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Nitrosation of Amines in AOT-Based Microemulsions

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Abstract

This chapter is a review of the kinetics of nitrosation of secondary amines by N-methyl-N-nitroso-p-toluenesulfonamide (MNTS) in AOT-based microemulsions. Three regions can be distinguished in these colloids: the internal aqueous nanocore, the micellar interface and the external organic phase. The amines were chosen on the basis of their degrees of solubility resulting in a different distribution. The MNTS has a very low degree of solubility in water and the nitrosation reactions take place at the interface of the aggregates. The polarity changes at the interface have very important effects on the chemical reactivity. This kinetic study compares the results obtained in AOT microemulsions where the polarity at the interface can be tuned by adding a cosurfactant or by changing the continuous medium.

Keywords: AOT, MNTS, nitrosation, kinetics, amines

1. Introduction

Microemulsions are macroscopically homogeneous, thermodynamically stable systems constituted by two immiscible solvents in the presence of a surfactant [1]. Water in oil microemulsions consist of nanodroplets of water dispersed in a nonpolar solvent stabilized by a surfactant monolayer. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) is the most widely used surfactant for preparing microemulsions. The simplest microstructure AOT-based systems are that of spherical water droplets of colloidal dimensions and possess a small degree of polydispersity [2]. The size can be accurately controlled by the water content or, that is, the molar ratio of water to AOT ($W = [H_2O]/[AOT]$).

Transparent water-in-oil dispersions were reported for the first time in 1943 [3]. Hoar and Schulman found that oil can be dissolved in bulk water or water in bulk oil in presence of a soap to produce a homogeneous solution. The oil-surfactant-water systems reported were transparent, electrically non-conducting dispersions, in which the oil was the continuous phase. Dilution of these systems with excess water inverted them to oil-in-water systems. The key factor was the oil/surfactant or water/surfactant ratio (W). Later, Schulman et al. [4], by electron microscopy technique established that such dispersions consist of uniform spherical droplets of either oil or water dispersed in the appropriate continuous phase and were defined as microemulsions.

The first use of AOT as appropriate surfactant in the preparation of ternary systems was published in 1970 [5]. The authors studied the phase equilibria diagram

of the following systems: p-xylene/AOT/water, caprylic acid/AOT/water, and n-decanol/AOT/water. However, isooctane is actually the most widely oil used in the preparation of AOT-based microemulsions, due to the fact that this solvent shows a large region of isotropic transparent solutions, thermodynamically stable. The complete phase equilibria diagram was reported in 1980 [6, 7]. **Figure 1** shows the structure of the isooctane/AOT/water microemulsion.

Among the many applications of these systems, the use of the water pool as a nanoreactor for the preparation of nanoparticles stands out. The nanoparticle size is mainly controlled by the microemulsion size. For instance, ZnS nanoparticles were synthesized and characterized in n-heptane/AOT/water microemulsions [8, 9] and the nanoparticle size can be controlled by the W parameter. Indium-tin oxide ($\text{In}_2\text{O}_3/\text{SnO}_2$) nanoparticles were prepared in isooctane/AOT/water system [10]. The molecular structure of AOT favors the interface curved on the water core. The result is that the monodispersed ultrafine indium-tin oxide particles show better physicochemical properties prepared in microemulsion than in bulk precipitation method. In the same system barium chromate nanostructures (linear chains, rectangular superlattices and long filaments) as a function of reactant molar ratio were prepared [11]. Another example is the synthesis of crystalline nanoparticles of three different molecule-based magnetic materials, cobalt hexacyanoferrate, cobalt pentacyanonitrosylferrate, and chromium hexacyanochromate, by coprecipitation reactions involving mixtures of water-in-oil microemulsions [12].

However, if the objective of the research is the study of microemulsions as chemical nanoreactors, it is necessary to study the details of the processes that take place inside them. Our research group has focused, for more than 20 years, on the study of reaction mechanisms in a wide variety of colloidal systems. From a kinetic point of view, microemulsions are more versatile than other colloids because they provide both organic and aqueous environments. Then, it's possible to simultaneously dissolve both hydrophobic and hydrophilic reagents, each compound being distributed among oil, water, and surfactant film in accordance with its physicochemical nature. In the case of water in oil microemulsions, the properties of the confined water are very different from those of the bulk water due to intermolecular interactions at the micellar interface and to the geometric size constraints of the environment [13]. This characteristic makes possible the use of

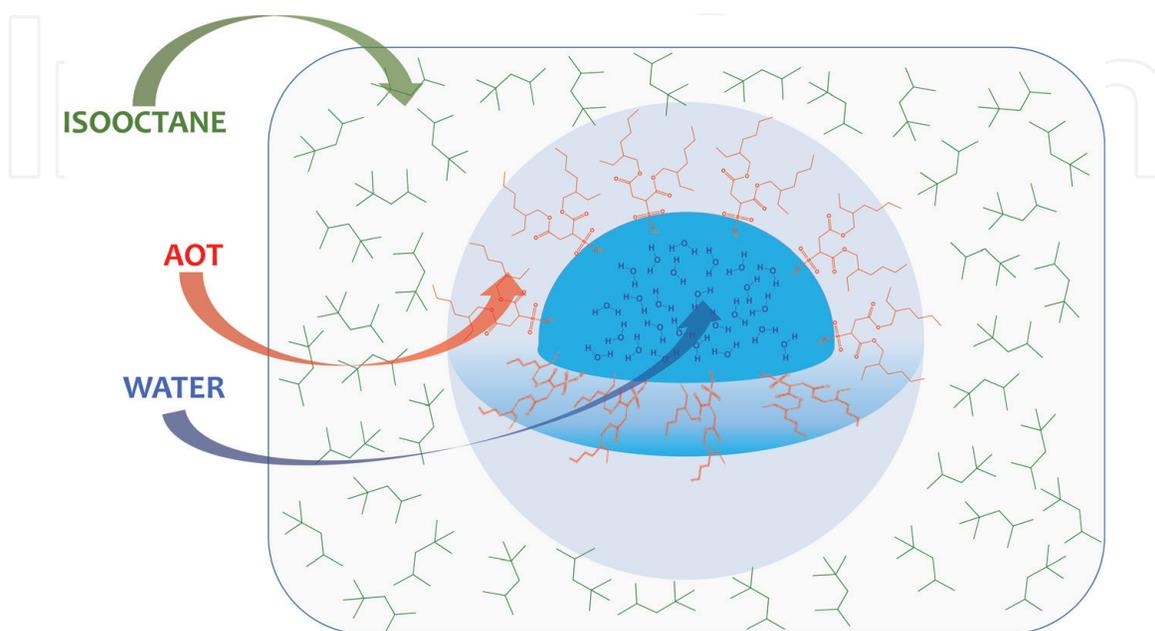


Figure 1.
Schematic illustration of a isooctane/AOT/water microemulsion.

microemulsions as biomimetic models for compartmentalization [14]. Most of these initial kinetic studies have not been able to explain the observed kinetic behavior quantitatively.

