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Simultaneous Effect of Microemulsions and Phase-Transfer Agents on Aminolysis Reactions

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The catalytic effect of triethylene glycol dimethyl ether (glyme) on the butylaminolysis of 4-nitrophenylcaprate (NPC) in water/AOT/chlorobenzene microemulsions has been studied. Experimental results show the existence of four simultaneous reaction pathways. One of them takes place at the microemulsion interphase where the rate-determining step of butylaminolysis is the formation of the addition intermediate, T^\pm . The locus of the other three pathways is the continuous medium of the microemulsion. These three pathways consist of the decomposition of the addition intermediate catalyzed by butylamine, by glyme, and by both of them. The kinetic model allows us to obtain the value of every rate and distribution constant involved in the overall reaction mechanism. We must emphasize that the reactions located in the continuous medium exhibit a kinetic behavior similar to the corresponding one found in pure chlorobenzene. On the basis of the pseudophase model, the percentage of reaction in each of the microdomains of the microemulsion has been calculated. Likewise, changes in the loci of reaction from the interphase to the continuous medium as a function of catalyst concentration have been proved.

Introduction

Microemulsions are defined as thermodynamically stable and optically transparent macroscopically homogeneous mixtures of oils, water, and surfactants.¹ Microemulsions, with droplet sizes in the range of 50–500 Å, are formed by adding an amphiphile to a system containing water and oil (usually a hydrocarbon). In a microemulsion, high concentrations of both water-soluble and water-insoluble compounds can be dissolved simultaneously.² Due to their large interfacial area, microemulsions have been used to accelerate chemical processes and to induce regioselectivity in organic reactions as a function of their composition.³ Microemulsions have also been used in various catalytic⁴ processes: oxidation,⁵ hydroformylation,⁶ carbonylation,⁷ dehalogenation,⁸ and free-radical chain polymerization,⁹ as well as a media for enzymatic¹⁰ reactions, for enhanced oil recovery,¹¹ and as a mobile phase in chromatographic solutions.¹² The microemulsion environment, although dynamic, could nevertheless influence catalyst–substrate orientations or conformational preferences and thereby affect the resultant enantioselectivity.¹³ Additionally, the unique properties of the water pool at the interior of these aggregates could play an important role in catalysis.

Use of a microemulsion as a reaction medium constitutes an alternative to phase-transfer catalysis.¹⁴ 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. The surface area between water and oil can reach values as high as 10^5 m²/L of microemulsion.¹⁵ In comparison with phase-transfer catalysis, several reactions show enhanced reaction rates in microemulsions, for instance, the oxidation of different hydrophobic

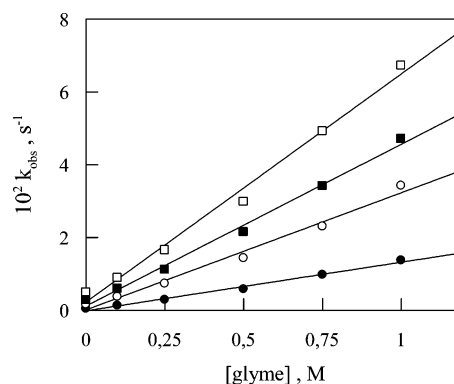


Figure 1. Influence of glyme concentration on NPC butylaminolysis rate constant, k_{obs} , in AOT/chlorobenzene/water microemulsions; $W = 2$, $[\text{AOT}] = 0.30$ M, $T = 25.0$ °C. (●) $[\text{BuNH}_2] = 0.10$ M; (○) $[\text{BuNH}_2] = 0.22$ M; (■) $[\text{BuNH}_2] = 0.30$ M; (□) $[\text{BuNH}_2] = 0.40$ M.

substrates,¹⁶ alkylation of phenol,¹⁷ nucleophilic substitution reactions,¹⁸ as well as catalytic, enantioselective oxidations of olefins.¹⁹

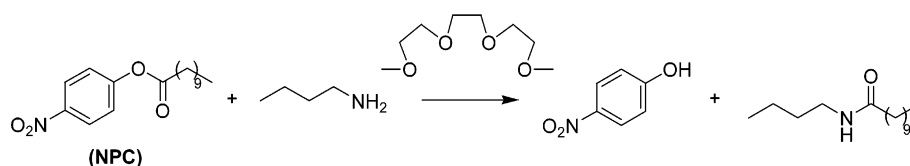
The microemulsion approach and the phase-transfer agent approach can be combined, yielding together the highest reaction rates.²⁰ Use of phase-transfer agents in the presence of micelles and macroemulsions is well documented;^{21,22} however, there are only a few reports in the literature on the use of phase-transfer agents in combination with microemulsions.^{20c,23} Häger and Holmberg^{20b} have studied the reaction between 4-*tert*-butylbenzyl bromide and potassium iodide in microemulsions and two-phase systems in the presence of phase-transfer agents. Likewise, they have shown that the combined approach, that is, the use of a microemulsion as a reaction medium together with the addition of a phase-transfer agent, gives the highest reaction rate. Berkessel²⁴ and co-workers have studied the epoxidation of α,β -unsaturated enones and alkaline hydrogen peroxide in the presence and absence of phase-transfer agents.

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SCHEME 1



Their results show a modest acceleration of the process in microemulsions due to the addition of phase-transfer agent.

