

## First Evidence of Simultaneous Different Kinetic Behaviors at the Interface and the Continuous Medium of w/o Microemulsions

Luis García-Río,<sup>\*,†</sup> Juan C. Mejuto,<sup>‡</sup> and Moisés Pérez-Lorenzo<sup>†</sup>

Departamento de Química Física, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago, Spain, and Departamento de Química Física, Facultade de Ciencias, Universidade de Vigo, Ourense, Spain

Received: September 16, 2005; In Final Form: October 31, 2005

A study was carried out on the butylaminolysis reaction of 4-nitrophenyl caprate in AOT/chlorobenzene/water microemulsions, with the observed rate constant,  $k_{\text{obs}}$ , showing both first- and second-order dependence on butylamine concentration. The first-order term in  $[\text{BuNH}_2]$  is due to the reaction occurring at the interface of the microemulsion while the second-order term is due to the reaction in the continuous medium. The different kinetic behavior is accounted for by the mechanism by which the reaction proceeds: at the interface of the microemulsion, the rate-determining step is the formation of the addition intermediate,  $\text{T}^\pm$ , whereas in the continuous medium the slow step is the base-catalyzed decomposition of this intermediate. The application of the pseudophase formalism allows the observed kinetic behavior to be explained and to obtain the rate constants at the interface,  $k_2^{\text{i}} = 0.13 \text{ M}^{-1} \text{ s}^{-1}$ , and in the continuous medium,  $k_2^{\text{o}} K^{\text{T}} = 2.46 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ . These values indicate that the reaction rate decreases approximately 23 times upon going from the aqueous medium to the interface of the microemulsion, whereas the rate constant in the continuous medium is consistent with that obtained in pure chlorobenzene,  $k_2^{\text{o}} K^{\text{T}} = 2.09 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ .

### Introduction

The use of microemulsions as reaction media has attracted considerable interest in recent years<sup>1</sup> due to the microheterogeneous nature of these systems. The great utility of microemulsions as solvents for organic reactions lies in their ability to solubilize polar and nonpolar substances and to compartmentalize and concentrate reagents.<sup>2</sup> Three main applications have been reported: (i) use of microemulsions to overcome reagent incompatibility problems,<sup>3</sup> (ii) reactions where a specific catalytic effect is obtained,<sup>4</sup> and (iii) use of microemulsions to influence reaction regioselectivity.<sup>5</sup> The use of a two-phase system with an added phase transfer agent and the use of a microemulsion are two alternatives to overcome reagent incompatibility problems in organic synthesis. Both routes have proven useful but on entirely different accounts. In phase transfer catalysis, the ionic reactant is carried into the organic phase, in which it becomes highly reactive. In the microemulsion approach, there is no transfer of reactant from one environment to another; the method relies on the creation of the very large oil–water interface at which the reaction occurs. There are a few reports in the literature on the use of phase transfer agents in combination with microemulsions<sup>6</sup> showing that the use of a microemulsion as reaction medium and the addition of a phase transfer agent gave the highest reaction rate.<sup>7</sup> Microemulsions have also found wide applications in enzymology<sup>8</sup> because several advantages can be achieved by using enzymes in media of low water content: increasing the solubility of nonpolar reagents, increasing the possibility of shifting thermodynamic equilibria in favor of condensation, and because of the improve-

ment of thermal stability of the enzymes, enabling reactions to be carried out at higher temperatures.

Microemulsions also are widely used as reaction media for carrying out polymerization reactions.<sup>9</sup> Reactions are performed in the aqueous micellar confinement within an oil phase. Ideally, the size of each single nanoparticle should be given by the number of precursor ions in each micelle. It was established that these systems are not nanoreactors in the strict sense, since objects synthesized that way are usually significantly larger than the original micelles. The reason for this is that those surfactant assemblies dissolve and reform on a rather short (millisecond) time scale. Any chemical reaction slower than this exchange time (practically all reactions) does not experience the compartmentalized structure of the medium but a quasi-continuous environment. The potential advantage of nanoreactors for polymer and colloid science is that a chemical reaction, confined to a nanosized environment, has a different outcome as compared to the same reaction or process in the continuous phase: (a) The size of the polymer or colloid to be made is limited by the size of the confinement and the number of precursor molecules in each nanoreactor. (b) The relation between inter- and intramolecular reactions can be shifted. (c) Nanoreactors allow the implementation of reactions in a medium where they otherwise cannot be performed.<sup>10</sup> Microemulsions, particularly of the (water/oil) w/o type, have become of interest as a medium for the synthesis of inorganic particles, ranging from metals to complex crystallites, of very small size.<sup>11</sup>

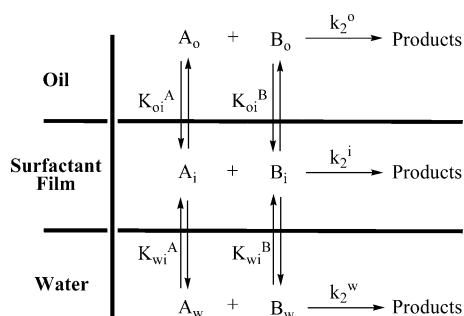
The compartmentalization of reactants in three pseudophases may not only alter the rate of certain reactions<sup>12</sup> but also modify the mechanism by which these reactions occur.<sup>13</sup> We have developed a kinetic model to quantitatively explain the influence of microemulsions on chemical reactivity. The model considers the distribution of the reactants throughout the different phases of the microemulsion and that the reaction is taking place

\* To whom correspondence should be addressed. E-mail: qflgr3cn@usc.es.

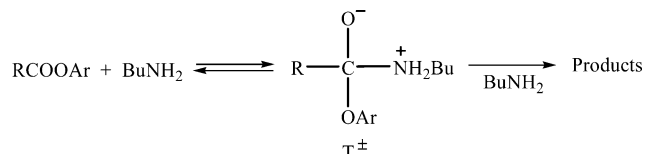
<sup>†</sup> Universidade de Santiago de Compostela.

<sup>‡</sup> Universidade de Vigo.