In 1993, in our laboratory, García-Río et al. [15] reported the use of the pseudophase formalism as modified for microemulsions. The reaction studied (see **Figure 2**) was the nitrosation of secondary amines by N-methyl-N-nitroso-p-toluenesulfonamide (MNTS) in isooctane/AOT/water microemulsions. The amines studied were piperazine, N-methylbenzylamine, piperidine, dimethylamine, morpholine, pyrrolidine, and diisopropylamine. In that work, the validity of the model for reactions taking place at interface between the water droplet and the isooctane was confirmed. The pseudo-phase model continued to be applied successfully in many reactions carried out in this type of microemulsions. For instance, for nitroso group transfer from 2-ethoxyethyl and 2-bromoethyl nitrite to the secondary amines piperazine, N-methylbenzylamine, and morpholine in isooctane/AOT/water microemulsions [16]. The diverse kinetic behavior was explained quantitatively based on the model considering the distribution of the amine among the aqueous and isooctane phases and their mutual interface; the reaction itself always takes place at the interface. Among all these reactions, we are especially interested in the MNTS reaction with piperazine (PIP), N-methylbenzylamine (NMBA), and morpholine (MOR) (see **Figure 3**). The reason is that these three species represent three different solubilities in water in oil microemulsions. Piperazine is practically insoluble in isooctane, N-methylbenzylamine is poorly soluble in water, and morpholine has considerable solubility in both water and isooctane.

In the kinetic studies carried out in microemulsions, the relative reactivities of the amines are discussed in comparison with those observed in bulk water. The comparison requires knowledge of the molar reaction volume at the interface. An estimation of this volume was made and yields a value of 0.37 M^{-1} for the molar volume of AOT in isooctane/AOT/water microemulsions. The nitroso transfer reactions are 58 times slower at the interface of the microemulsion, which can be attributed to the lower polarity of the interfacial region [17].

In this chapter our objective is to show how the reactivity of AOT-based microemulsions can change due to changes in the continuous medium or the introduction of an anionic cosurfactant at the interface. In colloidal systems, with applications in cosmetics and cleaning products, it is usual to use two surfactants with very different properties. In the case of micellar aggregation, mixtures of surfactants often work better than a single surfactant. For example, in detergents, anionic surfactants are included to maximize solubilization, and non-ionic surfactants to



Figure 2.
Nitrosation reaction of secondary amines by N-methyl-N-nitroso-p-toluenesulfonamide (MNTS).

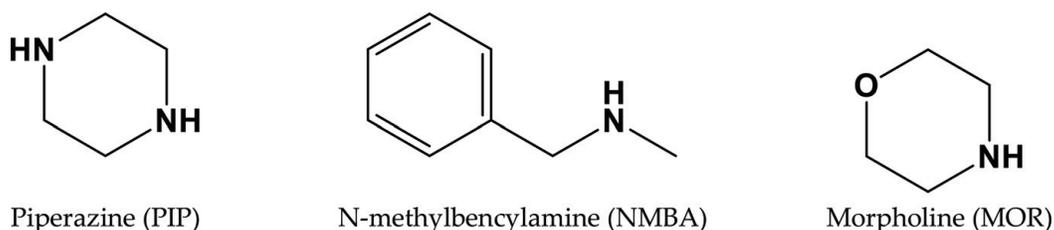


Figure 3.
Structure of the amines.

increase water hardness tolerance. Mixed microemulsions are formed generally by cationic surfactants and long-chain alcohols. Structural and physicochemical characterization of these systems have been published. For example, the position of the alcohol between the interfacial and the bulk oil phase was determined by different experimental techniques [18–21]. Kinetic studies in microemulsions with two surfactants were also carried out in our laboratory. For instance, García-Rio and Hervella reported the nitrosation of piperazine (PIP) and N-methylbenzylamine (NMBA) by N-methyl-N-nitroso-p-toluenesulfonamide (MNTS) in microemulsions of isooctane/tetradecyltrimethylammonium bromide (TTABr)/alcohol/water, varying nature of the alcohols: 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol and 1-decanol [22]. The main conclusion of this article is that the effect of the alcohols is the increase in volume of the interface with the consequent dilution of the reactants. The values of the rate constants obtained in TTABr/alcohol microemulsions were always lower than those obtained in AOT microemulsions. The incorporation of the alcohol into the interface of the microemulsion displaces the water molecules and increases its hydrophobic character.

In this chapter, we present the comparative review of the nitrosation of secondary amines by MNTS nitrosation in two clearly differentiated systems:

1. Microemulsions with AOT and SDS as surfactants [23]. The presence of SDS as a cosurfactant causes a sharp decrease in the electrical percolating temperature, that is, the surfactant film becomes less rigid favoring the transport of matter. The amines (piperazine, N-methylbenzylamine and morpholine) were chosen based on their degrees of solubility in the different components of the microemulsions.
2. AOT-based microemulsions with ortho-, meta- or para-xylene as continuous medium [24]. The use of an aromatic molecule as the continuous medium of a microemulsion modifies the reactivity. In addition, this type of microemulsions has the characteristic of being non-percolative. The amines were chosen based on their different degrees of solubility in the different components of the microemulsion and on the fact that numerous kinetic studies had already been carried out in “normal” microemulsions.

2. Percolation temperature

The first step, to characterize these systems is to analyze the effect of the co-surfactant or the oil on the microstructure of the aggregates. Microemulsions are dynamic structures and electrical conductivity measurements can be a useful method for characterizing aggregate interactions [25]. Microemulsions have a low electrical conductivity ($0.01\text{--}0.1\ \mu\text{S cm}^{-1}$), but higher than that of pure isooctane ($<1 \times 10^{-3}\ \mu\text{S cm}^{-1}$) because they are systems that contain charges. Increasing the temperature, the electrical conductivity of these systems increases gradually, at a temperature from which there is a marked increase in the variation of the electrical conductivity with temperature ($>100\ \mu\text{S cm}^{-1}$). This singularity is known as electrical percolation, and the temperature at which this occurs is known as the threshold of percolation or the temperature of percolation. The values of the threshold of percolation, in a certain microemulsion, can be modified by small quantities of additives. The electrical percolation phenomenon is explained assuming a mechanism involving the formation of channels through which mass is exchanged between disperse water droplets in the continuous phases. An effective collision between two water nanodroplets is necessary to allow the droplets to fuse together.

Then, mass transfer between the water droplets must take place to allow charge to be conducted and the droplets to separate by fission.

AOT-based microemulsions, thermodynamically stable over a wide range of water proportions, are the most extensively examined. The size of these aggregates can be controlled via the parameter W ($W = [\text{H}_2\text{O}]/[\text{AOT}]$) as the droplet radius is directly related to W , $\text{radius} = 1.5 W$ [26]. In the case of ternary isooctane/water/AOT microemulsions, the temperature of percolation decreases by the presence of formamides and urea [27]. However, the presence of amines increases the threshold of percolation [28]. An important effect is observed when adding SDS to water/AOT/isooctane. An increase in the molar ratio $\rho = [\text{SDS}]/[\text{AOT}]$, in isooctane/AOT/SDS/water/microemulsion corresponds with a strong decrease in the percolation threshold for these quaternary microemulsions (see **Figure 4**). The difference between the percolation threshold of a standard AOT-based microemulsion and the quaternary system is more than 40°C . A similar effect was found for the rate constant of matter exchange between droplets. In the case of heptane/AOT/SDS/water system, the value of the rate constant is $1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for $\rho = 0$ (ternary microemulsion) and $2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for $\rho = 0.1$ (quaternary microemulsion) [29]. The explanation was that SDS tends to locate at the water-hydrocarbon interface, thus causing a disruption of the surfactant head groups at the interface, which, in turn, promotes a more rapid exchange of pool components on pool encounters.

