

Michael addition and ester aminolysis in w/o AOT-based microemulsions†

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A kinetic study was carried out on the aminolysis of 4-nitrophenylacetate (NPA) by *N*-methylbenzylamine (NMB) and the Michael addition of piperazine to *N*-ethylmaleimide (NEM) in AOT–isooctane–water microemulsions. The experimental results show that the rate constant observed for the aminolysis of NPA increases together with the concentration of the surfactant and the water content of the system. Conversely, the values of k_{obs} obtained for the Michael addition to NEM decrease as the surfactant concentration increases. This difference in behavior must be a consequence of the different distribution of the reagents throughout the different microenvironments of the microemulsion. The application of the formalism of the pseudophase shows that the aminolysis of NPA takes place solely in the interface of the microemulsion, and the rate constant in this pseudophase increases along with the water content of the system, due to a greater hydration of the interface. The different distribution of the reagents in the Michael addition of piperazine to NEM makes it possible for the reaction to take place simultaneously in the interface and the aqueous microdroplet, increasing the percentage of the reaction on the interface while the water content of the system decreases. Thus, the difference in rate observed for the Michael addition between the interface and the aqueous microdroplet is twelve-fold, due to the smaller polarity of the interface with regard to the aqueous medium.

Introduction

Microemulsions are thermodynamically stable dispersions of either water-in-oil (w/o) or oil-in-water (o/w), their stability resulting from the presence of a suitable surfactant. The solutes can be located in three different compartments: (i) the internal aqueous core or water pool, (ii) the micellar interface formed by a monolayer of surfactant molecules with their polar head groups oriented toward the water pool, and (iii) the external organic pseudophase.¹ The use of microemulsions as a reaction medium has gained great importance in recent years. They have been used to synthesize nanomaterials in their interior, and in some cases a control of the size of the nanoparticles with the composition of the microemulsion has been achieved.² On the other hand, due to the structure presented by the microemulsions, compounds of a very different polarity will be able to come into contact with each other in the interior. Likewise, it has been observed that the use of microemulsions as a reaction medium can induce regiospecificity in some organic reactions^{3,4} and constitutes an alternative to phase transfer catalysts.⁵

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 pseudophases. Our research group has successfully applied the model of the pseudophases to a large number of reactions.⁶ Turco Liveri *et al.*⁷ have reached equivalent expressions using the fractions in volume of each of the pseudophases of the microemulsion. The model of the pseudophase has been successfully applied to solvolysis reactions,⁸ which show the variation in the properties of the water present in the interior of the microemulsions. Likewise it has been applied by other authors to explain decarboxylation reactions,⁹ reactions of aromatic nucleophilic substitution¹⁰ and, in a modified version, electronic transfer reactions.¹¹

In the present study we have successfully applied the model of the pseudophase to the aminolysis reactions of *p*-nitrophenylacetate (NPA) by *N*-methylbenzylamine (NMB) and to the Michael addition of piperazine (PIP) to *N*-ethylmaleimide. In both cases due to the solubility of the reagents in the different pseudophases of the microemulsion NPA and NEM are distributed amongst the three pseudophases of the microemulsion. The amines present strongly differentiated solubility: NMB is practically insoluble in water and is distributed between the continuous medium and the interface of the microemulsion, whereas PIP is insoluble in isooctane and is distributed between the aqueous microdroplet and the interface.

Experimental

AOT (Aldrich) was kept in a vacuum desiccator for two days, with no further purification. The microemulsions were

† Electronic supplementary information (ESI) available: Tables S1–S4 and Fig. S1. See DOI: 10.1039/b507190a

prepared by mixing isooctane (Aldrich), water and a solution of AOT 1.00 M in isooctane (Aldrich), in appropriate proportions. *p*-Nitrophenylacetate (Aldrich), *N*-methylbenzylamine (Aldrich), piperazine (Aldrich) and *N*-ethylmaleimide (Aldrich) used were of the maximum purity available and did not undergo further purification.