## SCHEME 1



## SCHEME 2

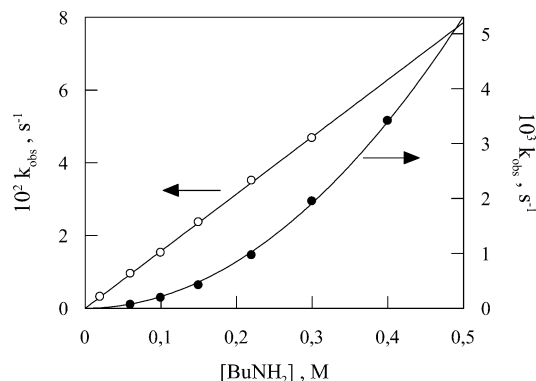


simultaneously at those phases where the reactants can come into contact with each other (Scheme 1).

The model has been successfully applied to reactions that take place in only one phase: reactions of anionic nucleophiles in the aqueous microdroplet<sup>14</sup> and processes of unimolecular solvolysis<sup>12</sup> or bimolecular<sup>15</sup> reactions at the interface. Recently, we have shown its application to aminolysis reactions occurring both in the aqueous microdroplet and at the interface of AOT-based microemulsions.<sup>16</sup> Equivalent expressions to those derived by us were obtained by Casavino and co-workers and applied to iron(III) oxidation of some alkyl-substituted ferrocenes<sup>17</sup> and the kinetics of substitution in palladium(II) complexes.<sup>18</sup> Sánchez et al. have shown that the Brönsted equation, which can be derived directly from the transition state theory, is an alternative to the pseudophase model to rationalize the observed kinetic effects in microemulsions. The model has been applied to  $I^- + \text{IrCl}_6^{2-}$ ,  $\text{Fe}(\text{CN})_6^{4-} + \text{S}_2\text{O}_8^{2-}$ ,  $\text{Fe}(\text{CN})_2(\text{bpy})_2 + \text{S}_2\text{O}_8^{2-}$ , and  $[\text{Ru}(\text{NH}_3)_5\text{pz}]^{2+} + \text{S}_2\text{O}_8^{2-}$  reactions,<sup>19</sup> where the reagents are distributed between the water droplet and the interface, showing that the microemulsions behave as concentrated salt solutions.

To explore the influence of the different microenvironments of the microemulsion on chemical reactivity, we focus our attention on the possibility of a reaction that takes place simultaneously by two different mechanisms in the continuous medium and the interface. Despite the large number of studies conducted to explain the influence of w/o microemulsions on chemical reactivity, we are not aware of any reports of reactions occurring simultaneously in the continuous medium and at the interface of the microemulsion. We have previously studied the aminolysis reaction of 4-nitrophenyl acetate by hydrophobic amines, *n*-decylamine,<sup>16</sup> and *N*-methylbenzylamine,<sup>20</sup> in AOT/isooctane/water microemulsions. However, the higher rate of reaction at the interface of the microemulsion compared to isooctane, together with a favorable distribution of reactants, caused the reaction to proceed only at the interface. In an attempt to shift the reaction to the continuous medium, the hydrophobic character of the ester was increased by replacing 4-nitrophenyl acetate with 4-nitrophenyl caprate (NPC), and the polarity of the continuous medium was increased by replacing isooctane with chlorobenzene.

The mechanism of ester aminolysis proceeds by an addition–elimination mechanism<sup>21</sup> (Scheme 2). In high-polarity solvents (acetonitrile or alcohol/water mixtures), the rate-determining step is the formation of the addition intermediate, T<sup>±</sup>, with the rate



**Figure 1.** Influence of *n*-butylamine concentration on  $k_{\text{obs}}$  for the aminolysis of NPC in chlorobenzene (●) and acetonitrile (○):  $[\text{NPC}] = 5 \times 10^{-5}$  M,  $T = 25.0$  °C.

equation showing first-order dependence on amine concentration. In low-polarity solvents, such as chlorobenzene, the rate-determining step is the base-catalyzed decomposition of T<sup>±</sup>, in such a way that the rate equation shows second-order dependence on amine concentration. The results obtained by studying the butylaminolysis of NPC in AOT/chlorobenzene/water microemulsions indicate both first- and second-order dependence on amine concentration, which correspond to the reaction occurring both at the interface and in the continuous medium of the reaction. These results constitute the first example of a reaction in w/o microemulsions where it exhibits different kinetic behavior at the interface and in the oil.

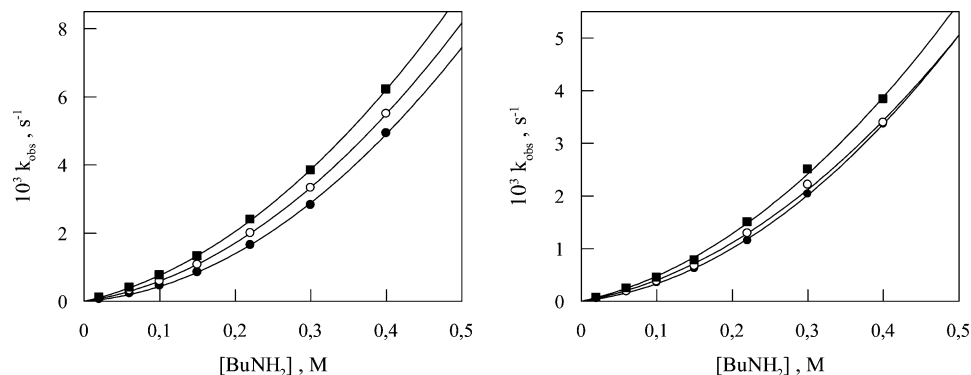
## Experimental Section

*N*-butylamine and *p*-nitrophenyl caprate (NPC) were supplied by Aldrich in the highest available purity and used as received. AOT (Aldrich) was dried in a vacuum desiccator for 2 days and then used without further purification. Microemulsions were prepared by mixing chlorobenzene (Aldrich), water, and 1.00 M AOT/chlorobenzene solution in appropriate proportions. Kinetic experiments were carried out by following the change in absorbance with time due to the formation of reaction products, at  $\lambda = 320$  nm for the reaction in chlorobenzene and  $\lambda = 390$  nm for the reaction in the microemulsions. All the measurements were recorded using a HP 8453 spectrophotometer thermostated at  $25.0 \pm 0.1$  °C. In all kinetic experiments, the NPC concentration,  $[\text{NPC}] = 5.00 \times 10^{-5}$  M, was much lower than that of butylamine. The absorbance–time data always fit the first-order integrated equation satisfactorily ( $r > 0.999$ ), and the observed rate constant,  $k_{\text{obs}}$ , was reproducible to within 3%. Moreover, the low  $[\text{NPC}]$  in comparison with  $[\text{AOT}]$  typically ranging from 0.1 to 0.60 M guarantees that the products of the reaction cannot alter the properties of the interface because their concentration will be less than 0.05% of the interfacial composition.