Maximum water solubilization capacity of the quaternary system was studied by adding an appropriate volume of water to samples containing known amounts of AOT, SDS and isooctane under continuous stirring until permanent turbidity was observed. An increase in W increases the overlap volume between two droplets as they approach each other to form a cluster, thereby increasing the interaction potential and facilitating percolation. While droplet attraction plays a prominent role in percolation, the nature of the interface is also relevant to the process because mass transfer is impossible unless the interface is ruptured in some way. In the case of isooctane/AOT/water microemulsions the presence in the aqueous phase of a moderate concentration of organic additives decreased the solubilization capacity and led to phase separation at a W value between 47 and 42 for thiourea compounds [30]. If the additive is an electrolyte (NaClO_4 , NH_4Cl , NaBr and Na_2SO_4) the water

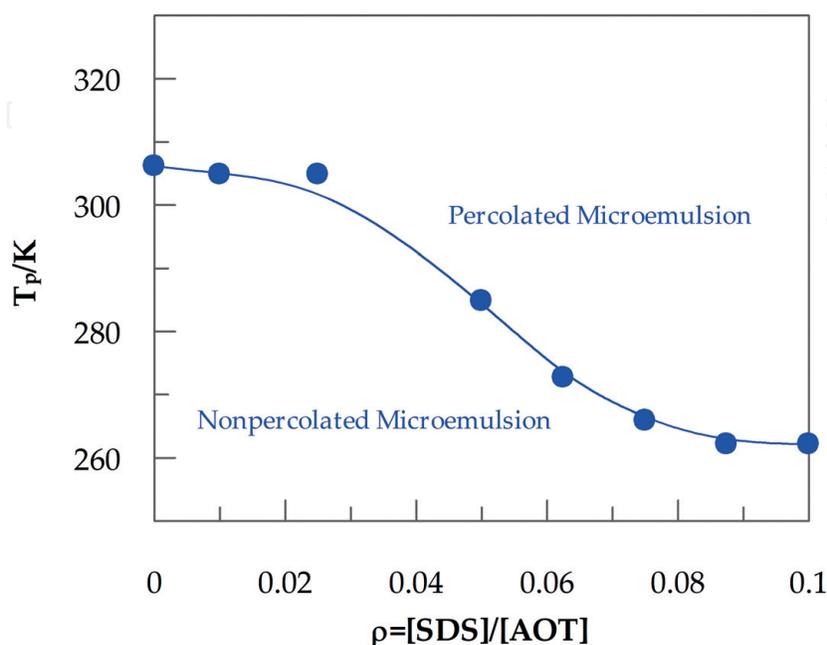


Figure 4. Changes in percolation temperatures of water/AOT/SDS/isooctane microemulsions for different ρ values ($\rho = [\text{SDS}]/[\text{AOT}]$). The solid line is a guide for the eye. $W = 22$, $[\text{AOT}] = 0.5 \text{ M}$.

solubilization capacity (W_{breakage}) decreases to $W = 36\text{--}30$. In our quaternary system, **Figure 5**, shows how W_{breakage} decreases by increasing the amount of SDS as cosurfactant. SDS modifies the natural negative curvature of the AOT by increasing the rigidity of its film and hindering its distortion, thereby decreasing interactions among droplets.

In this chapter, we also examined the xylene/AOT/water system, using o-, m-, and p-xylene. Percolation temperature of water in oil microemulsions is known to depend on the properties of the bulk solvent [31]. By using n-decane, n-octane, and n-heptane as continuous media, it was found that the percolation temperature to increase with decreasing length of the alkyl chain in the hydrocarbon. The strong attractive interaction between water nanodroplets was assumed to be the major

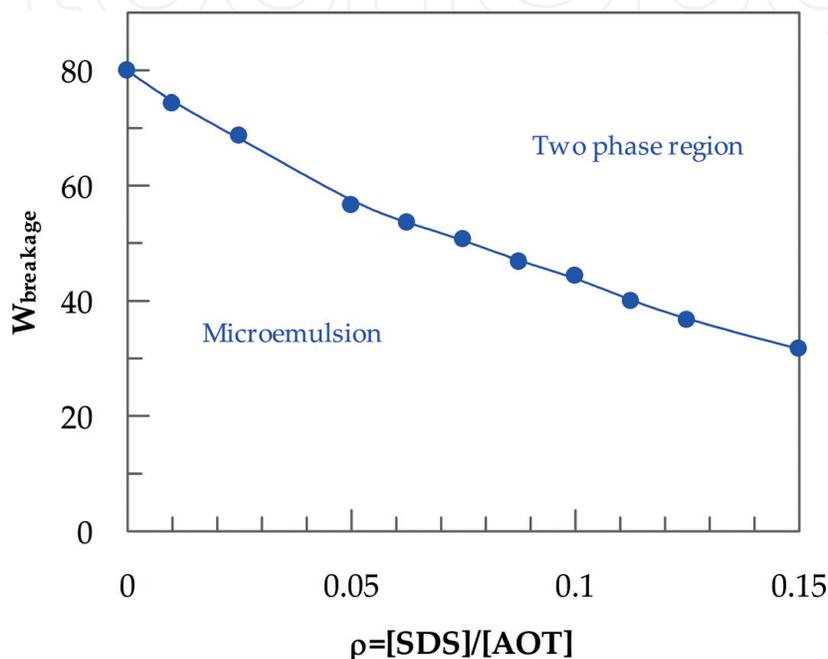


Figure 5. Influence of ρ ($\rho = [\text{SDS}]/[\text{AOT}]$) in the water solubilization capacity (W_{breakage}) of isooctane/AOT/SDS/water microemulsions. The solid line is a guide for the eye. $W = 22$, $[\text{AOT}] = 0.5 \text{ M}$.

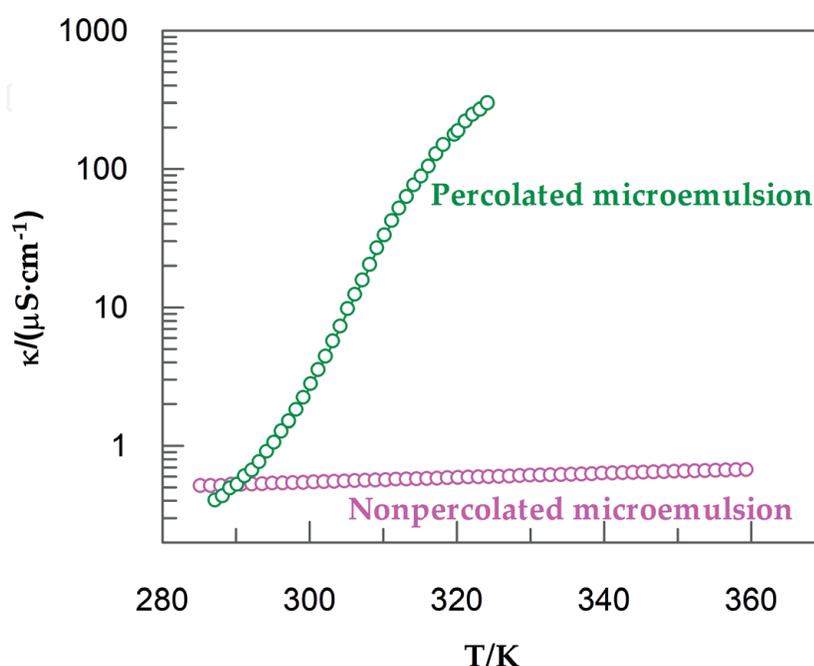


Figure 6. Conductivity vs. temperature plot for an isooctane/AOT/water microemulsion (O) and an o-xylene/AOT/water microemulsion (O). $[\text{AOT}] = 0.5 \text{ M}$, $W = 12$.

factor limiting microemulsion stability. An increase in molar mass of the hydrocarbon oil was found to decrease the density of the continuous phase and facilitate access of the interacting droplets for mass transfer. Microemulsions with xylenes as continuum medium are non-percolative and **Figure 6** shows the variation of conductivity with temperature for o-xylene/AOT/water and isooctane/AOT/SDS/water microemulsions.