The goal of this study will be a first approach to the phase-transfer catalysis in microemulsions making use of a simplified system. Our aim is not to study a process of phase-transfer catalysis but the behavior in microemulsions for a reaction that is catalyzed by the addition of phase-transfer agents. Thus, our study will be centered on the development of a kinetic model that allows explanation of the catalytic effect in microemulsions and analysis of the possibility of a displacement of the locus of reaction in the microemulsion as a result of the addition of a phase-transfer agent. This displacement of the reaction position will constitute the base for the possible synchronous action of phase-transfer and microemulsion catalysis.

With these aims, the effect of AOT-based microemulsions in chlorobenzene and triethylene glycol dimethyl ether (glyme) on the butylaminolysis of 4-nitrophenylcaprate (NPC) has been studied (Scheme 1). Catalysis by phase-transfer agents (crown ethers or glymes) of aminolysis reactions of carboxylic esters is a well-studied process.²⁵ Nucleophilic attack of *n*-butylamine on the ester generates a tetrahedral intermediate,²⁶ T^\pm . This intermediate may either proceed with the catalytic assistance of a second *n*-butylamine molecule or form a complex with the phase-transfer agent, $T^\pm G$. Subsequently, this complex gives rise to the reaction products in the rate-determining step. Recently, we have improved this reaction mechanism²⁷ by showing the existence of a reaction pathway exhibiting a first-order dependence on the concentration of the phase-transfer catalyst and a second-order dependence on the butylamine concentration.

Experimental Section

The *n*-butylamine, *p*-nitrophenylcaprate (NPC), and triethylene glycol dimethyl ether (glyme) were supplied by Aldrich in the highest 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 a 1.00 M AOT/chlorobenzene solution in the appropriate proportions. Kinetic experiments were carried out by following the change in absorbance with time due to the formation of the reaction products at $\lambda = 390$ nm. All of the measurements were recorded using a HP 8453 spectrophotometer thermostated at 25.0 ± 0.1 °C. In all kinetic experiments, the NPC concentration, $[NPC] = 5.00 \times 10^{-5}$ 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_{obs} , was reproducible to within 3%. Moreover, the low $[NPC]$ in comparison with $[AOT]$ typically ranging from 0.10 to 0.60 M guaranteed that the products of the reaction could not alter the properties of the interface because their concentration would be less than 0.05% of the interfacial composition.

The distribution coefficient of NPC between water and chlorobenzene, K_{ow}^{NPC} , was determined by mixing equal volumes of both solvents and adding a constant amount of NPC. 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 $K_{ow}^{NPC} = 8.90 \times 10^{-3}$ was obtained, indicative of the low solubility of NPC in water. The distribution coefficient of *n*-butylamine, K_{ow}^A , was previously calculated,²⁸ $K_{ow}^A = 1.70$. The chlorobenzene–water distribution constant for glyme was kinetically calculated by means of calibration of the catalytic effect of glyme on NPC butylaminolysis in chlorobenzene. After that, a fixed amount of glyme was added to a chlorobenzene–water system, and after equilibration, the catalytic effect of the glyme dissolved in the organic phase was determined. From the catalytic effect on NPC butylaminolysis, the glyme concentration in chlorobenzene was obtained, and therefore, a value of $K_{ow}^G = 0.38$ was calculated.

Results

The influence of phase-transfer catalysts on NPC butylaminolysis in AOT/chlorobenzene/water microemulsions has been investigated. With that purpose, the influence of glyme concentration on k_{obs} has been studied for different *n*-butylamine concentrations at different microemulsion compositions. The composition of the microemulsion was varied using two *W* values, $W = [H_2O]/[AOT]$, $W = 2$ and 6. In each case, the surfactant concentration ranged between $[AOT] = 0.10$ and 0.60 M. Figures 1 and 2 show, as an example, the k_{obs} values obtained for $W = 2$ and 6 at a constant surfactant concentration, $[AOT] = 0.30$ M. In both cases, the glyme concentration for different *n*-butylamine concentrations was varied. The k_{obs} obtained exhibited a linear relationship with the glyme concentration, with a remarkable catalysis. Thus, a 1.0 M glyme concentration implies a rate increase higher than 700%.

The observed kinetic behavior for the NPC butylaminolysis rate constant in AOT/chlorobenzene/water microemulsions in the presence of glymes can be easily rationalized by taking into account that the overall process rate constant, k_{obs} , shows two different contributions. One of them is due to the glyme noncatalyzed reaction,²⁸ $k_{obs}^{noncat} = k_A[BuNH_2] + k_B[BuNH_2]^2$, and the other one is due to the glyme-catalyzed pathways,

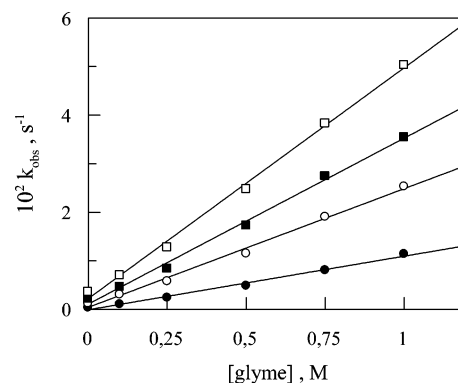


Figure 2. Influence of glyme concentration on NPC butylaminolysis rate constant, k_{obs} , in AOT/chlorobenzene/water microemulsions; $W = 6$, $[AOT] = 0.30$ M, $T = 25.0$ °C. (●) $[BuNH_2] = 0.1$ M; (○) $[BuNH_2] = 0.22$ M; (■) $[BuNH_2] = 0.3$ M; (□) $[BuNH_2] = 0.4$ M.