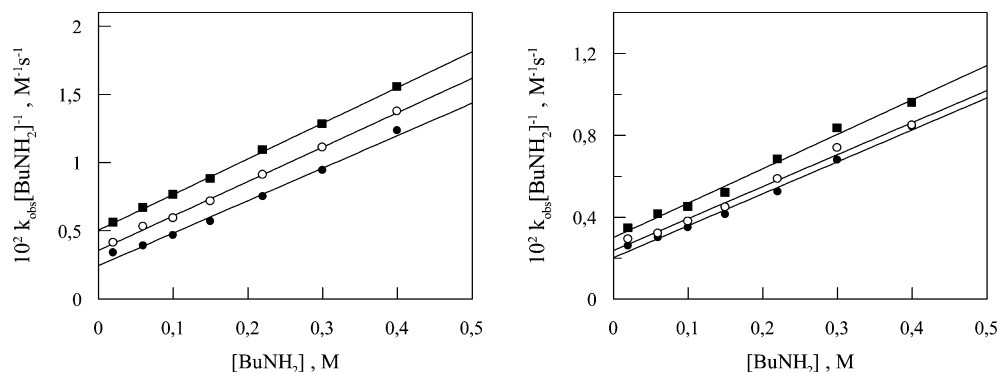
The distribution coefficient of NPC between water and chlorobenzene was determined by mixing equal volumes of both solvents to which a constant amount of NPC was added. After vigorous stirring, phase separation was allowed to proceed at a constant temperature (25.0 °C) and the NPC content of each phase was determined. An average value of  $K_o^w = 8.90 \times 10^{-3}$  was obtained, indicative of the low solubility of NPC in water.

## Results

**1. Butylaminolysis of NPC in Homogeneous Media.** Figure 1 shows the influence of  $[\text{BuNH}_2]$  on  $k_{\text{obs}}$  in the aminolysis of NPC in chlorobenzene. The existence of a quadratic dependence



**Figure 2.** Influence of *n*-butylamine concentration on  $k_{\text{obs}}$  for the aminolysis of NPC in AOT/chlorobenzene/water microemulsions:  $[\text{NPC}] = 5 \times 10^{-5} \text{ M}$ ,  $T = 25.0^\circ \text{C}$ , (left)  $W = 2$ , (right)  $W = 8$ , (●)  $[\text{AOT}] = 0.30 \text{ M}$ , (○)  $[\text{AOT}] = 0.45 \text{ M}$ , and (■)  $[\text{AOT}] = 0.60 \text{ M}$ .



**Figure 3.** Plot of experimental data according to eq 1 for the aminolysis of NPC in AOT/chlorobenzene/water microemulsions:  $[\text{NPC}] = 5 \times 10^{-5} \text{ M}$ ,  $T = 25.0^\circ \text{C}$ , (left)  $W = 2$ , (right)  $W = 8$ , (●)  $[\text{AOT}] = 0.30 \text{ M}$ , (○)  $[\text{AOT}] = 0.45 \text{ M}$ , and (■)  $[\text{AOT}] = 0.60 \text{ M}$ .

of  $k_{\text{obs}}$  on  $[\text{BuNH}_2]$  can be observed, corresponding to a process where the slow step is the base-catalyzed decomposition of the addition intermediate,  $\text{T}^\pm$  (Scheme 2). This kinetic behavior is interpreted in terms of a rate equation of the form:  $k_{\text{obs}} = k_{\text{B}} - [\text{BuNH}_2]^2$ . The value of  $k_{\text{B}}$  for the butylaminolysis of NPC in pure chlorobenzene can be obtained from the fit of the experimental data,  $k_{\text{B}} = 2.09 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ . As the polarity of the medium increases, so does the rate of decomposition of the addition intermediate,  $\text{T}^\pm$ , and the rate-determining step becomes the formation of this intermediate. This behavior has been observed using acetonitrile as solvent, and it is characterized by the existence of a linear dependence of  $k_{\text{obs}}$  on  $[\text{BuNH}_2]$  (see Figure 1):  $k_{\text{obs}} = k_{\text{A}}[\text{BuNH}_2]$ . From the fit of the data in Figure 1, the value of  $k_{\text{A}}$  can be determined,  $k_{\text{A}} = 1.57 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ .

**2. Butylaminolysis of NPC in AOT/Chlorobenzene/Water Microemulsions.** The influence of the microemulsion composition on the observed rate constant of butylaminolysis was studied using microemulsions where  $[\text{AOT}]$  was varied between  $[\text{AOT}] = 0.10$  and  $0.60 \text{ M}$  and the water content between  $W = 2$  and  $W = 8$  ( $W = [\text{H}_2\text{O}]/[\text{AOT}]$ ). The lower solubilization capacity of water in AOT-based microemulsions formed by aromatic hydrocarbons<sup>22</sup> as compared to alicyclic hydrocarbons did not allow us to use values of  $W > 8$ . The influence of  $[\text{BuNH}_2]$  on  $k_{\text{obs}}$  was studied for each microemulsion composition tested. As an example, Figure 2 shows the results obtained for  $W = 2$  ( $[\text{AOT}] = 0.30, 0.45, 0.60 \text{ M}$ ) and  $W = 8$  ( $[\text{AOT}] = 0.30, 0.45, 0.60 \text{ M}$ ).