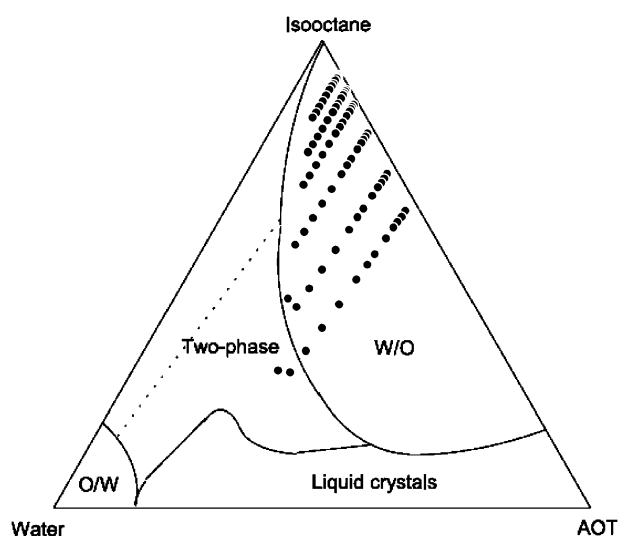
The reaction between NPA and *N*-methylbenzylamine was studied following the change in absorbance due to the appearance of the reaction products at $\lambda = 400$ nm, using a spectrophotometer Hewlett-Packard 8453. The reaction between piperazine and *N*-ethylmaleimide was followed at 298 nm using a spectrophotometer Varian Cary 50. In all the experiments the ester concentration, $[NPA] = 5 \times 10^{-5}$ M, is much smaller than amine, $[NMB] = 0.1$ M. For the reaction between PIP and NEM the following concentrations were used: $[PIP] = 6.03 \times 10^{-3}$ M and $[NEM] = 4.21 \times 10^{-4}$ M. In all the experiments the temperature was kept constant at $(25.0 \pm 0.1)^\circ\text{C}$. The kinetic absorbance-time data were always adjusted in accordance with the first order integrated equation ($r > 0.999$), giving the values of the first order pseudo rate constants, k_{obs} , which could be reproduced within a margin of 5%.

With the aim of determining the distribution constant of NEM between the aqueous pseudophase and the oil, K_o^w , a solution of NEM in water is prepared ($[NEM]_w = 5.59 \times 10^{-3}$ M) and another solution in isooctane ($[NEM]_o = 5.59 \times 10^{-3}$ M). The two solutions are mixed and shaken for at least 20 minutes. After the separation of the phases at 25°C the NEM present in each of the phases is determined. The distribution constant between the aqueous phase and the organic phase is defined as $K_o^w = [NEM]_w/[NEM]_o$, whence $K_o^w = 0.12$.

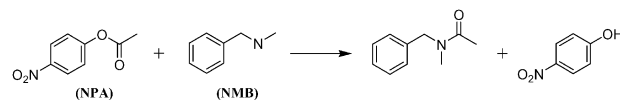
Results

A study was carried out on the influence of the composition of the microemulsion on the rate constant for both reactions. Scheme 1 shows the composition of the w/o microemulsions which were used for this study. The compositions were selected with the aim of covering a wide interval: the content of AOT varies between (12–65)% (w/w); that of water between (0.5–44)% (w/w) and that of isooctane between (3–87)% (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, saline content, etc.

In all cases it was found that the observed rate constant, k_{obs} , presents a linear dependency on the nucleophilic concentration when the reaction takes place in the microemulsion. This



Scheme 1



Scheme 2

behavior is consistent with that found in water and in other polar solvents¹² for ester aminolysis.

1. Aminolysis of NPA by NMB

A study has been carried out on the influence of the microemulsion composition on k_{obs} in the aminolysis of NPA by *N*-methylbenzylamine (Scheme 2), keeping constant the total amine concentration with regard to the total volume of the system, $[NMB] = 0.1$ M, and varying the composition of the microemulsion. For W values studied k_{obs} shows a linear dependence on amine concentration (see supplementary material†)

Fig. 1 shows us by way of example how k_{obs} varies with the composition of the microemulsion for four values of W . These results show that k_{obs} increases together with the concentration of AOT, tending to reach a limit value. Likewise k_{obs} can be observed to increase together with the water content of the microemulsion.

This behavior can be explained from a qualitative point of view: on increasing the concentration of the surfactant and the water content of the microemulsion, the incorporation of the reagents into the interface of the microemulsion is favored. In turn the local concentration of both reagents increases.

2. Aminolysis of NEM by PIP

To investigate the influence of the composition of the microemulsion on the aminolysis of NEM by piperazine (Scheme 3), experiments were carried out in which the composition of the microemulsion was varied, while keeping the concentration of NEM constant, $[NEM] = 4.21 \times 10^{-4}$ M, and also that of PIP, $[PIP] = 6.03 \times 10^{-3}$ M, with regard to the total volume of the system.

Fig. 2 shows, by way of example, the results obtained for $W = 5$, 20 and 35. As we can observe, k_{obs} decreases as the concentration of the surfactant increases.