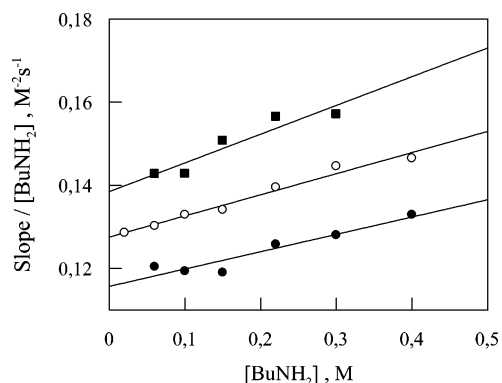


Figure 3. Representation of the obtained experimental results for NPC butylaminolysis in AOT/chlorobenzene/water microemulsions, in agreement with eq 3; $W = 2$; $T = 25.0\text{ }^{\circ}\text{C}$. (●) $[\text{AOT}] = 0.15\text{ M}$; (○) $[\text{AOT}] = 0.2\text{ M}$; (■) $[\text{AOT}] = 0.45\text{ M}$.

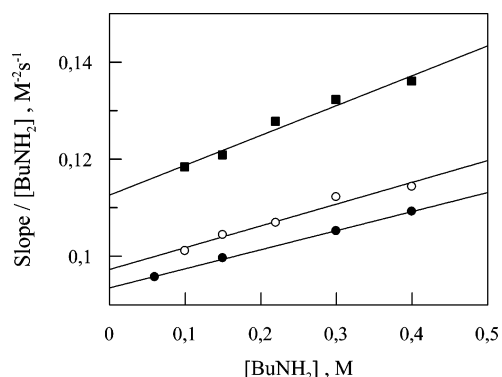


Figure 4. Representation of the obtained experimental results for NPC butylaminolysis in AOT/chlorobenzene/water microemulsions, in agreement with eq 3; $W = 6$; $T = 25.0\text{ }^{\circ}\text{C}$. (●) $[\text{AOT}] = 0.15\text{ M}$; (○) $[\text{AOT}] = 0.2\text{ M}$; (■) $[\text{AOT}] = 0.45\text{ M}$.

$k_{\text{obs}}^{\text{cat}} = (k_{\text{C}}[\text{BuNH}_2] + k_{\text{D}}[\text{BuNH}_2]^2)[\text{G}]$. Thus, the global process can be described by the following equation

$$k_{\text{obs}} = k_{\text{obs}}^{\text{noncat}} + k_{\text{obs}}^{\text{cat}} = k_{\text{A}}[\text{BuNH}_2] + k_{\text{B}}[\text{BuNH}_2]^2 + (k_{\text{C}}[\text{BuNH}_2] + k_{\text{D}}[\text{BuNH}_2]^2)[\text{G}] \quad (1)$$

Equation 1 predicts the existence of a linear relationship between k_{obs} and the glyme concentration. This relationship is confirmed in Figures 1 and 2. The slope of the linear fit of k_{obs} values against the glyme concentration, Figures 1 and 2, corresponds to the following equation

$$\text{slope} = k_{\text{C}}[\text{BuNH}_2] + k_{\text{D}}[\text{BuNH}_2]^2 \quad (2)$$

Equation 2 can be rearranged as

$$\frac{\text{slope}}{[\text{BuNH}_2]} = k_{\text{C}} + k_{\text{D}}[\text{BuNH}_2] \quad (3)$$

This equation predicts the existence of a linear relationship between the ratio $\text{slope}/[\text{BuNH}_2]$ and the amine concentration. From the linear fit of the experimental results to eq 3 (Figures 3 and 4), we can obtain the apparent rate constant values k_{C} and k_{D} (see Table 1). The rate constant k_{C} corresponds to the reaction pathway where the complex T^{\pm}G evolves directly to products. On the other hand, k_{D} corresponds to the macroscopic rate constant in which the reaction pathway implies the assistance of a second amine molecule in the evolution of the T^{\pm}G complex to products.

As it is deduced from the data shown in Table 1, there is no clear dependence between k_{C} and k_{D} with surfactant concentration, although the increase of W yields a slight decrease of these macroscopic rate constants. This behavior may be due to a displacement of the amine and glyme toward the aqueous microphase. This displacement hinders the reaction in the continuous medium. As a comparison, k_{C} and k_{D} values obtained in pure chlorobenzene are shown in Table 1. The values obtained in the continuous medium are close to the corresponding ones determined in pure chlorobenzene.

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 organic solvent (o), and an interface formed fundamentally by the surfactant (i). As usual, upon studying the reactivity in colloidal systems (micelles, vesicles, and microemulsions), the activity coefficients of the components in these systems are independent of their concentrations. There is a controversy in the scientific community about the microstructure of water in oil microemulsions, mainly at very low water contents. In fact, some authors have suggested that for low water contents, the aggregate microstructure will deviate from the droplet model. Therefore, the pseudophase model considering the existence of three pseudophases should be wrong. However, recent results from our laboratory studying the effect of AOT-based microemulsions on the reaction between crystal violet and the sulfite ion have shown irrefutable evidence of the existence of three well-differentiated microenvironments in the AOT-based microemulsions, even at very low water contents.²⁹ The existence of three well-differentiated microenvironments is also supported by the degree of counterion binding to the surfactant,³⁰ FT-IR studies,^{31,32} photon correlation spectroscopy,³³ SAXS, and SANS,³⁴ as well as by the use of microemulsions as templates for the synthesis of nanoparticles.³⁴