The observed rate constants,  $k_{\text{obs}}$ , exhibit a linear and quadratic dependence on  $[\text{BuNH}_2]$ :  $k_{\text{obs}} = k_{\text{A}}[\text{BuNH}_2] + k_{\text{B}} - [\text{BuNH}_2]^2$ . The experimental data can be analyzed using eq 1

(Figure 3), which predicts the existence of a linear dependence between  $k_{\text{obs}}/[\text{BuNH}_2]$  and  $[\text{BuNH}_2]$ .

$$k_{\text{obs}}/[\text{BuNH}_2] = k_{\text{A}} + k_{\text{B}}/[\text{BuNH}_2] \quad (1)$$

From the intercepts and slopes of plots analogous to those in Figure 3, we can obtain the values of  $k_{\text{A}}$  and  $k_{\text{B}}$  for each microemulsion composition. The values obtained are listed in Table 1.

## Discussion

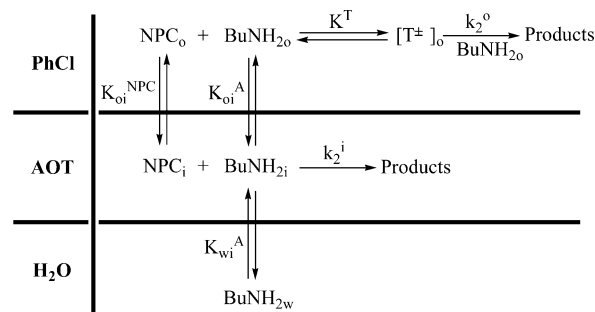
Figure 4 shows the influence of microemulsion composition on the  $k_{\text{A}}$  and  $k_{\text{B}}$  terms (Table 1). As can be observed, the first-order rate constant with respect to amine,  $k_{\text{A}}$ , increases with an increase in AOT concentration and a decrease in the water content of the microemulsion. However, the rate constant exhibiting second-order dependence on amine concentration,  $k_{\text{B}}$ , decreases slightly as  $[\text{AOT}]$  and  $W$ ,  $W = [\text{H}_2\text{O}]/[\text{AOT}]$ , increase (note the different Y-scales in Figure 4, left and right). This behavior has to be interpreted by taking into account that the reaction takes place simultaneously in the continuous medium and at the interface of the microemulsion. Nucleophilic attack of *n*-butylamine on the ester generates a tetrahedral intermediate,<sup>23–26</sup>  $\text{T}^\pm$ , whose base-catalyzed decomposition is the rate-determining step in chlorobenzene and is responsible for the second-order term in  $\text{BuNH}_2$ . We can therefore relate the rate constant  $k_{\text{B}}$  to the process occurring in the continuous medium of the microemulsion. When the polarity of the reaction medium is increased, the formation of the intermediate,  $\text{T}^\pm$ , becomes the rate-determining step, which is made clear by the first-order term in  $\text{BuNH}_2$ . Therefore, the rate constant  $k_{\text{A}}$  can be related to the butylaminolysis process occurring at the interface of the microemulsion.

**TABLE 1: Influence of Microemulsion Composition on  $k_A$  and  $k_B$  for Butylaminolysis of NPC**

$W^a$	[AOT], M	$Z^b$	$k_A, M^{-1} s^{-1}$	$k_B, M^{-2} s^{-1}$
2	0.10	92.9	$8.47 \times 10^{-4}$	$2.59 \times 10^{-2}$
2	0.15	60.1	$1.27 \times 10^{-3}$	$2.48 \times 10^{-2}$
2	0.20	44.1	$1.88 \times 10^{-3}$	$2.40 \times 10^{-2}$
2	0.30	28.1	$2.46 \times 10^{-3}$	$2.38 \times 10^{-2}$
2	0.45	17.7	$3.57 \times 10^{-3}$	$2.52 \times 10^{-2}$
2	0.60	12.3	$5.05 \times 10^{-3}$	$2.61 \times 10^{-2}$
3	0.10	92.0	$7.84 \times 10^{-4}$	$2.61 \times 10^{-2}$
3	0.15	59.9	$1.22 \times 10^{-3}$	$2.19 \times 10^{-2}$
3	0.20	43.9	$1.58 \times 10^{-3}$	$2.16 \times 10^{-2}$
3	0.30	27.9	$2.31 \times 10^{-3}$	$2.02 \times 10^{-2}$
3	0.45	17.2	$3.32 \times 10^{-3}$	$2.08 \times 10^{-2}$
3	0.60	11.9	$4.61 \times 10^{-3}$	$2.25 \times 10^{-2}$
4	0.10	91.8	$8.26 \times 10^{-4}$	$2.22 \times 10^{-2}$
4	0.15	59.8	$1.22 \times 10^{-3}$	$2.06 \times 10^{-2}$
4	0.20	43.7	$1.46 \times 10^{-3}$	$2.05 \times 10^{-2}$
4	0.30	27.7	$2.03 \times 10^{-3}$	$1.97 \times 10^{-2}$
4	0.45	17.0	$2.88 \times 10^{-3}$	$1.99 \times 10^{-2}$
4	0.60	11.7	$3.70 \times 10^{-3}$	$2.38 \times 10^{-2}$
6	0.10	91.5	$7.34 \times 10^{-4}$	$2.20 \times 10^{-2}$
6	0.15	59.4	$1.06 \times 10^{-3}$	$2.05 \times 10^{-2}$
6	0.20	43.4	$1.38 \times 10^{-3}$	$1.91 \times 10^{-2}$
6	0.30	27.4	$2.19 \times 10^{-3}$	$1.66 \times 10^{-2}$
6	0.45	16.7	$2.57 \times 10^{-3}$	$1.58 \times 10^{-2}$
6	0.60	11.3	$3.75 \times 10^{-3}$	$1.80 \times 10^{-2}$
8	0.10	91.1	$5.59 \times 10^{-4}$	$2.16 \times 10^{-2}$
8	0.15	59.1	$8.67 \times 10^{-4}$	$1.98 \times 10^{-2}$
8	0.20	43.0	$1.18 \times 10^{-3}$	$1.79 \times 10^{-2}$
8	0.30	27.0	$2.02 \times 10^{-3}$	$1.56 \times 10^{-2}$
8	0.45	16.3	$2.37 \times 10^{-3}$	$1.56 \times 10^{-2}$
8	0.60	11.0	$3.01 \times 10^{-3}$	$1.68 \times 10^{-2}$

<sup>a</sup>  $W = [H_2O]/[AOT]$ . <sup>b</sup>  $Z = [PhCl]/[AOT]$ .