This behavior is contrary to that which is observed in the aminolysis of NPA by NMB (see Fig. 1) and must be a consequence of the different distribution of the reagents. As the surfactant concentration increases, so too does the con-

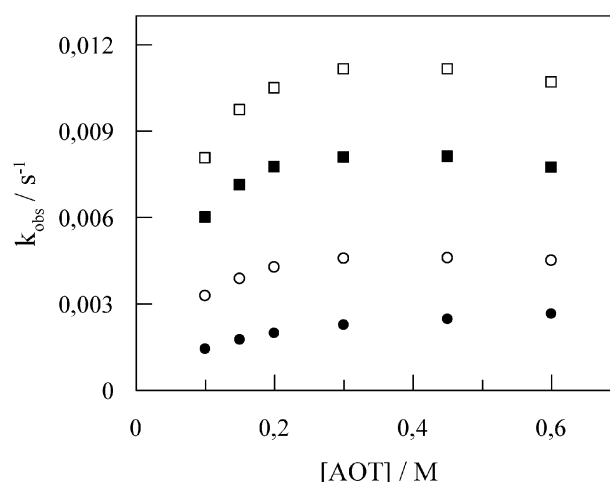
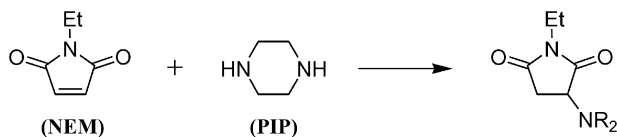


Fig. 1 Influence of the composition of the microemulsion on k_{obs} in the aminolysis of NPA by *N*-methylbenzylamine. $[NMB] = 0.1$ M referred to the total volume of the system. $T = 25^\circ\text{C}$. (●) $W = 2$; (○) $W = 7$; (■) $W = 20$ and (□) $W = 40$.



centration of piperazine in the interface of the microemulsion, with the resulting decrease in its concentration in the aqueous microdroplet. This decrease in concentration will cause a decrease in the reaction rate, given that the rate in the aqueous microdroplet must be greater than in the interface of the microemulsion, as a consequence of its different solvation capacity.

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. To apply the pseudophase formalism we must 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). 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.

1. Aminolysis of NPA by NMB

The experimental results obtained in the aminolysis of NPA by *N*-methylbenzylamine can be interpreted from Scheme 4. The low solubility of NMB in water allows us to exclude the possibility that it is distributed across the three pseudophases of the microemulsion. In this way NPA and NMB can only come into contact in the continuous medium and in the interface of the microemulsion. The possibility that the reaction takes place in the continuous medium can be discarded due to the existence of a linear dependency between k_{obs} and the amine concentration when the reaction takes place in microemulsions (not shown). This result contrasts with the behavior observed in pure isooctane where k_{obs} presents a quadratic dependency on the amine concentration. This different kinetic behavior is a consequence of a change in the determining step

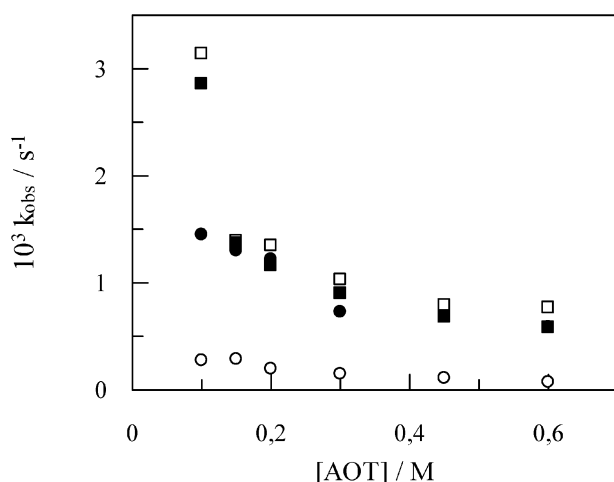
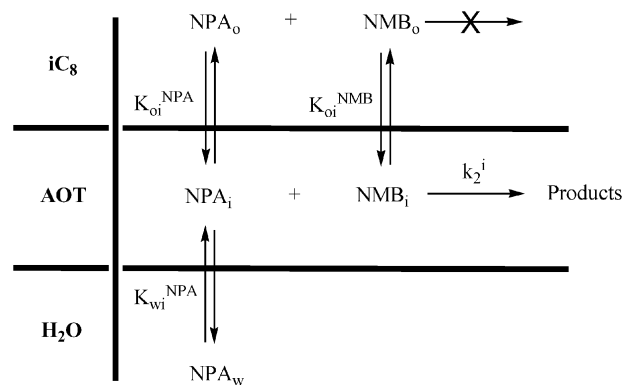


Fig. 2 Influence of the composition of the microemulsion on k_{obs} in the aminolysis of NEM by piperazine. [PIP] = 0.1 M referred to the total volume of the system. $T = 25^\circ\text{C}$. (○) $W = 5$; (●) $W = 10$; (□) $W = 20$ and (■) $W = 35$.



of the reaction rate as the polarity of the medium changes. In solvents of a low polarity, such as isooctane, the reaction occurs by the formation of an addition intermediate, T^\pm , the decomposition of which is catalyzed by bases in the rate determining step of the process.¹³ As the polarity of the medium increases, the slow step becomes the formation of the intermediate, and consequently k_{obs} shows a linear dependency on the amine concentration.