The goal of this chapter is to conduct a comparative kinetic study on percolative and nonpercolative microemulsions. The difference in composition between the systems should result in differences in structure and physical properties as the ease with which the oil can penetrate the surfactant layer will vary markedly with the steric hindrance it encounters.

3. Nitrosation in isooctane/AOT/SDS/water microemulsions

The kinetics, at 25°C, of the transfer of the nitroso group from MNTS to secondary amines (PIP, NMBA and MOR) was studied using a wide variety of quaternary microemulsions as reaction media. MNTS reacts with secondary amines by transnitrosation to give carcinogenic *N*-nitrosamines [32] and, for this reason, the chemistry of MNTS has received increasing interest. The reactivity, in water, between MNTS and amines has been reported in our laboratory [33]. Kinetic studies were carried out in AOT-based microemulsions and micellar media [34–38]. The rate constants obtained for the reactions in microemulsions were in all cases like those in water, with first-order terms in MNTS and total amine concentration. The pseudophase model allows us to provide a quantitative explanation of the experimental results. The model considers the distribution of the amine between the oil, the surfactant film and the water nanodroplet. The MNTS has a very low degree of solubility in water and the nitrosation reaction always takes place at the interface. The presence of SDS changes the properties at the interface of the microemulsion, and thus the reactivity.

The influence of the composition of the quaternary system on the rate of transnitrosation of PIP, NMBA and MOR by MNTS was studied in a series of experiments in which the nanodroplet size varied from series to series over the range $W = 7.4\text{--}25.8$. The total surfactant concentration was varied between 0.443 and 0.544. The mole ratio ρ ($\rho = [\text{SDS}]/[\text{AOT}]$) was varied from series to series between 0 and 0.15.

The reaction kinetics was followed by monitoring the decrease in absorbance, at the appropriate wavelength, due to MNTS consumption. The concentration of MNTS was always much lower than the concentration of amine. The absorbance-time data of all kinetic experiments were fitted by first-order integrated equations, and the values of the pseudo-first-order rate constants, k_o , were reproducible to within 5%.

3.1 Reaction with piperazine (PIP)

The influence of the structure of the quaternary system on the rate of transnitrosation of PIP by MNTS was studied in a series of experiments in which total concentration of piperazine was 0.05 M. **Figure 7** shows that the value of pseudo-first-order rate constants (k_o) increases by increasing total surfactant concentration. However, k_o decreases by increasing the nanodroplet size (W).

Kinetic studies of reactions AOT-based microemulsions can be analyzed 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: a continuous medium formed

fundamentally by organic solvent (oil) an aqueous pseudophase (water) and an interface formed fundamentally by the surfactants (interface). Because of the very low water solubility of MNTS it will partition between the continuous medium and surfactant film, where the reaction is taking place. However, PIP is distributed between water and the surfactant film. **Figure 8** shows schematically the distribution of PIP and MNTS between the three phases of the microemulsion.

The partition coefficients that define the distribution of the reagents among the three pseudophases are defined in terms of their mole per mole concentrations in the pseudophases:

$$K_1 = \frac{[Amine]_{interface}}{[Amine]_{water}} W \quad (1)$$

$$K_4 = \frac{[MNTS]_{interface}}{[MNTS]_{oil}} Z \quad (2)$$

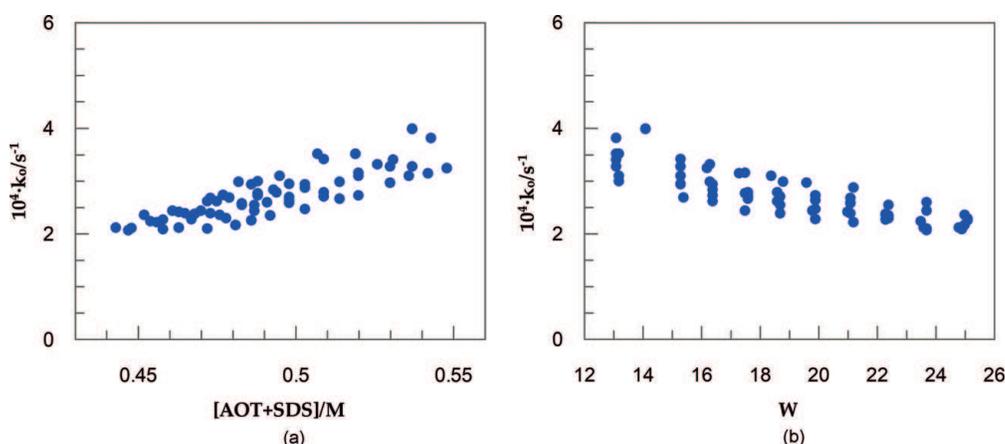


Figure 7. Left: influence of the concentration of surfactant upon k_o , at 25°C, for the nitrosation of piperazine by MNTS. Right: influence of the amount of water (W , $W = [H_2O]/([AOT] + [SDS])$) upon k_o , at 25°C, for the nitrosation of piperazine by MNTS.

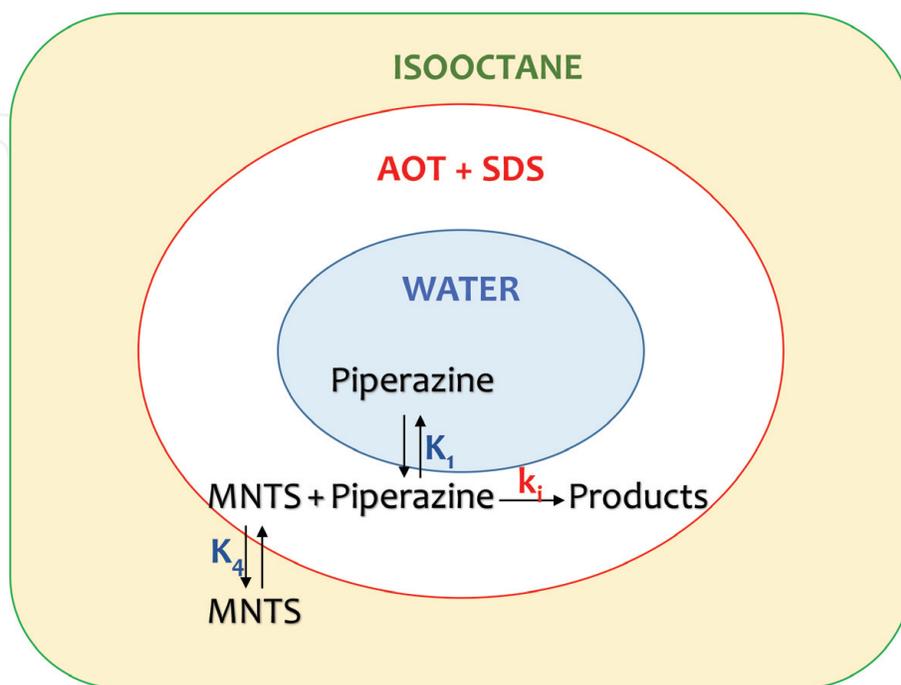


Figure 8. Pseudophase model for the nitrosation of Piperazine in isooctane/AOT/SDS/water microemulsions.