An increase in the surfactant concentration results in an increase in  $k_A$  with AOT concentration (Figure 4, left) due to the incorporation of BuNH<sub>2</sub> and NPC into the interface and, hence, in an increase in the rate of the process due to the higher polarity of the interface as compared to chlorobenzene. The increase of  $k_A$  with [AOT] contrasts with the behavior observed for  $k_B$ , which decreases as the surfactant concentration increases reaching a minimum value and then  $k_B$  increases upon increasing the surfactant concentration. This behavior is due to the incorporation of the reactants into the interface, which results in a decrease of the concentrations in the continuous medium. Moreover, increasing the surfactant concentration increases the volume of the disperse phase and consequently decreases the volume of the continuous medium increasing the reagent concentrations in the oil pseudophase. The balance between these two effects is responsible for the behavior shown in Figure 4, right. Both rate constants,  $k_A$  and  $k_B$ , decrease with increasing  $W$  values, which is attributed to the incorporation of BuNH<sub>2</sub> into the aqueous microdroplet, with the resulting decrease of

**SCHEME 3**

BuNH<sub>2</sub> in the continuous medium and at the interface of the microemulsion.

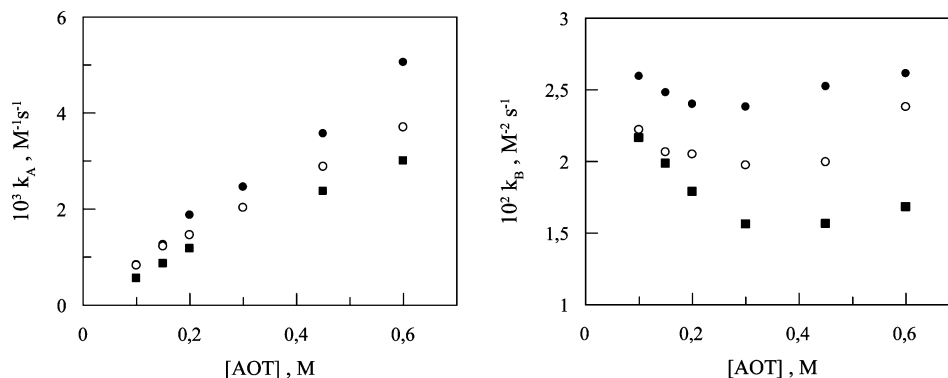
To carry out a quantitative interpretation of the observed behavior, it is necessary to propose a reaction scheme which allows the possibility for butylaminolysis to take place simultaneously in the continuous medium and at the interface of the microemulsion and where the rate-determining step corresponds to the decomposition and formation of  $T^\pm$ , respectively (Scheme 3).

The low solubility of NPC in water excludes the possibility of its distribution between the three pseudophases of the microemulsion. Thus, NPC and BuNH<sub>2</sub> will only come into contact with each other at the interface and in the continuous medium. The distribution of BuNH<sub>2</sub> throughout the three pseudophases of the microemulsion is governed by the equilibrium constants corresponding to its incorporation at the interface from the aqueous microdroplet,  $K_{wi}^A = ([BuNH_2]_i/[BuNH_2]_w)W$ , and from the continuous medium,  $K_{oi}^A = ([BuNH_2]_i/[BuNH_2]_o)Z$ , respectively, where  $Z$  is defined as the molar ratio:  $Z = [PhCl]/[AOT]$ . From these equilibrium constants, the following expressions for butylamine concentration in the continuous medium, interface, and aqueous microdroplet of the microemulsion can be determined in terms of the total concentration of BuNH<sub>2</sub>.

$$[BuNH_2]_o = \frac{Z[BuNH_2]_T}{K_{oi}^A + Z + K_{ow}^A W} \quad (2)$$

$$[BuNH_2]_i = \frac{K_{oi}^A [BuNH_2]_T}{K_{oi}^A + Z + K_{ow}^A W} \quad (3)$$

$$[BuNH_2]_w = \frac{K_{ow}^A W [BuNH_2]_T}{K_{oi}^A + Z + K_{ow}^A W} \quad (4)$$



**Figure 4.** Influence of AOT concentration on  $k_A$  (left) and  $k_B$  (right): (●)  $W = 2$ , (○)  $W = 4$ , and (■)  $W = 8$ .



Where  $K_{ow}^A$  is the relationship between the distribution constants of butylamine:  $K_{ow}^A = K_{oi}^A/K_{wi}^A$ .

The equilibrium constant for the formation of the addition intermediate,  $T^\pm$ , in the continuous medium,  $K_T$ , is defined as:  $K_T = [T^\pm]_o/[NPC]_o[BuNH_2]_o$ . This equilibrium constant is expressed in terms of concentrations in the continuous medium referred to the volume of the continuous medium in the microemulsion. They can be converted into concentrations related to the total volume of the microemulsion just by considering that the volume of the continuous medium can be defined as the product of the concentration and molar volume of chlorobenzene.

$$K_T = \frac{[T^\pm]_o}{[NPC]_o[BuNH_2]_o} \bar{V}_o [PhCl] \quad (5)$$

The distribution constants of NPC between the continuous medium and the interface of the microemulsion are defined analogously to those for  $BuNH_2$ . Similarly, as with butylamine, the NPC concentration in the continuous medium and the interface as well as the  $T^\pm$  concentration in the continuous medium can be determined in terms of the total concentration of NPC.

$$[NPC]_o = \frac{Z[NPC]_T}{K_{oi}^{NPC} + Z} \quad (6)$$

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

$$[T^\pm]_o = \frac{ZK^T[BuNH_2]_o[NPC]_T}{\bar{V}_o[PhCl](K_{oi}^{NPC} + Z) + ZK^T[BuNH_2]_o} \cong \frac{ZK^T[BuNH_2]_o[NPC]_T}{\bar{V}_o[PhCl](K_{oi}^{NPC} + Z)} \quad (8)$$

The simplification in eq 8 is consistent with the experimental behavior, where at high butylamine concentration  $k_{obs}$  shows no tendency to reach a limiting value.