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

$$K_{wi}^{NPA} = \frac{[NPA]_i}{[NPA]_w} W \quad K_{oi}^{NPA} = \frac{[NPA]_i}{[NPA]_o} Z \quad (1)$$

where $[NPA]_w$, $[NPA]_i$, and $[NPA]_o$ are the concentrations of NPA in the aqueous pseudophase, in the interface and in the continuous medium, referred to the total volume of the microemulsion. The parameter Z is defined as the molar relationship $Z = [\text{isooctane}]/[\text{AOT}]$, by analogy with the parameter W . It is possible to evaluate the concentrations of NPA in the aqueous pseudophase and in the interface of the microemulsion considering that the total concentration of NPA can be expressed as the sum of the concentration in each of the three pseudophases of the system:

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

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

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

where the concentrations are referred to the total volume of the microemulsion. The eqn (3) can be simplified taking into account the values obtained previously¹⁴ for K_{oi}^{NPA} and K_{wi}^{NPA} ($K_{oi}^{NPA} = 25.9$ and $K_{wi}^{NPA} = 996$):

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

From Scheme 4 we can obtain the following expression for the rate constant observed, k_{obs} .

$$k_{\text{obs}} = k'_i \frac{K_{oi}^{NPA}}{K_{oi}^{NPA} + Z} \quad (5)$$

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 :

$$k'_i = k_2^i [NMB]_i = k_2^i \frac{V_{\text{tot}}}{V_i} [NMB]_i = k_2^i \frac{[NMB]_i}{\bar{V}_{\text{AOT}} [\text{AOT}]} \quad (6)$$

where $[NMB]_i$ is the concentration of *N*-methylbenzylamine in the interface of the microemulsion referred to the total volume of the interface, while $[NMB]_i$ is the concentration of the amine 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 AOT. In this way $V_{tot}/V_i = 1/\bar{V}_{AOT}[AOT]$ where \bar{V}_{AOT} represents the molar volume of the surfactant, $\bar{V}_{AOT} = 0.34 \text{ M}^{-1}$ and $[AOT]$ represents the total concentration of AOT referred to the total volume of the microemulsion.

Taking into account the distribution equilibrium of *N*-methylbenzylamine between the interface and the continuous medium of the microemulsion, we can obtain the following expression:

$$[NMB]_i = \frac{K_{oi}^{NMB}}{K_{oi}^{NMB} + Z} [NMB]_T \quad (7)$$

Combining eqn (5)–(7) we can write:

$$k_{obs} = \frac{k_2^i}{\bar{V}_{AOT}[AOT]} \frac{K_{oi}^{NPA}}{(K_{oi}^{NPA} + Z)} \frac{K_{oi}^{NMB} [NMB]_T}{(K_{oi}^{NMB} + Z)} \quad (8)$$

The rate equation can be reordered thus:

$$\frac{[NMB]_T}{k_{obs} \bar{V}_{AOT} [AOT]} = \frac{(K_{oi}^{NPA} + Z)(K_{oi}^{NMB} + Z)}{k_2^i K_{oi}^{NPA} K_{oi}^{NMB}} \quad (9)$$

This expression predicts the existence of a linear and quadratic dependence of $[NMB]_T/(k_{obs} \bar{V}_{AOT} [AOT])$ on parameter Z . Fig. 3 shows a series of examples in which we can see the existence of a good fit of the experimental results to the previous equation.

From the adjustments carried out in Fig. 3, and using the value of $K_{oi}^{NPA} = 25.9$, we can obtain the values of the distribution constant of *N*-methylbenzylamine between the continuous medium and the interface, K_{oi}^{NMB} , and of the rate constant of the aminolysis in the interface, k_2^i . The values obtained for K_{oi}^{NMB} are independent of W (see Fig. 4), allowing us to calculate a mean value of $K_{oi}^{NMB} = 29.1$. However, the values obtained for k_2^i present a clear variation with W , as shown in Fig. 5. As the water content of the system increases, there is also an increase in the rate constant of aminolysis in the interface, due to a progressive increase in the hydration of the interface.

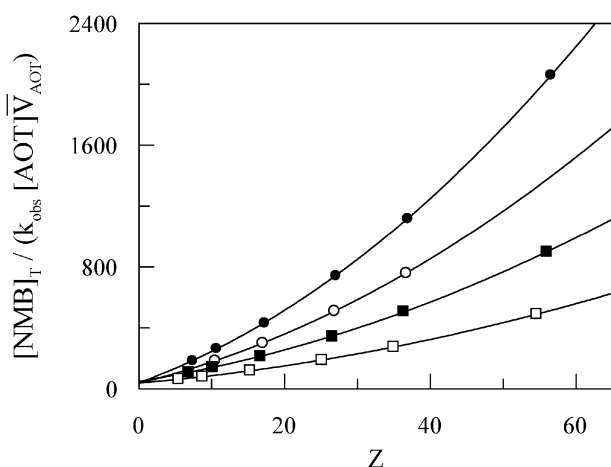


Fig. 3 Representation of the experimental results obtained for the aminolysis of NPA by *N*-methylbenzylamine in AOT–isooctane–water microemulsions in accordance with the eqn (9). $[NMB] = 0.1 \text{ M}$ referred to the total volume of the system. $T = 25^\circ\text{C}$. (●) $W = 2$; (○) $W = 7$; (■) $W = 20$ and (□) $W = 40$.