1. Kinetic Parameters. The low solubility of NPC in water excludes the possibility of its distribution between the three pseudophases of the microemulsion. Thus, NPC and BuNH_2 will only come into contact with each other at the interface and in the continuous medium. Previous studies²⁸ carried out in our laboratory in the absence of a phase-transfer catalyst have shown that butylaminolysis of NPC takes place simultaneously at the continuous medium and the interface of the microemulsion, where the rate-determining step corresponds to the decomposition and formation of T^{\pm} , respectively. On the other hand, NPC aminolysis can exhibit catalysis by phase-transfer agents (crown ether or glymes) in chlorobenzene.²⁷

In order to raise a mechanism for NPC butylaminolysis in AOT-based microemulsions catalyzed by glymes, we must consider the simultaneous effect of the microemulsion and the glyme. As glyme is distributed between the three pseudophases, it can take part in the aminolysis reaction both at the AOT film and in the continuous medium. Nevertheless, bibliographic results³⁵ show that catalysis by crown ethers and glymes is not appraised when the rate-determining step is the formation of the addition intermediate, T^{\pm} . Therefore, we can exclude the possibility that glyme acts as a catalyst at the interphase. Hence, its only function will be to catalyze the reaction pathways

TABLE 1: Macroscopic Rate Constants for NPC Aminolysis for Different Microemulsion Compositions Obtained from the Fit of the Experimental Results to Eq 5

<i>W</i>	[AOT], M	<i>Z</i>	$k_C, M^{-2} s^{-1}$	$k_D, M^{-3} s^{-1}$
2	0.10	82.915	$(1.14 \pm 0.03) \times 10^{-1}$	$(4.28 \pm 1.07) \times 10^{-2}$
2	0.15	53.947	$(1.16 \pm 0.02) \times 10^{-1}$	$(4.16 \pm 0.07) \times 10^{-2}$
2	0.20	39.463	$(1.28 \pm 0.01) \times 10^{-1}$	$(5.08 \pm 0.36) \times 10^{-2}$
2	0.30	24.979	$(1.29 \pm 0.01) \times 10^{-1}$	$(6.76 \pm 0.55) \times 10^{-2}$
2	0.45	15.323	$(1.38 \pm 0.03) \times 10^{-1}$	$(6.94 \pm 1.43) \times 10^{-2}$
2	0.60	10.495	$(1.52 \pm 0.03) \times 10^{-1}$	$(8.14 \pm 1.51) \times 10^{-2}$
6	0.10	88.934	$(7.89 \pm 0.38) \times 10^{-2}$	$(2.86 \pm 1.46) \times 10^{-2}$
6	0.15	56.229	$(9.35 \pm 0.02) \times 10^{-2}$	$(3.93 \pm 0.07) \times 10^{-2}$
6	0.20	39.877	$(9.72 \pm 0.12) \times 10^{-2}$	$(4.51 \pm 0.46) \times 10^{-2}$
6	0.30	24.272	$(1.01 \pm 0.03) \times 10^{-1}$	$(4.96 \pm 1.34) \times 10^{-2}$
6	0.45	14.616	$(1.13 \pm 0.02) \times 10^{-1}$	$(6.16 \pm 0.61) \times 10^{-2}$
6	0.60	10.161	$(1.08 \pm 0.12) \times 10^{-1}$	$(6.13 \pm 1.43) \times 10^{-2}$
PhCl			$(9.40 \pm 0.07) \times 10^{-2}$	$(3.17 \pm 0.30) \times 10^{-2}$

located in the continuous medium. Taking into account these factors, we can propose the following reaction mechanism (Scheme 2).

This complex reaction mechanism assumes the existence of a four-pathway reaction. There are two non-glyme-catalyzed pathways, one at the AOT film, k_2^i , and another in the continuous medium, k_2^o . Also, there are two glyme-catalyzed pathways in the continuous medium. These two go through the complex formation between the addition intermediate, $[T^\pm]_o$, and the catalyst; one of them goes through a spontaneous decomposition of $[T^\pm G]_o$, $(k_1^G)^o$, while the other one goes through the assistance of a second butylamine molecule upon this complex, $(k_2^G)^o$. From this mechanism, the following rate equation can be obtained (see Supporting Information for a complete deduction of eq 4)³⁶

$$k_{\text{obs}} = \frac{k_2^i K_{\text{oi}}^{\text{NPC}} K_{\text{oi}}^{\text{A}} [\text{BuNH}_2]_{\text{T}}}{\bar{V}_{\text{AOT}} [\text{AOT}] (K_{\text{oi}}^{\text{NPC}} + Z) (K_{\text{oi}}^{\text{A}} + Z + K_{\text{ow}}^{\text{A}} W)} + \frac{k_2^o K^{\text{T}} Z [\text{BuNH}_2]_{\text{T}}^2}{\bar{V}_o [\text{AOT}]^2 (K_{\text{oi}}^{\text{NPC}} + Z) (K_{\text{oi}}^{\text{A}} + Z + K_{\text{ow}}^{\text{A}} W)^2} + \frac{(k_1^G)^o K^{\text{T}} K^{\text{TG}} Z [\text{BuNH}_2]_{\text{T}} [G]_{\text{T}}}{\bar{V}_o^2 [\text{AOT}]^2 (K_{\text{oi}}^{\text{NPC}} + Z) (K_{\text{oi}}^{\text{A}} + Z + K_{\text{ow}}^{\text{A}} W) (K_{\text{oi}}^{\text{G}} + Z + K_{\text{ow}}^{\text{G}} W)} + \frac{(k_2^G)^o K^{\text{T}} K^{\text{TG}} Z [\text{BuNH}_2]_{\text{T}}^2 [G]_{\text{T}}}{\bar{V}_o^3 [\text{AOT}]^3 (K_{\text{oi}}^{\text{NPC}} + Z) (K_{\text{oi}}^{\text{A}} + Z + K_{\text{ow}}^{\text{A}} W)^2 (K_{\text{oi}}^{\text{G}} + Z + K_{\text{ow}}^{\text{G}} W)} \quad (4)$$