On the basis of Scheme 3, the following rate equation can be obtained

$$r = k'_i [NPC]_i + k'_o [T^\pm]_o \quad (9)$$

Where  $k'_i$  and  $k'_o$  are the pseudo-first-order rate constants referred to the interface and the continuous medium, respectively. These rate constants can be expressed as bimolecular rate constants at the interface,  $k_2^i$ , and in the continuous medium,  $k_2^o$ , as

$$k'_i = k_2^i [BuNH_2]_i = k_2^i \frac{V_{tot}}{V_i} [BuNH_2]_i = k_2^i \frac{[BuNH_2]_i}{V_{AOT}[AOT]} \quad (10)$$

$$k'_o = k_2^o [BuNH_2]_o = k_2^o \frac{V_{tot}}{V_o} [BuNH_2]_o = k_2^o \frac{[BuNH_2]_o}{V_o[PhCl]} \quad (11)$$

Where  $[BuNH_2]_i$  and  $[BuNH_2]_o$  refer to the  $BuNH_2$  concentrations at the interface and in the continuous medium related to the volumes of the phases, whereas  $[BuNH_2]_i$  and  $[BuNH_2]_o$  correspond to the  $BuNH_2$  concentrations at the interface and in the continuous medium referred to the total volume of the

system. As is usual in micellar systems and microemulsions,<sup>27</sup> the interface is assumed to consist of only the surfactant, in such a way that the volume of the interface is given by the volume occupied by AOT. Thus,  $V_{tot}/V_i = 1/V_{AOT}$  [AOT] where  $V_{AOT}$  stands for the molar volume of the surfactant,  $V_{AOT} = 0.34 \text{ M}^{-1}$ , and [AOT] stands for the total concentration of AOT referred to the total volume of the microemulsion. Similarly, the continuous medium is assumed to consist solely of chlorobenzene, in such a way that its volume is given by the volume occupied by PhCl. Therefore,  $V_{tot}/V_o = 1/\bar{V}_o$  [PhCl], where  $\bar{V}_o$  is the molar volume of chlorobenzene,  $\bar{V}_o = 0.102 \text{ M}^{-1}$ , and [PhCl] represents the chlorobenzene concentration referred to the total volume of the system.

Hence, the rate equation (9) can be rewritten as

$$r = k_2^i \frac{[BuNH_2]_i}{V_{AOT}[AOT]} [NPC]_i + k_2^o \frac{[BuNH_2]_o}{V_o[PhCl]} [T^\pm]_o \quad (12)$$

Combining this expression with eqs 2, 3, 7, and 8 leads to the following expression for the observed rate constant,  $k_{obs}$

$$k_{obs} = \frac{k_2^i K_{oi}^{NPC} K_{oi}^A}{V_{AOT} [AOT] (K_{oi}^{NPC} + Z) (K_{oi}^A + Z + K_{ow}^A W)} \frac{[BuNH_2]_{tot} + \frac{k_2^o K^T Z^3}{V_o^2 [PhCl]^2 (K_{oi}^{NPC} + Z) (K_{oi}^A + Z + K_{ow}^A W)^2}}{[BuNH_2]_{tot}^2} \quad (13)$$

This allows the first- and second-order terms in butylamine to be identified as

$$k_A = \frac{k_2^i K_{oi}^{NPC} K_{oi}^A}{V_{AOT} [AOT] (K_{oi}^{NPC} + Z) (K_{oi}^A + Z + K_{ow}^A W)} \quad (14)$$

$$k_B = \frac{k_2^o K^T Z^3}{V_o^2 [PhCl]^2 (K_{oi}^{NPC} + Z) (K_{oi}^A + Z + K_{ow}^A W)^2} \quad (15)$$

The analysis of these terms will be performed independently.

**1. Reaction at the Interface.** To analyze the behavior observed for the butylaminolysis reaction at the interface of the microemulsion, eq 14 can be rewritten as follows<sup>28</sup>

$$\frac{1}{k_A V_{AOT} [AOT] Z} = \frac{K_{oi}^A + K_{oi}^{NPC} + K_{ow}^A W}{k_2^i K_{oi}^{NPC} K_{oi}^A} + \frac{1}{k_2^i K_{oi}^{NPC} K_{oi}^A} Z \quad (16)$$

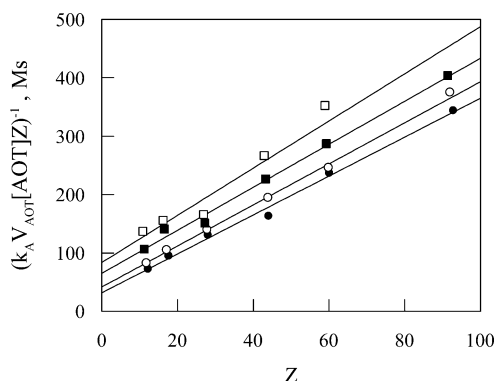
Figure 5 shows a good fit of eq 16 to the experimental data for different values of  $W$ .