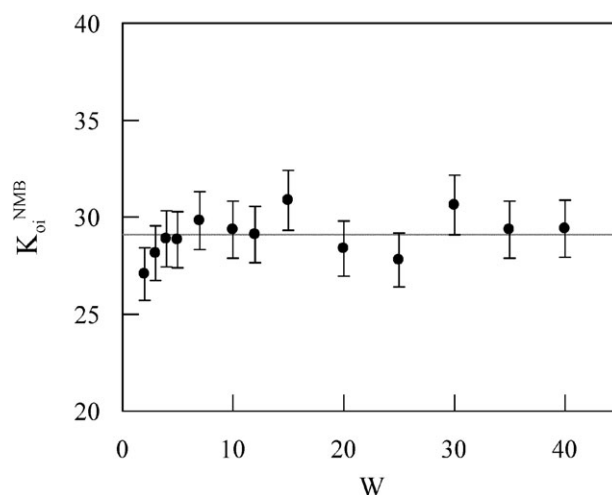


Fig. 4 Influence of W on the distribution constant of NMB in AOT–isooctane–water microemulsions at 25°C .

2. Aminolysis of NEM by PIP

The Michael addition of amines to NEM in water and in various solvents is a well known process.¹⁵ To investigate the influence of microemulsions on the rate of this process it is necessary to propose a reaction scheme, Scheme 5. The insoluble nature of piperazine in isooctane means that piperazine is found only between the interface and the aqueous pseudo-phase of the system.

In the same way as we obtained the NPA concentrations in the previous section, we can obtain the PIP concentrations:

$$[PIP]_i = \frac{K_{wi}^{PIP} [PIP]_T}{K_{wi}^{PIP} + W} \quad [PIP]_w = \frac{W [PIP]_T}{K_{wi}^{PIP} + W} \quad (10)$$

In accordance with the mechanism of Scheme 5, the reaction will take place simultaneously in the interface and in the aqueous microdroplet of the microemulsion. Therefore, on the basis of equations analogous to [2]–[3] for NEM, we can propose the following expression for the observed rate constant, k_{obs} :

$$k_{obs} = \frac{k'_w K_{oi}^{NEM} W + k'_i K_{oi}^{NEM} K_{wi}^{NEM}}{K_{oi}^{NEM} K_{wi}^{NEM} + K_{wi}^{NEM} Z + K_{oi}^{NEM} W} \quad (11)$$

where k'_i and k'_w are the first order rate pseudoconstants referred to the interface and the aqueous microdroplet, respectively. These rate constants can be expressed as bimolecular

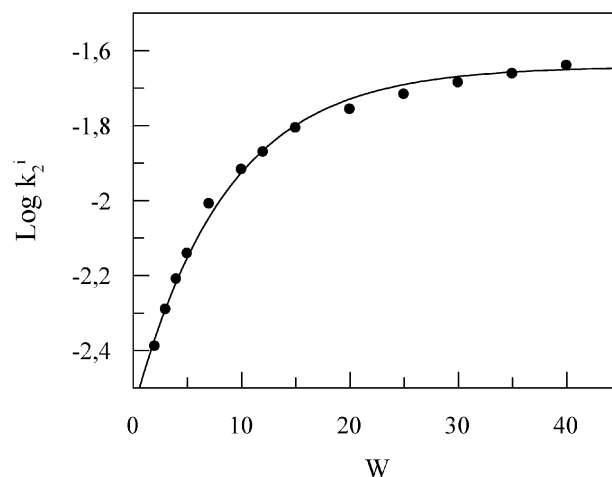
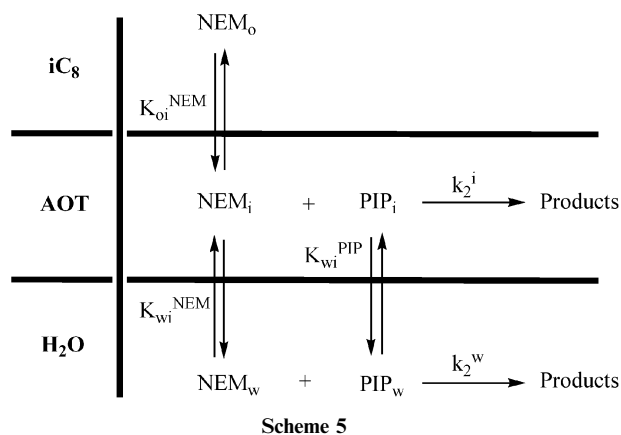