This equation is analogous to the empirical equation obtained previously, eq 1. The apparent rate constants, k_A , k_B , k_C , and k_D can be expressed as a function of the real rate constants in the

different microemulsion pseudophases, the reactant distribution constants, and the microemulsion composition parameters

$$k_A = \frac{k_2^i K_{\text{oi}}^{\text{NPC}} K_{\text{oi}}^{\text{A}}}{\bar{V}_{\text{AOT}} [\text{AOT}] (K_{\text{oi}}^{\text{NPC}} + Z) (K_{\text{oi}}^{\text{A}} + Z + K_{\text{ow}}^{\text{A}} W)} \quad (5)$$

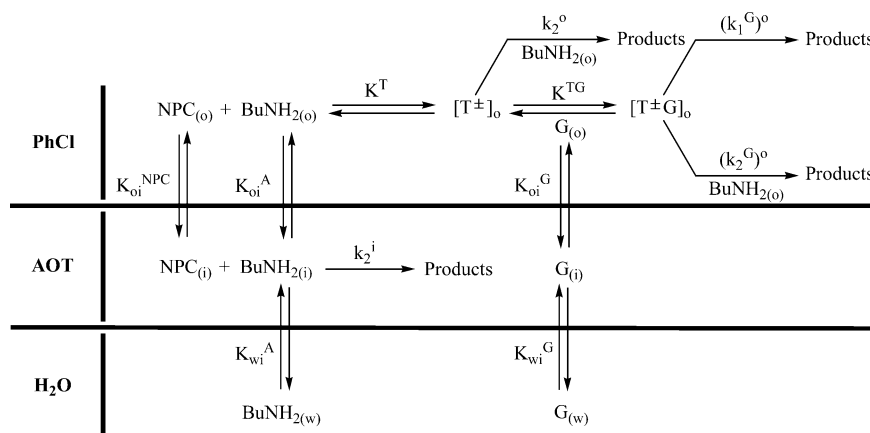
$$k_B = \frac{k_2^o K^{\text{T}} Z}{\bar{V}_o^2 [\text{AOT}]^2 (K_{\text{oi}}^{\text{NPC}} + Z) (K_{\text{oi}}^{\text{A}} + Z + K_{\text{ow}}^{\text{A}} W)^2} \quad (6)$$

$$k_C = \frac{(k_1^G)^o K^{\text{T}} K^{\text{TG}} Z}{\bar{V}_o^2 [\text{AOT}]^2 (K_{\text{oi}}^{\text{NPC}} + Z) (K_{\text{oi}}^{\text{A}} + Z + K_{\text{ow}}^{\text{A}} W) (K_{\text{oi}}^{\text{G}} + Z + K_{\text{ow}}^{\text{G}} W)} \quad (7)$$

$$k_D = \frac{(k_2^G)^o K^{\text{T}} K^{\text{TG}} Z}{\bar{V}_o^3 [\text{AOT}]^3 (K_{\text{oi}}^{\text{NPC}} + Z) (K_{\text{oi}}^{\text{A}} + Z + K_{\text{ow}}^{\text{A}} W)^2 (K_{\text{oi}}^{\text{G}} + Z + K_{\text{ow}}^{\text{G}} W)} \quad (8)$$

At this point, we must prove if our experimental results (shown in Table 1) verify the predicted behaviors of eqs 7 and 8.³⁷ These equations can be simplified by taking into account the distribution constants of NPC and *n*-butylamine that were previously determined:²⁸ $K_{\text{oi}}^{\text{NPC}} = 5.6$, $K_{\text{oi}}^{\text{A}} = 0.28$, $K_{\text{ow}}^{\text{A}} = 1.70$. The glyme constant distribution value in a water/chlorobenzene biphasic system has been obtained ($K_{\text{ow}}^{\text{G}} = 0.38$). With these values, eq 7 can be written as³⁸

SCHEME 2



$$k_C = \frac{(k_1^G)^\circ K^T K^{TG} Z}{0.102^2 [\text{AOT}]^2 (5.6 + Z)(0.28 + Z + 1.70W)(K_{oi}^G + Z + 0.38W)} \quad (9)$$

This expression can be rearranged as eq 10. This equation predicts the existence of a linear relationship between Y_C , $Y_C = 0.102^2 [\text{AOT}]^2 (5.6 + Z)(0.28 + Z + 1.70W)(Z + 0.38W)k_C$, and Z , $Z = [\text{Oil}]/[\text{AOT}]$

$$Y_C = 0.102^2 [\text{AOT}]^2 (5.6 + Z)(0.28 + Z + 1.70W)(Z + 0.38W)k_C = (k_1^G)^\circ K^T K^{TG} Z \quad (10)$$

Figure 5 (Table 1 values) shows the good agreement of our data with eq 10, and it allows us to obtain a value of $(k_1^G)^\circ K^T K^{TG}$, $(k_1^G)^\circ K^T K^{TG} = (9.66 \pm 0.03) \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$, which is compatible with the corresponding one in pure chlorobenzene, $(k_1^G)^\circ K^T K^{TG} = (9.40 \pm 0.07) \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$.

