor should be compared to the desolvation of the OH$^-$ by the DMSO, finding that the enthalpy of solvent transfer, $\delta\Delta H_{DMSO\rightarrow Ethanol}^{OH^-} = -14.24$ kcal mol^{-1}. It thus appears that if the desolvation of the base were the only factor causing a solvent effect on rate and on $\Delta H^{\neq}$ in this reaction, then a far larger effect would be expected than is actually observed. Haberfield's results show that the enthalpy of solvent transfer from 60% aqueous DMSO to 60% aqueous ethanol for ethyl acetate is $\delta\Delta H_{DMSO\rightarrow Ethanol}^{Ethylacetate} = 0.23$ kcal mol^{-1}. As might be expected, the enthalpies of transfer of the esters do not contribute significantly to the differences in the enthalpies of the reactants in these solvents. This smaller degree of sensitivity of the enthalpy of transfer of the ester in comparison with OH$^-$ or the transition state is the reason why the distribution constants K_{oi}^{NPA} and K_{wi}^{NPA} are not modified when the reactivity is altered.

4. Influence of dynamical phenomena on the basic hydrolysis of NPA

Dynamical measurements have been used to characterize the intramicellar water in w/o microemulsions. These studies all find that the water inside the micelles moves differently from bulk water. Using viscosity sensitive probes, Hasegawa *et al.*[32] have measured the microviscosity inside reverse micelles of varying size. Their results indicate that the water inside micelles with $W < 10$ has a higher viscosity than that of the bulk, a fact that they ascribe to water bound to the AOT polar headgroups. For microemulsions larger than $W = 10$, the viscosity decreases slowly as the size of the microemulsions increases. Solvent relaxation with fluorescence probes[33] reveals two different solvation rates inside the microemulsions that authors attribute to water bound to the polar headgroups of AOT and bulk-like water. The results from these and other studies[34] indicate that water in AOT microemulsions moves more slowly than bulk water. While ordinary water molecules relax in the subpicosecond time scale, inside microemulsions the solvation dynamics becomes several thousand times slower and occurs in the nanosecond time scale.[34a,35] Water motion in the low water content microemulsions was essentially frozen while in higher ones additional bulk-like relaxation components developed. However the time scale for water relaxation remains below that for the basic hydrolysis of NPA. Due to this, during the reaction time we observe an average of the dynamical properties of water. The observation of an average value of the physical properties is also consistent with the ^{1}H-NMR observed behavior. There is a large body of evidence showing the existence of

several water states inside AOT-based microemulsions. However the rate of exchange between these water states is too fast for the NMR time scale so that only one average signal is observed. This signal is W-dependent because of the different percentages of these water states.

The internal dynamics of microemulsions is a well-known process that is related to percolation phenomena. Several research groups have studied this process in the presence and absence of additive.[36] This process occur as the result of inter-droplet channels opening in droplet clusters that allows transport of materials between them as has been showed by Moulik and coworkers.[37] Lang, Zana and coworkers have related electrical percolation to the rate constant governing the exchange of materials between droplets.[38] For AOT/isooctane/water microemulsions the rate of exchange of materials between droplets has been obtained as $\cong 10^9$ $M^{-1}s^{-1}$. It means that this phenomenon will be relevant only to fast reactions, whose rate may totally or partially depend on material exchange rates. Our kinetic results for nitrophenyl acetate hydrolysis are far away from a diffusion controlled reaction (by 10^{12} times) so that changes in the internal dynamics of the microemulsion are not relevant in our case.