Fig. 5 Influence of W on $\text{Log } k_2^i$ for the aminolysis of NPA by *N*-methylbenzylamine in AOT–isooctane–water microemulsions. $[NMB] = 0.1 \text{ M}$ referred to the total volume of the system. $T = 25^\circ\text{C}$



rate constants in the interface, k_2^i and in the aqueous microdroplet, k_2^w , thus:

$$k'_i = k_2^i [\text{PIP}]_i^i = k_2^i \frac{V_{\text{tot}}}{V_i} [\text{PIP}]_i$$

$$= \frac{k_2^i}{\bar{V}_{\text{AOT}} [\text{AOT}]} \frac{K_{\text{wi}}^{\text{PIP}} [\text{PIP}]_T}{(K_{\text{wi}}^{\text{PIP}} + W)} \quad (12)$$

$$k'_w = k_2^w [\text{PIP}]_w^w = k_2^w \frac{V_{\text{tot}}}{V_{\text{H}_2\text{O}}} [\text{PIP}]_w$$

$$= \frac{k_2^w}{\bar{V}_{\text{H}_2\text{O}} [\text{AOT}]} \frac{[\text{PIP}]_T}{(K_{\text{wi}}^{\text{PIP}} + W)} \quad (13)$$

where $[\text{PIP}]_i^i$ and $[\text{PIP}]_w^w$ correspond to the concentrations of PIP in the interface and in the aqueous microdroplet referred to the volume of these pseudophases. These concentrations are referred to the total volume of the system, taking into account just the volumes of the pseudophases. Combining the eqn (11)–(13) we can obtain the following rate equation:

$$k_{\text{obs}} = \frac{k_2^i \frac{K_{\text{oi}}^{\text{NEM}} K_{\text{wi}}^{\text{NEM}} K_{\text{wi}}^{\text{PIP}}}{\bar{V}_{\text{AOT}} [\text{AOT}]} + k_2^w \frac{K_{\text{oi}}^{\text{NEM}} W}{\bar{V}_{\text{H}_2\text{O}} [\text{AOT}]} [\text{PIP}]_T}{K_{\text{oi}}^{\text{NEM}} K_{\text{wi}}^{\text{NEM}} + K_{\text{wi}}^{\text{NEM}} Z + K_{\text{oi}}^{\text{NEM}} W (K_{\text{wi}}^{\text{PIP}} + W)} \quad (14)$$

This equation can be written thus:

$$\frac{[\text{PIP}]_T}{k_{\text{obs}} [\text{AOT}] \bar{V}_{\text{H}_2\text{O}} \bar{V}_{\text{AOT}}} = \frac{(K_{\text{wi}}^{\text{PIP}} + W) [K_{\text{oi}}^{\text{NEM}} K_{\text{wi}}^{\text{NEM}} + K_{\text{oi}}^{\text{NEM}} W + K_{\text{wi}}^{\text{NEM}} Z]}{k_2^i K_{\text{oi}}^{\text{NEM}} K_{\text{wi}}^{\text{NEM}} K_{\text{wi}}^{\text{PIP}} \bar{V}_{\text{H}_2\text{O}} + k_2^w K_{\text{oi}}^{\text{NEM}} \bar{V}_{\text{AOT}} W} \quad (15)$$

It predicts the existence of a linear dependency between $[\text{PIP}]_T / k_{\text{obs}} [\text{AOT}] \bar{V}_{\text{H}_2\text{O}} \bar{V}_{\text{AOT}}$ and the parameter Z of composition of the microemulsion. Fig. 6 shows, by way of example, the good fit of the eqn (15) for values of $W = 15, 27$ and 40 .

The ordinates and the slopes of Fig. 6 show a dependency on W , as predicted by eqn (15). To carry out a quantitative analysis we will make use of the ordinates in the origin. The intercepts in Fig. 6, eqn (15), can be rewritten thus:

$$\frac{(K_{\text{wi}}^{\text{PIP}} + W) (K_{\text{wi}}^{\text{NEM}} + W)}{\text{Intercept}} = k_2^i \bar{V}_{\text{H}_2\text{O}} K_{\text{wi}}^{\text{PIP}} K_{\text{wi}}^{\text{NEM}} + k_2^w \bar{V}_{\text{AOT}} W \quad (16)$$