Also, from the ratio k_C/k_D , we can obtain the following equation

$$\frac{k_C/k_D}{V_o[\text{AOT}]} = \frac{(k_1^G)^\circ (K_{oi}^A + K_{ow}^A W)}{(k_2^G)^\circ} + \frac{(k_1^G)^\circ}{(k_2^G)^\circ} Z \quad (11)$$

This expression predicts the existence of a linear relationship between $(k_C/k_D)/(\bar{V}_o[\text{AOT}])$ and Z . Figure 6 shows the good agreement of the experimental results with eq 11 for $W = 2$ and 6. Zero-compatible values for intercepts are due to $(K_{oi}^A + K_{ow}^A W) \ll Z$.

From the slopes of Figure 6, we can evaluate the ratio of the rate constants of the tetrahedral intermediate–glyme complex that yields the products. At $W = 2$, $(k_1^G)^\circ/(k_2^G)^\circ = 2.93 \pm 0.13 \text{ M}$. At $W = 6$, $(k_1^G)^\circ/(k_2^G)^\circ = 2.91 \pm 0.07 \text{ M}$. These values are compatible with the corresponding one obtained in pure chlorobenzene, $(k_1^G)^\circ/(k_2^G)^\circ = 2.97 \pm 0.03 \text{ M}$. This implies that the reaction pathway through a spontaneous decomposition of an intermediate–glyme complex is favored against the pathway through the assistance of a second butylamine molecule on this complex to form an amide.

Using an average value of $(k_1^G)^\circ/(k_2^G)^\circ = 2.92 \pm 0.07 \text{ M}$ and $(k_1^G)^\circ K^T K^{TG} = (9.66 \pm 0.03) \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$, we obtain $(k_2^G)^\circ K^T K^{TG} = (3.30 \pm 0.08) \times 10^{-2} \text{ M}^{-3} \text{ s}^{-1}$, which is compatible with the corresponding one in pure chlorobenzene, $(k_2^G)^\circ K^T K^{TG} = (3.17 \pm 0.30) \times 10^{-2} \text{ M}^{-3} \text{ s}^{-1}$. Also, the rate constants of NPC butylaminolysis in AOT-based microemulsions in chlorobenzene in the absence of glymes are $k_2^I = 0.15 \text{ M}^{-1} \text{ s}^{-1}$ at the interphase²⁸ and $k_2^G K^T = 2.09 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ in the continuous medium²⁸. In this way, we can know the values of all of the distribution and rate constants implied in Scheme 2 (Table 2).

2. Reaction Locus Displacement. From the Table 2 values, we can calculate the percentage of reaction which takes place at the interphase. This percentage changes with the microemulsion composition and also with the catalyst concentration.

The interfacial reaction percentage is calculated as the % interfacial reaction = $100k_A/(k_A + k_B[\text{BuNH}_2])$ for the reaction in the absence of a phase-transfer catalyst. Figure 7 shows the changes in the percentage with amine concentration and microemulsion composition parameters. We must emphasize that the percentage of interfacial reaction decreases upon increasing amine concentration in the microemulsion. This behavior is due to the two different pathways of reaction at the interphase and

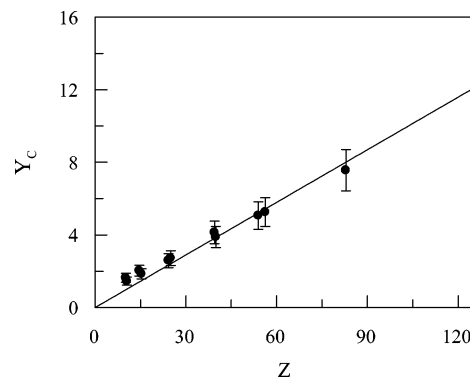


Figure 5. Representation of $Y_C = 0.102^2 [\text{AOT}]^2 (5.6 + Z)(0.28 + Z + 1.70W)(Z + 0.38W)k_C$ versus Z (eq 10).

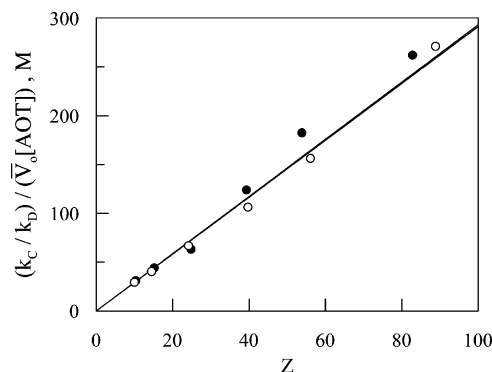


Figure 6. Linear relationship (eq 11) for NPC butylaminolysis in AOT/chlorobenzene/water microemulsions; $T = 25^\circ \text{C}$. (●) $W = 2$; (○) $W = 6$.

the continuous medium. At the interphase, the reaction rate presents a linear relationship with amine concentration, where the rate-determining step is the intermediate formation, T^\pm . In the continuous medium, the rate exhibits a quadratic dependence with the amine concentration, which implies that the rate-determining step would be the catalyzed decomposition of T^\pm . As the increase in the amine concentration yields an increase of the importance of the catalyzed pathway, it would be reasonable that the percentage of reaction in the continuous medium increases too.