The lack of influence of electrical percolation phenomena upon chemical controlled reactions has been probed by our research group by studying the nitroso group transfer from N-methyl-N-nitroso-p-toluenesulfonamide to several secondary amines at $25°$ and $35°C$. Under the experimental conditions we have used percolated and non-percolated microemulsions and the kinetic results show consistent kinetic parameters.[15] We have also studied the influence of electrical percolation on the kinetic parameters in microemulsions where percolation is promoted by additives. We compare the solvolysis of 4-nitrophenyl chloroformate in AOT-based microemulsions in the absence and the presence of 1,3-dimethylurea ([dimethylurea] = 0–0.50 M). Under these experimental conditions the percolation temperature changes by more than $20°C$ and no influence is observed on the kinetic parameters.[10] Finally, the nitroso group transfer reactions were also studied in water/AOT/SDS/isooctane quaternary microemulsions. In this system a change of $44°C$ on the percolation temperature had no influence on the kinetic parameters.[39] The very large difference in time scale for internal dynamics of the microemulsion and chemical controlled reactions is responsible for the absence of percolation influence on reaction rates.

Conclusions

The results obtained on studying the basic hydrolysis of the NPA in microemulsions of AOT/isooctane/water can be summarized as follows:

1. When studying the basic hydrolysis of the NPA in AOT-based microemulsions it is found that the rate constant observed is approximately 100 times lower than in bulk water and depends on the composition of the microemulsion. To interpret these results the formalism of the pseudophase has been applied, considering the distribution of the NPA throughout the three pseudophases of the microemulsion and reaction in the aqueous microdroplet. The model proposed has allowed us to obtain the distribution constants of the NPA throughout the three pseudophases of the microemulsion and the second order rate constant in the aqueous microdroplet, k_2^w.

2. The second order rate constant in the aqueous microdroplet increases as the water content of the system decreases. This behavior is due to the alteration of the physical properties of the water of the microemulsion. As W decreases the structure of the hydrogen bond is broken, and consequently the solvation capacity of the transition state decreases. However, the effect which has the greatest contribution to the increase of k_2^w is the partial desolvation of the hydroxide ion as W decreases.

This behavior means that the reactivity in the aqueous micro-droplet of a microemulsion of $W = 2$ is approximately equal to that found in 75% aqueous DMSO.

3. The comparison of the enthalpy of solvent transfer from 60% aqueous DMSO to 60% aqueous ethanol for ethyl acetate, OH^- and transition state shows that the contribution of the enthalpy of solvent transfer for the ester to the activation enthalpy of the reaction is negligible. The value of $\delta\Delta H_{DMSO \to Ethanol}^{Ethylacetate} = 0.23$ kcal mol^{-1} in comparison with $\delta\Delta H_{DMSO \to Ethanol}^{OH^-} = -14.24$ kcal mol^{-1} allows us to explain the variation of the rate of reaction as W decreases while the distribution constants of the NPA do not alter.

Acknowledgements

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17 As will be shown, the experimental results obtained will be consistent with the fact that K_{wi}^{NPA} and K_{oi}^{NPA} do not vary along with the composition of the microemulsion. This behavior is in accordance with the fact that the enthalpy of solvent transfer between aqueous DMSO and aqueous ethanol is very small by comparison with the enthalpy of solvent transfer for the transition state or the enthalpy of solvent transfer for the hydroxide ions.

18 There is a large body of studies showing the validity of the droplet model as a good description of the microheterogeneous structure of 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 and H. F. Eicke, *J. Phys. Chem.*, 1979, **83**, 480). SAXS and SANS studies have also shown the existence of

a linear dependence of the water pool radius with W (M. P. Pileni, *J. Phys. Chem.*, 1993, **97**, 6961 and references therein). Infra-red 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 show that the fraction of bound water is as much as half of the water content for very small W-values (M. B. Temsamani, I. El Hassani and H. D. Hurwith, *J. Phys. Chem. B*, 1998, **102**, 3335 and references therein);

19 There is already evidence of the variation of rate constants with the W parameter of microemulsion composition. In fact, studies on solvolysis in AOT/isooctane/water microemulsions show that the rate constant at the interface of the microemulsion increases as W decreases as a consequence of the changes in the physical properties of the water, see ref. 10.

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