Previous studies^{6a} have allowed us to determine the value of the distribution constant of the piperazine between the continuous medium and the interface of the microemulsion $K_{\text{wi}}^{\text{PIP}}$, $K_{\text{wi}}^{\text{PIP}} = 9.5$ at 25°C . The value of the distribution constants of NEM can be determined from the Intercept/slope quotient¹⁶ and amount to $K_{\text{wi}}^{\text{NEM}} = 133$ and $K_{\text{oi}}^{\text{NEM}} = 16$. Using these

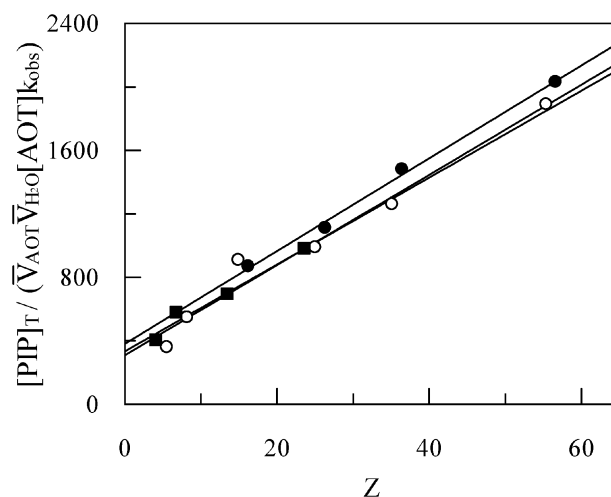


Fig. 6 Verification of the fit of the eqn (15) for the aminolysis of NEM by PIP in microemulsions AOT–isooctane–water. $[\text{PIP}] = 6.03 \times 10^{-3}$ M referred to the aqueous pseudophase of the system. $T = 25^\circ\text{C}$. (●) $W = 15$; (○) $W = 27$ and (■) $W = 40$.

values, we can rewrite the eqn (16) as:

$$\frac{(9.5 + W)(133 + W)}{\text{Intercept}} = k_2^i \bar{V}_{\text{H}_2\text{O}} K_{\text{wi}}^{\text{PIP}} K_{\text{wi}}^{\text{NEM}} + k_2^w \bar{V}_{\text{AOT}} W \quad (17)$$

This expression predicts the existence of a linear dependency between $(9.5 + W)(133 + W)/\text{Intercept}$ and the parameter W of the composition of the microemulsion. Fig. 7 shows the behavior observed for the aminolysis of NEM by piperazine.

As we can observe, there exists a clear linear dependency for values of $W > 10$, while there is a negative divergence of the linearity for $W < 10$. From this linear adjustment, and considering the values of $K_{\text{wi}}^{\text{NEM}}$ ($K_{\text{wi}}^{\text{NEM}} = 133$) obtained previously, we can obtain the rate constants k_2^w y k_2^i : $k_2^w = 1.41 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2^i = 0.113 \text{ M}^{-1} \text{ s}^{-1}$. The difference in reactivity between the interface and the aqueous pseudophase of the microemulsion is of $k_2^w/k_2^i = 12.5$, this result is compatible with the 17-fold decrease in the rate constant when passing from the aqueous pseudophase to the interface of the microemulsion in the aminolysis of NPA with PIP in AOT–isooctane–water microemulsions.¹⁷

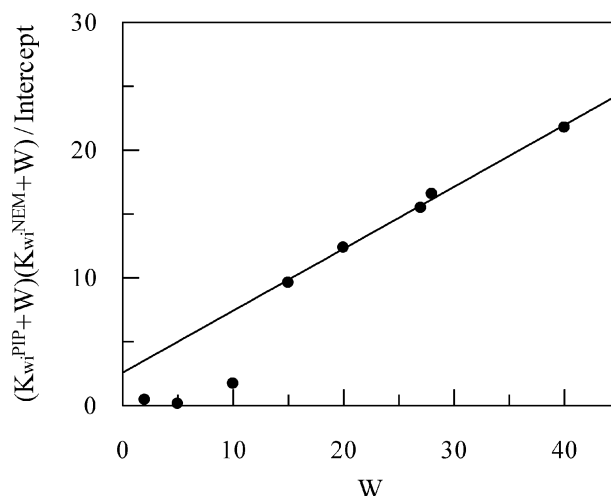


Fig. 7 Influence of W on $(K_{\text{wi}}^{\text{PIP}} + W)(K_{\text{wi}}^{\text{NEM}} + W)/\text{Intercept}$ (eqn (16)) for the aminolysis of NEM by piperazine in AOT/isooctane/water microemulsions. $[\text{PIP}] = 6.03 \times 10^{-3}$ M referred to the total volume of the system. $T = 25^\circ\text{C}$. The line represents the fit of the eqn (16) to the experimental results, considering only the values obtained for $W > 10$.