The subscripts interface, water and oil indicate quantities in the surfactant film, water and isooctane respectively, square brackets, as usual, indicate concentrations referred to the total volume of microemulsion, and Z is defined, in analogy with W, as the ratio [isooctane]/([AOT] + [SDS]). Based on these definitions, the model of **Figure 8** implies that the overall pseudo-first-order rate constant is given by Eq. (3):

$$k_o = k'_i \frac{1}{1 + \left(\frac{Z}{K_4}\right)} \quad (3)$$

where k'_i is the pseudo-first-order rate constant in the interface. This constant is expressed in terms of the bimolecular rate constant k_i as:

$$k'_i = k_i \frac{[Amine]_{interface}}{[AOT] + [SDS]} \quad (4)$$

The rate constant at the interface, k_i , is defined in terms of mole per mole concentration in the corresponding microphases. Then Eq. (3) can be rewritten as:

$$k_o = \left(\frac{[Amine]_{TOTAL}}{[AOT] + [SDS]} \right) \left(\frac{k_i K_1 K_4}{(K_1 + W)(K_4 + Z)} \right) \quad (5)$$

The results obtained by fitting Eq. (5) to the experimental data, at each mole ratio ρ , provides the kinetic parameters k_i , K_1 and K_4 . **Table 1** shows the values of the rate constant at the interface. The values of the partition constant of the amine, K_1 , are independent of the amount of SDS, and are between 9.5 and 10. In addition, the value of the MNTS distribution constant varies between 9 and 12. This result is compatible with those previously obtained in AOT-based microemulsion ($K_4 = 11$). The average value of K_4 is also in good agreement with the value estimated for isooctane/AOT/water system by analysis of changes in the UV spectrum of MNTS at 265–275 nm [39].

3.2 Reaction with N-methylbenzylamine (NMBA)

The influence of the presence of SDS on the rate of transnitrosation of NMBA by MNTS was studied in a series of experiments in which the total concentration of NMBA was always 0.1 M. The reactions in isooctane/AOT/SDS/water

ρ	\bar{V}/M^{-1}	PIPERAZINE + MNTS		NMBA + MNTS		MORPHOLINE + MNTS	
		k_i/s^{-1}	$k'_i/M^{-1}s^{-1}$	k_i/s^{-1}	$k'_i/M^{-1}s^{-1}$	k_i/s^{-1}	$k'_i/M^{-1}s^{-1}$
0.1500	0.336	$(1.57 \pm 0.07) \cdot 10^{-2}$	$5.3 \cdot 10^{-3}$	$(4.4 \pm 0.1) \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$(8.8 \pm 0.5) \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$
0.1250	0.341	$(1.64 \pm 0.08) \cdot 10^{-2}$	$5.6 \cdot 10^{-3}$	$(4.2 \pm 0.2) \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	$(9.3 \pm 0.6) \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$
0.1125	0.344	$(1.55 \pm 0.05) \cdot 10^{-2}$	$5.3 \cdot 10^{-3}$	$(2.8 \pm 0.1) \cdot 10^{-3}$	$9.5 \cdot 10^{-4}$	$(8.1 \pm 0.4) \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$
0.1000	0.347	$(1.56 \pm 0.06) \cdot 10^{-2}$	$5.4 \cdot 10^{-3}$	-	-	$(8.8 \pm 0.4) \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$
0.0875	0.350	-	-	$(3.1 \pm 0.1) \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	$(8.4 \pm 0.5) \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$
0.0750	0.353	$(1.57 \pm 0.06) \cdot 10^{-2}$	$5.5 \cdot 10^{-3}$	-	-	$(8.3 \pm 0.5) \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$
0.0625	0.356	-	-	$(3.7 \pm 0.2) \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$(8.2 \pm 0.5) \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$
0.0500	0.359	$(1.50 \pm 0.05) \cdot 10^{-2}$	$5.4 \cdot 10^{-3}$	$(4.7 \pm 0.2) \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	$(8.8 \pm 0.6) \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$
0.0250	0.364	$(1.50 \pm 0.06) \cdot 10^{-2}$	$5.5 \cdot 10^{-3}$	$(3.5 \pm 0.1) \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$(8.9 \pm 0.7) \cdot 10^{-4}$	$3.3 \cdot 10^{-4}$
0.0100	0.368	$(1.47 \pm 0.08) \cdot 10^{-2}$	$5.4 \cdot 10^{-3}$	$(4.0 \pm 0.2) \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$(8.8 \pm 0.6) \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$
0.0000	0.370	$(1.45 \pm 0.08) \cdot 10^{-2}$	$5.4 \cdot 10^{-3}$	$(3.1 \pm 0.1) \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	$(6.5 \pm 0.6) \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$

Table 1.
 Kinetic values for the transnitrosation between MNTS and PIP, NMBA, and MOR according to Eqs. (5), (7), and (8).

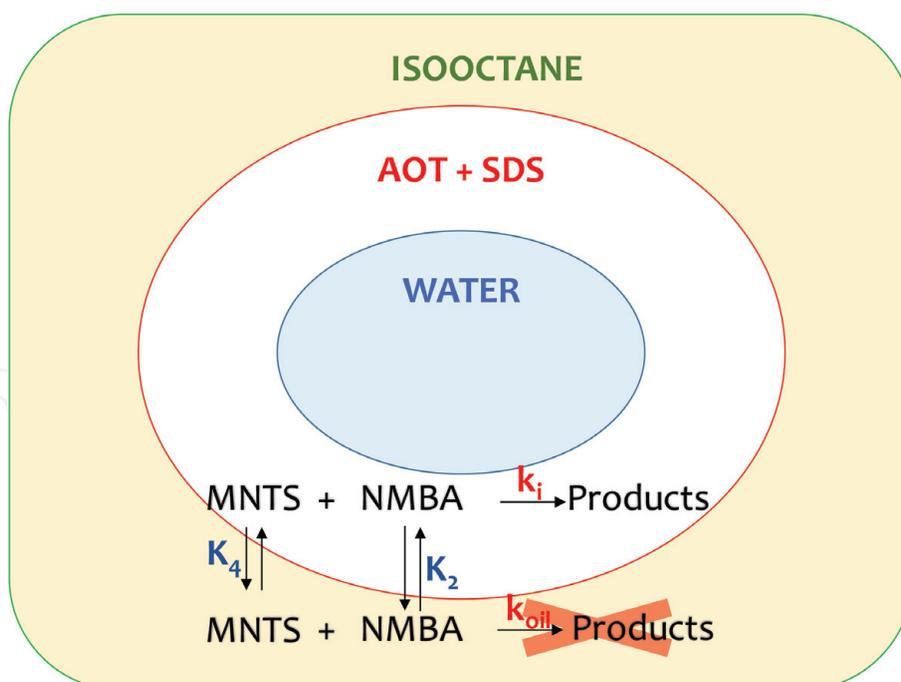


Figure 9. Pseudophase model for the nitrosation of *N*-methylbenzylamine in isooctane/AOT/SDS/water microemulsions.

microemulsions were studied by means of series of reactions analogous to those described for piperazine. In this case, no clear trend was observed in the variation of the pseudo-first-order rate constants with *W* or surfactant concentration.