Keeping a constant BuNH_2 concentration, the percentage of interfacial reaction seems independent of W (Figure 7, left). This behavior is due to the reactant distribution, mainly in the continuous medium and at the interphase. Figure 7, right, shows that by keeping a constant $[\text{BuNH}_2]$, the percentage of interfacial reaction increases upon increasing the AOT concentration (due to the incorporation of the reactants in the interphase, which implies the increase of their local concentrations). The increase of interfacial reaction is much greater as the butylamine concentration decreases. This behavior is due to the contribution of the amine in the displacement of the reaction loci to the continuous medium.

The addition of a phase-transfer catalyst exerts a very significant effect on the percentage of interfacial reaction. In this case, the percentage of interfacial reaction is calculated by $\% = 100k_A/(k_A + k_B[\text{BuNH}_2] + (k_C + k_D[\text{BuNH}_2])[G])$. Figure 8 shows the displacement of the reaction loci from the interphase to the continuous medium upon increasing the glyme concentration because glyme catalysis is only effective on the reaction in the continuous medium where the rate-limiting step is the addition intermediate decomposition, T^\pm . In the absence of glyme (Figure 8, top), 90% of the reaction takes place at the interface, and at $[\text{glyme}] = 1.00 \text{ M}$, 95% of the reaction takes

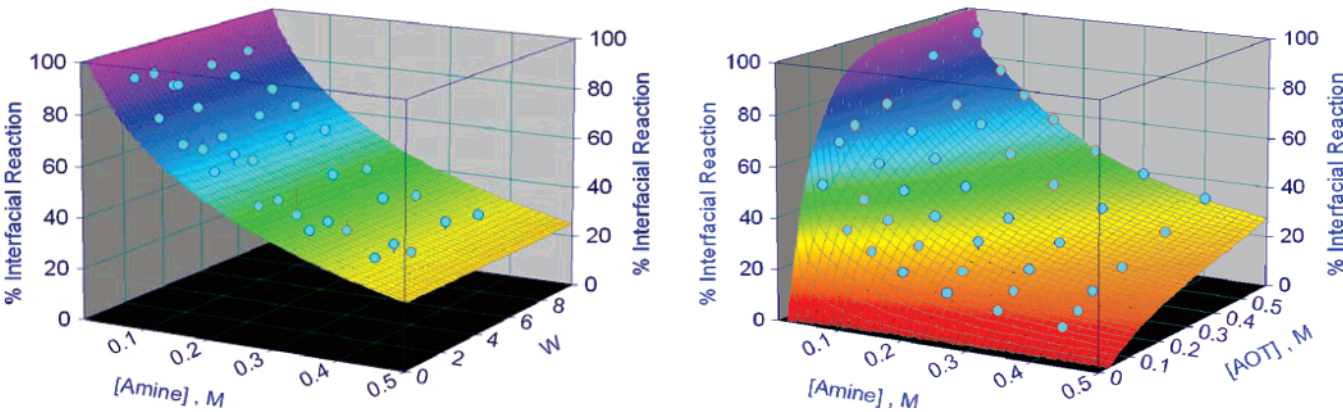


Figure 7. Influence of [BuNH₂], [AOT], and W on the percentage of interfacial reaction for butylaminolysis of NPC in water/AOT/chlorobenzene microemulsions at 25.0 °C.