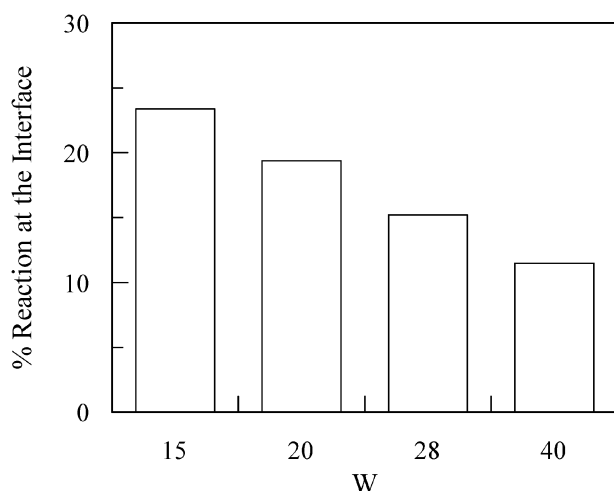
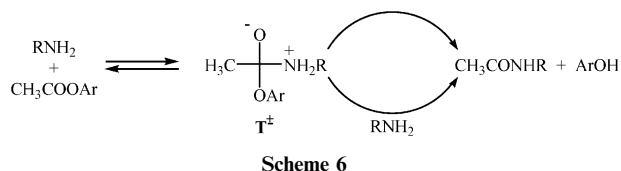


Fig. 8 Variation of the % of reaction at the interface with the water content of the AOT-based microemulsion for the Michael addition of piperazine to *N*-ethylmaleimide at 25 °C.

3. Influence of *W* on the rate constants in the interface and in the aqueous microdroplet

The rate limiting step for aminolysis of substituted phenylacetates in aqueous solution is first order in amine concentrations and leads to the formation of a tetrahedral intermediate (T^{\pm})^{12,13a} (Scheme 6).

When studying the aminolysis of NPA by NMB in AOT-based microemulsions we found that the rate constant in the interface increases along with *W*, Fig. 5. This behavior can be explained as a consequence of the changes in the properties of the water as *W* varies. 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 electrophilic character decreases, so too does the reaction rate. This behavior has also been shown in the study of the solvolysis reaction of the diphenylmethyl chloride^{8a} 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 has been observed between $\text{Log}k_2$ for the aminolysis of NPA by NMB and $\text{Log}k_1$ for the solvolysis of the diphenylmethyl chloride (not shown). The existence of this correlation shows that the decrease in the aminolysis rate constant of 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 shown in Fig. 5 are consistent with the fact that the greatest changes in the physical properties of the water of the microemulsions are observed for values of *W* < 15, these values being where the greatest variation of $\text{Log}k_2$ with *W* can be observed. The results shown in Fig. 7 show that for values of *W* > 15 both the rate constant in the interface and the rate constant in water scarcely change with *W*. In this way, we can obtain a good linear dependence as predicted by eqn (17). However, for values of *W* < 15 we can expect a decrease in the rate constant in the interface, analogous with that observed for

the aminolysis of NPA by NMB. This decrease in the rate constant in the interface means that the values determined experimentally diverge negatively from the behavior predicted by eqn (17). The divergence is more important if we consider that as the water content of the system decreases, there is an increase in the percentage of the reaction which takes place in the interface of the microemulsion (Fig. 8).

Conclusions

The aminolysis rate constant of NPA by NMB in the interface of AOT-based microemulsions increases together with *W*. This behavior is parallel with 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} . The aminolysis of NEM by piperazine 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 NPA by NMB.

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- 16 From the *Intercept/Slope* quotient of the representations of Fig. 6 and eqn (15) we can obtain $\text{Intercept/Slope} = K_{\text{oi}}^{\text{NEM}} + (K_{\text{oi}}^{\text{NEM}}/K_{\text{wi}}^{\text{NEM}})W$ which predicts the existence of a linear dependency on the quotient *Intercept/Slope* with *W*. The experimental results show that this quotient is independent of *W*. This result is due to the fact that $K_{\text{oi}}^{\text{NEM}} \gg K_{\text{oi}}^{\text{NEM}}$ in such a way as to verify the inequality $K_{\text{oi}}^{\text{NEM}} \gg K_{\text{oi}}^{\text{NEM}}W/K_{\text{wi}}^{\text{NEM}}$ making $\text{Intercept/Slope} = K_{\text{oi}}^{\text{NEM}} = 16$. Once the value of $K_{\text{oi}}^{\text{NEM}}$ is known, and using the value of the distribution constant of NEM between water and isooctane, $K_{\text{o}}^{\text{w}} = 0.120$, we can calculate $K_{\text{wi}}^{\text{NEM}}$, considering that $K_{\text{wi}}^{\text{NEM}} = K_{\text{oi}}^{\text{NEM}}/K_{\text{o}}^{\text{w}}$. In this way we can obtain the value of $K_{\text{wi}}^{\text{NEM}} = 133$.
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