From the ratio between the intercept and the slope of plots such as those in Figure 5 (eq 16), the following equation can be obtained

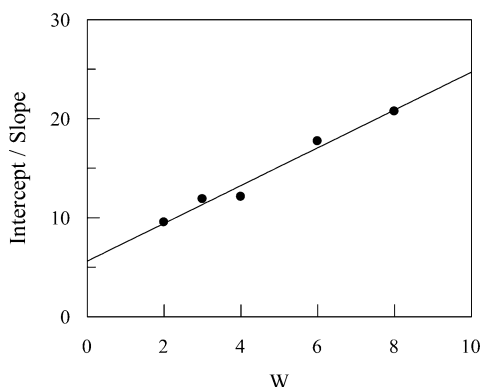
$$\text{intercept/slope} = K_{oi}^{NPC} + K_{oi}^A + K_{ow}^A W \quad (17)$$

As will be demonstrated later, it is clear that eq 17 can be rewritten as

$$\text{intercept/slope} = K_{oi}^{NPC} + K_{ow}^A W \quad (18)$$



**Figure 5.** Plot of experimental data according to eq 16 for the aminolysis of NPC in AOT/chlorobenzene/water microemulsions: [NPC] =  $5 \times 10^{-5}$  M,  $T = 25.0$  °C, (●)  $W = 2$ , (○)  $W = 3$ , (■)  $W = 6$ , and (□)  $W = 8$ .



**Figure 6.** Verification of eq 18 with the values obtained from Figure 5 for the aminolysis of NPC in AOT/chlorobenzene/water microemulsions,  $T = 25.0$  °C.

Figure 6 shows how the experimental data satisfy eq 18 and how the values of  $K_{oi}^{NPC}$ ,  $K_{oi}^{NPC} = 5.6 \pm 0.9$ , and  $K_{ow}^A$ ,  $K_{ow}^A = 1.9 \pm 0.2$ , can be obtained.

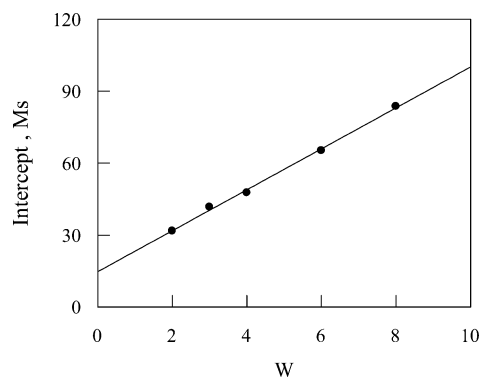
Similarly, from the intercepts of eq 16 (Figure 5), the following equation can be derived

$$\text{intercept} = \frac{K_{oi}^A + K_{oi}^{NPC}}{k_2^i K_{oi}^{NPC} K_{oi}^A} + \frac{K_{ow}^A}{k_2^i K_{oi}^{NPC} K_{oi}^A} W \cong \frac{1}{k_2^i K_{oi}^A} + \frac{K_{ow}^A}{k_2^i K_{oi}^{NPC} K_{oi}^A} W \quad (19)$$

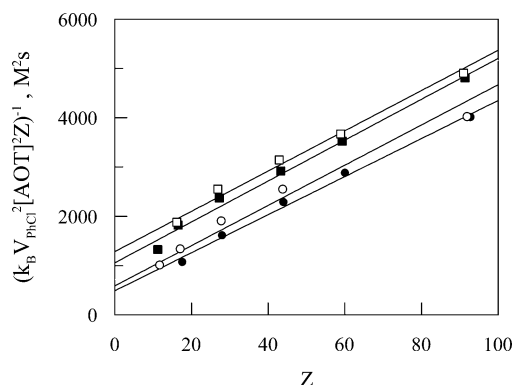
This predicts the existence of a linear dependence between the intercepts of Figure 5 and the  $W$  parameter of microemulsion composition. Figure 7 illustrates the satisfactory fulfillment of eq 19.

To obtain the values of the rate constant at the interface of the microemulsion, it is necessary to know the value of  $K_{oi}^A$ . As will be seen later, we can estimate a maximum value of  $K_{oi}^A = 0.28$ , which allows us to determine a value for the rate constant of  $k_2^i = 0.13 \text{ M}^{-1} \text{ s}^{-1}$  using eq 19 and the values of the intercept and slope of the plot in Figure 7. This value for the rate constant approaches that observed for the aminolysis of 4-nitrophenyl acetate by piperazine in AOT/isooctane/water microemulsions,  $k_2^i = 0.39 \text{ M}^{-1} \text{ s}^{-1}$ .

Due to the micellization of NPC in aqueous medium, it is difficult to determine its butylaminolysis rate constant. However, a value of  $k_2^w = 3 \text{ M}^{-1} \text{ s}^{-1}$  can be extrapolated from its aminolysis rate constants by decyl-, nonyl-, octyl-, heptyl-, and



**Figure 7.** Verification of eq 19 with the values obtained from Figure 5 for the aminolysis of NPC in AOT/chlorobenzene/water microemulsions,  $T = 25.0$  °C.



**Figure 8.** Plot of experimental data according to eq 20 for the aminolysis of NPC in AOT/chlorobenzene/water microemulsions: [NPC] =  $5 \times 10^{-5}$  M,  $T = 25.0$  °C, (●)  $W = 2$ , (○)  $W = 3$ , (■)  $W = 6$ , and (□)  $W = 8$ .

hexylamine.<sup>29</sup> Thus, we can estimate that the decrease in the rate constant is 23 times on going from the aqueous medium to the interface of the microemulsion, an inhibition that is entirely consistent with the behavior observed for other aminolysis reactions in AOT-based microemulsions.<sup>16</sup>

**2. Reaction in the Continuous Medium.** On the basis of eq 15 and taking into account that under our experimental conditions the following inequality is satisfied

$$(2K_{oi}^A + 2K_{ow}^A W + K_{oi}^{NPC})Z^2 + Z^3 \gg (K_{oi}^{A^2} + 2K_{oi}^A K_{ow}^A W + K_{ow}^{A^2} W^2)K_{oi}^{NPC} + \{(K_{oi}^{A^2} + 2K_{oi}^A K_{ow}^A W + K_{ow}^{A^2} W^2) + (2K_{oi}^A + 2K_{ow}^A W)K_{oi}^{NPC}\}Z$$

we can obtain

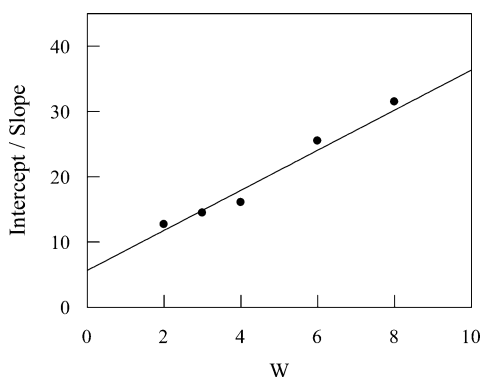
$$\frac{1}{k_B V_o^2 [AOT]^2 Z} = \frac{K_{oi}^{NPC} + 2K_{oi}^A + 2K_{ow}^A W}{k_2^o K^T} + \frac{1}{k_2^o K^T} Z \quad (20)$$

This equation predicts the existence of a linear dependence between  $1/(k_B V_o^2 [AOT]^2 Z)$  and the  $Z$  parameter of microemulsion composition, as shown by Figure 8.