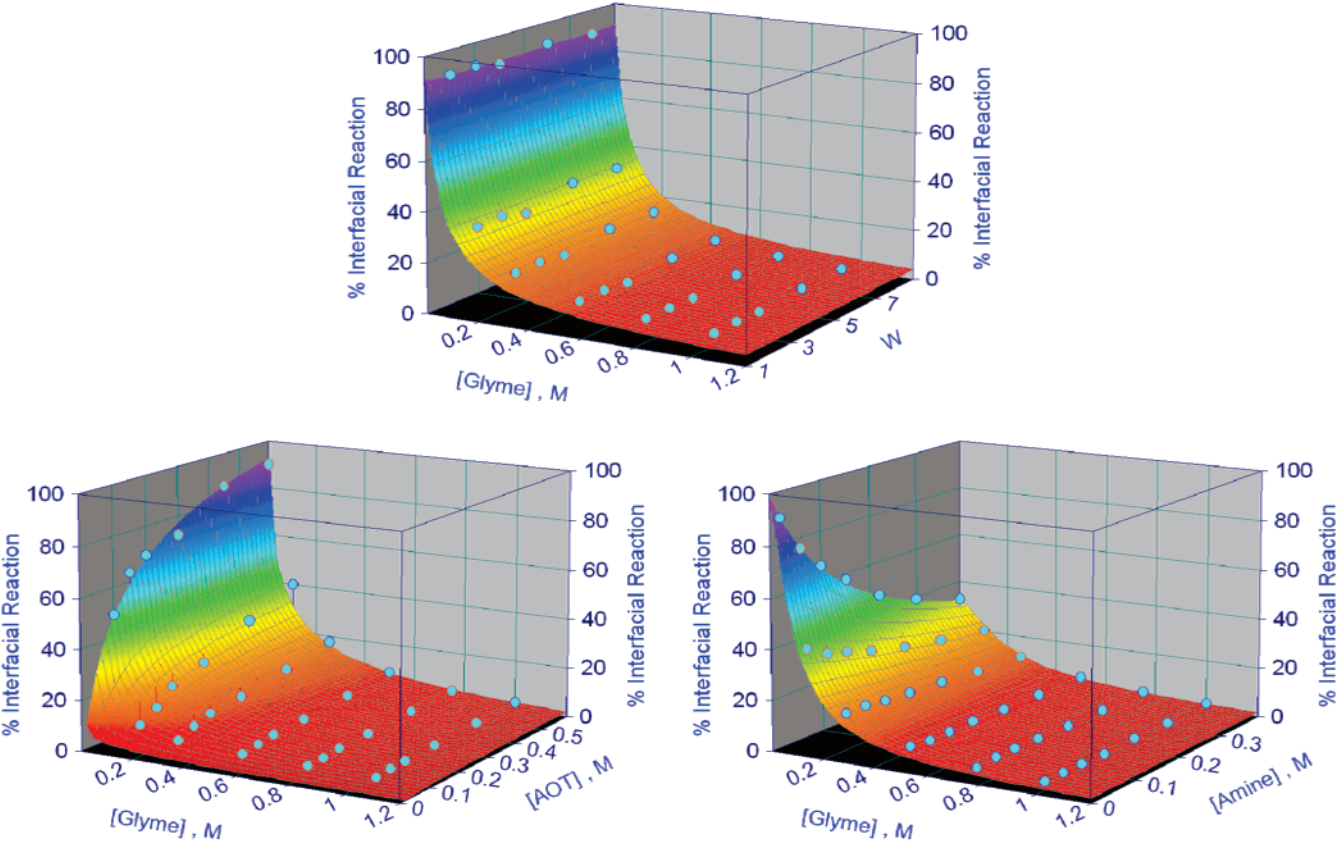


Figure 8. Influence of [BuNH₂], [glyme], [AOT], and W on the percentage of interfacial reaction for butylaminolysis of NPC in water/AOT/chlorobenzene microemulsions at 25.0 °C.

TABLE 2: Rate and Distribution Constants for NPC Butylaminolysis in Water/AOT/Chlorobenzene Microemulsions

distribution constants					
K_{oi}^{NPC}	K_{ow}^{NPC}	K_{oi}^A	K_{wi}^A	K_{ow}^A	K_{ow}^G
5.60 ± 0.92	$(8.90 \pm 0.25) \times 10^{-3}$	≤ 0.28	0.16 ± 0.01	1.70 ± 0.14	0.38 ± 0.03
rate constants					
	k_2^i , $M^{-1} s^{-1}$	$k_2^o K^T$, $M^{-2} s^{-1}$	$(k_1^G)^o K^T K^{TG}$, $M^{-2} s^{-1}$	$(k_2^G)^o K^T K^{TG}$, $M^{-3} s^{-1}$	
microemulsion	0.15	$(2.46 \pm 0.23) \times 10^{-2}$	$(9.66 \pm 0.03) \times 10^{-2}$	$(3.30 \pm 0.08) \times 10^{-2}$	
chlorobenzene		$(2.09 \pm 0.04) \times 10^{-2}$	$(9.40 \pm 0.07) \times 10^{-2}$	$(3.17 \pm 0.30) \times 10^{-2}$	

place in the continuous medium. As the reactants involved in the NPC butylaminolysis are present in the aqueous nanodroplet at very low concentrations, the interfacial reaction percentage will be independent of W.

Figure 8, left, shows the influence of surfactant concentration on the interfacial reaction percentage in the presence of glyme. At low glyme concentrations, the increase of surfactant concentration yields a displacement of the reaction locus to the

interface. However, at high glyme concentrations, the percentage of interfacial reaction is independent of [AOT]. This behavior is due to the increase in glyme concentration that pushes the reaction toward the continuous medium more than the increase in AOT concentration displaces the reaction locus toward the interphase. Figure 8, right, shows the influence of amine concentration on the percentage of interfacial reaction in the presence of glyme. Both the increase of glyme and amine concentration displaces the reaction to the continuous medium.

Conclusions

We have developed a kinetic model that assumes the existence of four simultaneous reaction pathways. One of them takes place at the microemulsion interphase where the rate-determining step of butylaminolysis is the addition intermediate formation, T^\pm . The locus of the other three pathways is the continuous medium of the microemulsion. These pathways consist of the decomposition of the addition intermediate, which is catalyzed by butylamine, by glyme, and by both of them. The reactions located in the continuous medium exhibit a kinetic behavior similar to the corresponding one found in pure chlorobenzene.

The kinetic model proposed has allowed us to obtain the value of every rate and distribution constant involved in the global reaction mechanism. On the basis of the pseudophase model, the percentage of reaction in each of the microdomains of the microemulsion has been calculated. Likewise, changes in the loci of reaction from the interphase to the continuous medium as a function of catalyst concentration have been proved. The locus of reaction is independent of nanodroplet size, but the addition of amine and glyme implies a displacement of the reaction to the continuous medium due to the catalysis of T^\pm decomposition. Surfactant addition displaces the reaction to the interphase, increasing the local concentrations of reactants. The global results would be a combination of both factors.

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Supporting Information Available: A compilation of observed rate constants for different microemulsion compositions and derivation of eq 4 are reported. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(37) Equations 5 and 6 correspond to the reaction in the absence of catalyst, and their validity has been verified in our laboratory.²⁸

(38) The high solubility of glyme in both water and chlorobenzene implies that $K_{oi}^G \ll (K_{ow}^G W + Z)$.