NMBA is poorly soluble in water. **Figure 9** shows schematically the distribution of the substrates between the continuous medium and the interface of the microemulsion. The pseudophase model for this reaction considers simultaneous reactions in the isooctane and the surfactant film. However, the reaction rate in isooctane (k_{oil}) is several orders of magnitude less than those observed in this system [40–42]. The equilibrium constant K_2 is the partition constant of the amine between the continuous medium and the interface:

$$K_2 = \frac{[Amine]_{interface} Z}{[Amine]_{oil}} \quad (6)$$

Calculations analogous to those described for piperazine lead to the following expression for the rate constant:

$$k_o = \left(\frac{[Amine]_{TOTAL}}{[AOT] + [SDS]} \right) \left(\frac{k_i K_2 K_4}{(K_2 + Z)(K_4 + Z)} \right) \quad (7)$$

In this case, K_4 was fixed as 11. Then, the fit of Eq. (7) to the experimental data provides the kinetic parameters k_i and K_2 . The values of the partition constant of the amine, K_2 , vary between 24 and 28. The value is compatible with the K_2 value obtained previously for the isooctane/AOT/water ternary system ($K_2 = 25$). **Table 1** shows the values of the rate constant at the interface.

3.3 Reaction with morpholine (MOR)

In experiments on the reaction between morpholine and MNTS, the behavior is similar to that of piperazine: by increasing *W* the rate constant decreases and by increasing surfactant concentration the rate constant also increases. Morpholine is

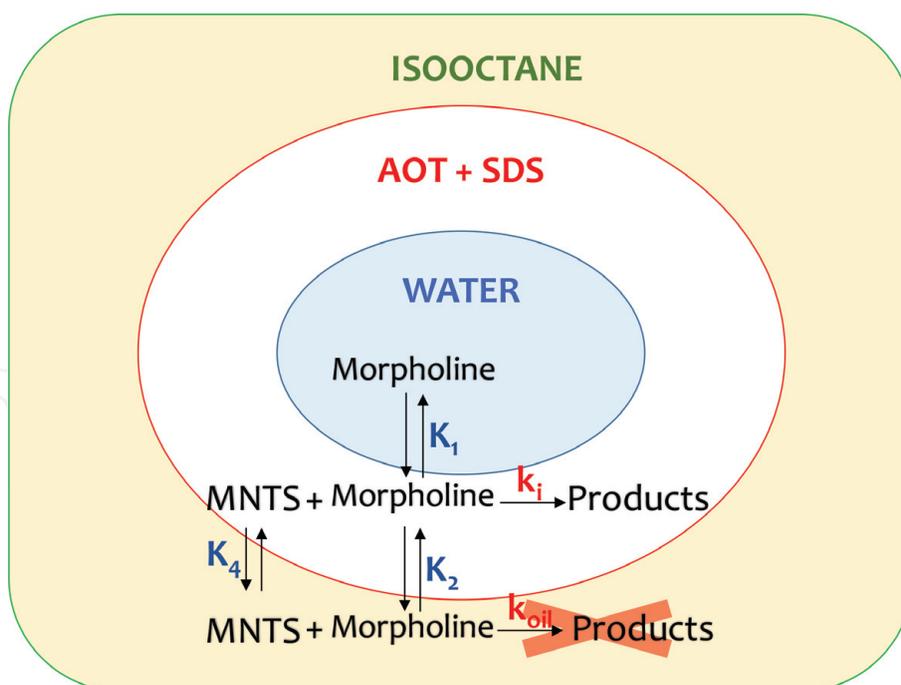


Figure 10. Pseudophase model for the nitrosation of morpholine in isooctane/AOT/SDS/water microemulsions.

distributed in all three pseudophases in the microemulsion, a more complex situation than any of those considered above. However, the effective reaction region is still constituted by the interface of surfactants, because reaction in isooctane (k_{oil}) is much slower than the observed rates. Taking these considerations into account, the pseudophase model applied is that shown in **Figure 10**.

Calculations analogous to those described for piperazine and N-methylbenzilamines lead to the following expression:

$$k_o = \left(\frac{[Amine]_{TOTAL}}{[AOT] + [SDS]} \right) \left(\frac{k_i K_1 K_2 K_4}{(K_1 K_2 + K_2 W + K_1 Z)(K_4 + Z)} \right) \quad (8)$$

The meaning of the constants K_1 , K_2 and K_4 was discussed previously. It is considered a known K_4 value equal to 11. The fit of Eq. (8) to the experimental data allows to obtain the other kinetic parameters. The fit, as in the previous cases, is carried out separately for each value of ρ . The distribution constants obtained were $K_1 = 45\text{--}48$ and $K_2 = 600$. The consistency between the experimental and predicted values (see **Figure 11**) confirms the accuracy of the micellar pseudophase model.

In order to compare the reactivity at the interface of the microemulsion it is necessary to know the molar volume. Furthermore, comparison of reactivity of the amines at the interface with the corresponding reactivity in bulk water needs that k_i (expressed in s^{-1}) must be converted to conventional reaction rates expressed in $M^{-1} s^{-1}$. The bimolecular rate constant is:

$$k_2^i = k_i \bar{V} \quad (9)$$

The molar volume of AOT was experimentally determined (given by its density) as $0.37 M^{-1}$. For the quaternary system the molar volume can be written as:

$$\bar{V} = \rho \bar{V}_{SDS} + (1 - \rho) \bar{V}_{AOT} \quad (10)$$

Table 1 shows the k_2^i values obtained from the fit of the experimental results to Eqs. (5), (7) and (8) and considering the Eq. (9). The nitroso transfer reactions are 20–50 times slower in isooctane/AOT/SDS/water microemulsions than in bulk

water due to the lower polarity of this microregion. The transition state for the transnitrosation reactions of MNTS requires a certain degree of charge separation, and reduction of the polarity will cause a decrease in reaction rate [33]. However, there is no significant difference of the bimolecular rate constants (k_2^i) between isooctane/AOT/water ($\rho = 0$) and isooctane/AOT/SDS/water microemulsions ($\rho = 0.01-0.15$). It is important to remember that in quaternary microemulsions, with $\rho > 0.3$, the kinetics is followed in percolated systems. For piperazine the rate constant is the same ($5.4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) in AOT and AOT/SDS microemulsions. For morpholine and NMBA the average value of bimolecular rate constant increases