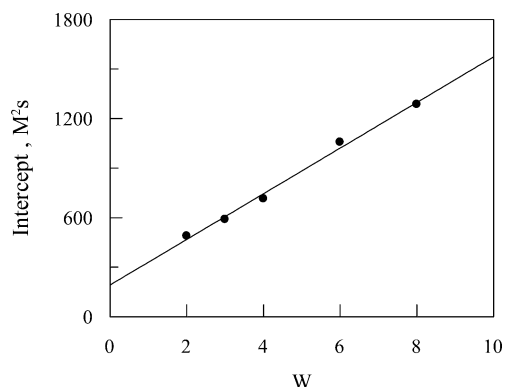
From the intercept/slope ratio of the plots in Figure 8, the following relationship can be derived

$$\text{intercept/slope} = K_{oi}^{NPC} + 2K_{oi}^A + 2K_{ow}^A W \quad (21)$$

which, as will be seen below, can be simplified to: intercept/slope =  $K_{oi}^{NPC} + 2K_{ow}^A W$ . Figure 9 shows the existence of a



**Figure 9.** Verification of eq 21 with the values obtained from Figure 8 for the aminolysis of NPC in AOT/chlorobenzene/water microemulsions,  $T = 25.0\text{ }^{\circ}\text{C}$ .



**Figure 10.** Verification of eq 22 with the values obtained from Figure 8 for the aminolysis of NPC in AOT/chlorobenzene/water microemulsions,  $T = 25.0\text{ }^{\circ}\text{C}$ .

good linear dependence between the intercept/slope ratio and the  $W$  parameter of microemulsion composition.

On the basis of the plot in Figure 9, the values of  $K_{oi}^{NPC}$ ,  $K_{oi}^{NPC} = 5.6 \pm 1.6$ , and  $K_{ow}^A$ ,  $K_{ow}^A = 1.5 \pm 0.2$ , can be obtained. The values obtained for  $K_{oi}^{NPC}$  and  $K_{ow}^A$  are in agreement with those previously obtained by studying the reaction at the interface of the microemulsion:<sup>30</sup>  $K_{oi}^{NPC} = 5.6 \pm 0.9$  and  $K_{ow}^A = 1.9 \pm 0.2$ .

By the use of the approach of  $K_{oi}^{NPC} \gg K_{oi}^A$ , the intercepts of eq 20 (Figure 8) can be rewritten as

$$\text{intercept} = \frac{K_{oi}^{NPC}}{k_2^o K^T} + \frac{2K_{ow}^A}{k_2^o K^T} W \quad (22)$$

Figure 10 shows the good fulfillment of eq 22. Through the use of the previously obtained values of  $K_{oi}^{NPC} = 5.6$  and  $K_{ow}^A = 1.7$ , it is possible to obtain the value of the product  $k_2^o K^T$ ,  $k_2^o K^T = 2.46 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ , which is in good agreement with that obtained in pure chlorobenzene,  $k_2^o K^T = 2.09 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ . This result allows us to conclude that the properties of the continuous medium in w/o microemulsions are equal to those of the pure solvent.

## Conclusions

The application of the pseudophase formalism has allowed us to explain the kinetic behavior observed in w/o microemulsions where the reaction takes place simultaneously at the interface and in the continuous medium, exhibiting a different kinetic behavior which can be attributed to the fact that the rate-determining steps are different in both media. At the interface of the microemulsion, the rate-determining step is the formation

of the addition intermediate,  $T^{\pm}$ , whereas in the continuous medium the rate-determining step is the base-catalyzed decomposition of this intermediate. From the analysis of the kinetic data, we have been able to determine the value of the rate constant at the interface, which is in agreement with the results reported for other aminolysis reactions of carboxylic esters.

The value obtained for the rate constant in the continuous medium is perfectly consistent with that obtained in pure solvent, suggesting that its properties are not affected by the microemulsion.

**Acknowledgment.** Financial support from the Xunta de Galiza (PGIDT03-PXIC20905PN and PGIDT04TMT209003PR) and Ministerio de Ciencia y Tecnología (Project BQU2002-01184 and HP03-34) is gratefully acknowledged.

**Supporting Information Available:** Tables showing the influence of *n*-butylamine concentration on two observed rate constants in NPC aminolysis in AOT/chlorobenzene/water microemulsions at various  $W$  values. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(28) To obtain eq 16, we have assumed that  $(K_{oi}^{NPC} + K_{oi}^A + K_{ow}^A)Z + Z^2 \gg K_{oi}^{NPC}(K_{oi}^A + K_{ow}^A W)$  whose validity can be checked on the basis of the values of the different distribution constants and the parameters of microemulsion composition.

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(30) The values obtained for  $K_{oi}^{NPC}$  allow us to justify the approximations made in eqs 17, 19, and 21. In eq 17, we can obtain  $K_{oi}^{NPC} + K_{oi}^A = 5.6 \pm 0.9$  for the reaction at the interface, whereas for the reaction in the continuous medium we can obtain  $K_{oi}^{NPC} + 2K_{oi}^A = 5.6 \pm 1.6$ , which indicates that  $K_{oi}^{NPC} \gg K_{oi}^A$ . Thus, we can estimate a maximum value of  $K_{oi}^A$ ,  $K_{oi}^A = 0.28$ .