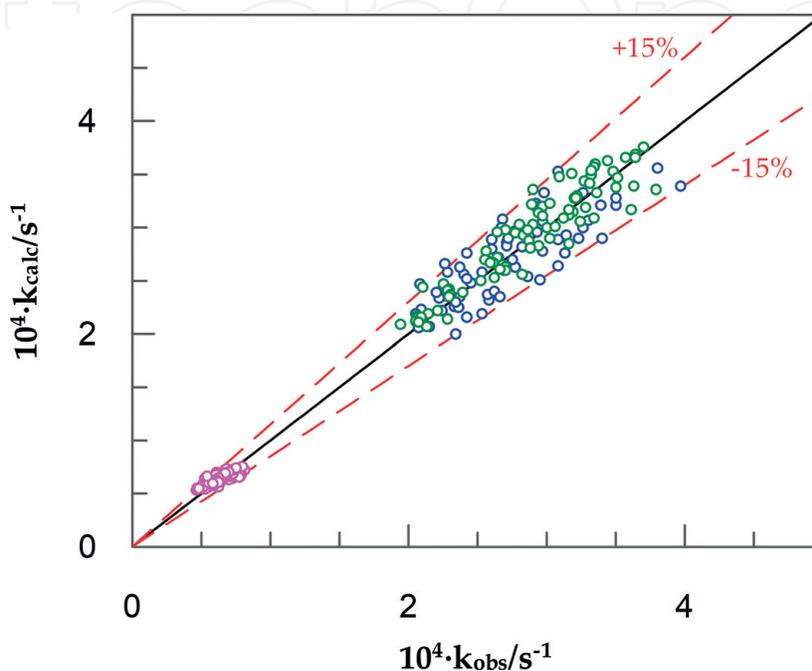


Figure 11.

Plot of experimental vs. calculated rate constants, at 25°C, for the transnitrosation reaction between MNTS and amines in isooctane/AOT/SDS/water microemulsions: piperazine (○), N-methylbenzilamine (○) and morpholine (○).

	Microemulsion	K_1	K_2	K_3	$k_2^i / \text{M}^{-1} \text{s}^{-1}$	Temperature	Relative k_2^i
Piperazine+MNTS	isooctane/AOT/water	9.6		11	$5.40 \cdot 10^{-3}$	25°C	1.00 ^a
	isooctane/AOT/SDS/water	9.6		11	$5.43 \cdot 10^{-3}$	25°C	1.00 ^a
	o-xylene/AOT/water	10.6		2.3	$2.94 \cdot 10^{-2}$	50°C	0.66 ^b
	isooctane/AOT/water	20.6		7.7	$4.48 \cdot 10^{-2}$	50°C	1.00 ^b
NMBA+MNTS	isooctane/AOT/water		25.0	11	$1.20 \cdot 10^{-3}$	25°C	1.00 ^a
	isooctane/AOT/SDS/water		25.5	11	$1.33 \cdot 10^{-3}$	25°C	1.11 ^a
	o-xylene/AOT/water		20.1	2.3	$4.07 \cdot 10^{-3}$	50°C	0.40 ^b
	m-xylene/AOT/water		12.8	2.3	$4.44 \cdot 10^{-3}$	50°C	0.43 ^b
	p-xylene/AOT/water		12.5	2.3	$4.81 \cdot 10^{-3}$	50°C	0.47 ^b
	isooctane/AOT/water		13.8	7.7	$1.03 \cdot 10^{-2}$	50°C	1.00 ^b
Morpholine+MNTS	isooctane/AOT/water	49	600	11	$2.40 \cdot 10^{-4}$	25°C	1.00 ^a
	isooctane/AOT/SDS/water	46.4	600	11	$3.03 \cdot 10^{-4}$	25°C	1.26 ^a

^aRelative $k_2^i \frac{k_2^i}{(k_2^i)_{\text{isooctane/AOT/water}}}$ at 25°C.

^bRelative $k_2^i \frac{k_2^i}{(k_2^i)_{\text{isooctane/AOT/water}}}$ at 50°C.

Table 2.

Kinetic parameter for the transnitrosation between MNTS and PIP, NMBA, and MOR according to Eqs. (5), (7), and (8).

slightly (see **Table 2**). For instance, in the case of morpholine the presence of SDS as cosurfactant increases the k_2^i value from $2.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ to $3.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (average value). This behavior is the result of two opposite effects: (1) a larger amount of SDS provides a lower molar volume of the surfactant film (see **Table 1**), and (2) by increasing ρ , the polarity at the interface increases. The presence of SDS as cosurfactant increases the small amount of water trapped between surfactant chains. If microemulsions of AOT are compared with those of AOT/SDS, the polarity is likely to increase slightly. For piperazine both effects are compensated and there is no difference in reactivity. The small increase in polarity due the presence of SDS is more important for the amines with solubility in oil: morpholine and NMBA.

4. Nitrosation in xylene/AOT/water microemulsions

The kinetic study of the nitroso group transfer from MNTS to the secondary amines piperazine (PIP) and N-methylbenzylamine (NMBA) in water/AOT/xylene was carried out. For PIP we used only o-xylene/AOT/water microemulsions. For NMBA we used o-xylene, m-xylene and p-xylene as continuous medium. Previously it was shown that these systems are non-percolative. In microemulsions where isooctane provides the continuous medium, W can be as large as 80 at a surfactant concentration of 0.5 M (see **Figure 5**). In contrast, W can barely reach 20 at identical surfactant concentrations in water/AOT/xylene microemulsions at 25°C. Raising the temperature slightly increases the solubility of water in the microemulsion. The kinetic study was conducted at 50°C, above the percolation temperature for isooctane/AOT/water and isooctane/AOT/SDS/water microemulsions.

The influence of the nature of the continuous medium on various properties of a wide range of water-in-oil (w/o) microemulsions was studied in our laboratory [43]. ^1H NMR spectroscopy allowed to determine the properties of water in the nanodroplet and the way they are affected by the bulk solvent. Changes in interfacial polarity were examined from the ^{13}C NMR signals of the surfactant molecule AOT. The variation of the carbon chemical shift as a function of the water content (W) was used as a measure of polarity changes at the interface. The reactions of solvolysis of anisoyl chloride were studied in oil/AOT/water microemulsions. The AOT-based microemulsions involved various continuous media, including trichloromethane, tetrachloromethane, alkanes (n-heptane, isooctane, and n-dodecane), cycloalkanes (cyclopentane, cyclohexane, and cycloheptane), and aromatic hydrocarbons (toluene as well as o-xylene, m-xylene and p-xylene). It was found that the solvolysis rate constants of anisoyl chloride depend on the penetration of the oil into the interface.

The kinetic study of PIP reactivity was conducted using o-xylene as the continuous medium in the microemulsions, W values over the range 7.4–15.7 and variable AOT concentrations from 0.1 to 0.7 M. PIP and MNTS concentrations were kept constant at $5 \times 10^{-2} \text{ M}$ and $2 \times 10^{-3} \text{ M}$, respectively. The value of pseudo-first-order rate constants (k_o) increase by increasing total surfactant concentration and decreases by increasing the water content (W).

A figure very similar to that used for PIP in the AOT/SDS quaternary system (**Figure 8**) describes the distribution of PIP and MNTS between the three phases of the microemulsion: water, AOT and oil (xylene). Therefore, the pseudo-first-order rate constant will be given by Eq. (5) by substituting $[\text{AOT}] + [\text{SDS}]$ for $[\text{AOT}]$. Kinetic (k_i) and equilibrium constants (K_1 and K_4) were obtained from fitting experimental data to Eq. (5). The bimolecular rate constant (k_2^i) is estimated from k_i according to Eq. (9) and assuming a value of 0.37 M^{-1} for $\overline{V_{\text{AOT}}}$. **Table 2** lists the

kinetic parameters for the transnitrosation reaction between PIP and MNTS in *o*-xylene/AOT/water microemulsion. **Figure 12** compares the experimental rate constants with that calculated. The satisfactory fit obtained for these experiments supports the validity of the model employed.

To compare results, we carried out a kinetic study in isooctane/AOT/water microemulsions at 50°C. Kinetic parameters were determined by following the same procedure as used previously. As can be seen from **Table 2**, the partition equilibrium constant of PIP, K_1 , between water and the AOT interface was greater in the *o*-xylene microemulsions. However, the reaction rate constant at the interphase, k_2^i , was smaller in the interface of the water/AOT/*o*-xylene microemulsions.

The NMBA reactivity was studied with *o*-xylene, *m*-xylene and *p*-xylene as the continuous medium of the water in oil microemulsion. Nanodroplet size, through the W parameter, varied between 7 and 18 and surfactant concentrations over the range 0.2–0.7 M. NMBA and MNTS concentrations were kept constant at 0.103 M and 2×10^{-3} M, respectively. Pseudo-first order rate constants increased markedly with increasing surfactant concentration at a constant value of W and more slightly with increase in water content at a constant AOT concentration. NMBA and MNTS are virtually insoluble in water and both are distributed between the interface and the oil. The reaction between MNTS and NMBA in xylenes was found to be very slow and, hence, was discarded. Thus, **Figure 9**, is valid for these systems. From the mechanistic proposal shown in **Figure 9** and considering that the surfactant is only AOT, Eq. (7) can be obtained. Kinetics parameters were obtained from fitting experimental data to Eq. (7). The consistency between the experimental and predicted values (see **Figure 12**) confirms the accuracy of the model for xylene/AOT/water microemulsions. **Table 2** compares kinetic and thermodynamic parameters for the microemulsions reviewed in this chapter.

Table 2 shows that the changes in the equilibrium constants (K_1 , K_2 and K_4) depend on their distribution between the three pseudophases. The lower values of K_4 in microemulsions with xylenes, at 50°C, may be related with the increased rigidity of the surfactant film due to the penetration of the oil. Similar effect was observed for the distribution constant of the NMBA (K_2). The equilibrium partition

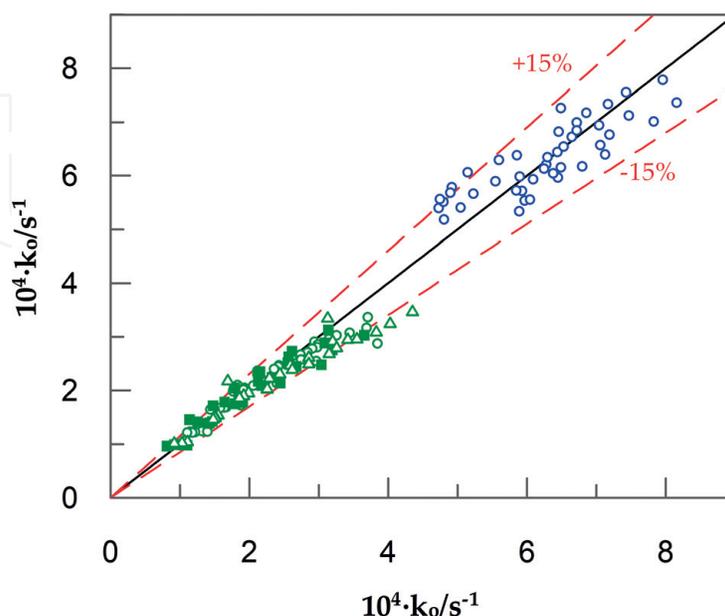


Figure 12.

Plot of experimental vs. calculated rate constants, at 50°C, for the following reactions: PIP + MNTS in *o*-xylene/AOT/water microemulsions (○), NMBA + MNTS in *o*-xylene/AOT/water microemulsions (○), NMBA + MNTS in *m*-xylene/AOT/water microemulsions (■), NMBA + MNTS in *p*-xylene/AOT/water microemulsions (△).

constant between water and PIP, K_1 , exhibits a different behavior; thus, an increase in temperature facilitates the migration of PIP to the pseudo-reaction phase in water/AOT/isooctane microemulsions. This result also seems to confirm the presence of an amount of water at the interphase that increases as the temperature is raised. However, no effect was observed on K_1 , K_2 and K_4 for isooctane/AOT/SDS/water microemulsions.

The relative bimolecular rate constant for PIP in o-xylene microemulsions is lower (0.66) than in isooctane microemulsions. This may be a result of a less polar interface by effect of the penetration of the continuous medium. The reaction between MNTS and NMBA was found to be more markedly inhibited in the xylene microemulsions. For NMBA the reaction was 2.1–2.5 times faster in the isooctane microemulsions than in the o-xylene, m-xylene and p-xylene microemulsions. The polarity of the interphase is a function of the amount of oil and water present. Structural evidence suggests that penetration of the continuous medium into the AOT film is easier for the aromatic medium than for isooctane. NMR and kinetic experiments confirm this prediction [43]. Highly polarizable solvents such as benzene, toluene, and tetrachloromethane penetrate the amphiphilic layer presumably up to the water core boundary. The resonance signals for the water H atoms in toluene, m-xylene, and p-xylene microemulsions are suggested an increasing penetration into the oil. The resonance signals for the water H atoms suggest that penetration is slightly deeper with o-xylene than with the other aromatic solvents. The oil penetration increased in the sequence o-xylene > m-xylene > p-xylene [43]. The relative biomolecular rate constants for the reaction between MNTS and NMBA in o-xylene, m-xylene and p-xylene are 0.40, 0.43 and 0.47 respectively.

5. Conclusions

In this chapter we have reviewed the reactions nitrosation of secondary amines by MNTS in AOT-based microemulsions. The reactivity of traditional microemulsions (isooctane/AOT/water) was compared with systems where the interface has been modified by the addition of a cosurfactant or by the substitution of isooctane for xylenes. The presence of SDS as a co-surfactant has important effects on the stability of the microemulsion. An increase in its relative concentration results in a significant decrease in its percolation temperature. The water solubilization capacity also decreases by the presence of SDS. Despite these important effects in the stability of the system, no significant differences are observed in the reactivity. The pseudophase model has been used to quantitatively evaluate the kinetic parameters, but the results are practically the same in isooctane/AOT/SDS/water microemulsions than in isooctane/AOT/water traditional systems.

The substitution of isooctane by xylene gives rise to nonpercolated microemulsions. Xylene/AOT/water microemulsions showed a remarkable effect in the reactivity. The ratio between the bimolecular rate constants allowed to compare the inhibitory effect of isooctane/AOT/water and xylene/AOT/water microemulsions. Thus, the reactions of MNTS with NMBA and PIP were found to be more strongly inhibited in the xylene microemulsions than in the isooctane microemulsions. The increased inhibitory effect of the xylene microemulsions is a result of the decreased polarity at the reaction site: the interphase between the continuous medium and the water.

Finally, we highlight the validity of the kinetic model for percolated and nonpercolated microemulsions. The pseudophase model is independent of structural connotations and internal dynamics of the system and assumes the water, surfactant, and continuous medium to be separate continuous phases.

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