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Influence of Anionic and Cationic Reverse Micelles on Nucleophilic Aromatic Substitution Reaction between 1-Fluoro-2,4-dinitrobenzene and Piperidine

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The nucleophilic aromatic substitution (S_NAr) reaction between 1-fluoro-2,4-dinitrobenzene and piperidine (PIP) were studied in two different reverse micellar interfaces: benzene/sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT)/water and benzene/benzyl-*n*-hexadecyl dimethylammonium chloride (BHDC)/water reverse micellar media. The kinetic profiles of the reactions were investigated as a function of variables such as surfactant and amine concentration and the amount of water dispersed in the reverse micelles, $W_0 = [H_2O]/[\text{surfactant}]$. In the AOT system at $W_0 = 0$, no micellar effect was observed and the reaction takes place almost entirely in the benzene pseudophase, at every AOT and PIP concentration. At $W_0 = 10$, a slight increment of the reaction rate was observed at low [PIP] with AOT concentration, probably due to the increase of micropolarity of the medium. However, at [PIP] $\geq$ 0.07 M the reaction rates are always higher in pure benzene than in the micellar medium because the catalytic effect of the amine predominates in the organic solvent. In the BHDC system the reaction is faster in the micellar medium than in the pure solvent. Increasing the BHDC concentration accelerates the overall reaction, and the saturation of the micellar interface is never reached. In addition, the reaction is not base-catalyzed in this micellar medium. Thus, despite the partition of the reactants in both pseudophases the reactions effectively take place at the interface of the aggregates. The kinetic behavior can be quantitatively explained taking into account the distribution of the substrate and the nucleophile between the bulk solvent and the micelle interface. The results were used to evaluate the amine distribution constant between the micellar pseudophase and organic solvent and the second-order rate coefficient of S_NAr reaction in the interface. A mechanism to rationalize the kinetic results in both interfaces is proposed.

Introduction

Reverse micellar systems are powerful models for biological compartmentalization studies, enzymatic catalysis, and separation of biomolecules.[1−7] Also, these micellar systems have been proven very useful to obtain new inorganic materials such as nanocrystallites[8] and polymers under mild conditions.[9]

Two clearly differentiated phases (aqueous and organic) present in reversed micelles allow compartmentalization of solubilized species at the microscopic level. Solubilization of a reactant in the same region of the surfactant assembly can lead to significant acceleration of reaction rates, while the rates of reactions of segregated reactants are retarded. When both reactants are in the water droplet, they are concentrated as in a nanoreactor, and since the size of this reactor is easily varied, the influence of the properties of the micellar system is relatively easy to assess.[8,10]

In previous works, we have been interested in bimolecular aromatic nucleophilic substitution (S_NAr) reactions between several nitro-substituted aromatic substrates and aliphatic amines in nonpolar[11−13] and polar aprotic solvents[14,15] and the sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT)/*n*-hexane system.[16]

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Diverse studies of S_NAr reaction between haloaromatic derivatives and anionic nucleophiles in reverse micellar media showed that the reactions were faster in the cationic media than in the aqueous phase or anionic micelles.[7,17−19] It has been proposed that the catalytic effect observed in the cationic systems could be explained considering that the positively charged head of the surfactant is capable of stabilizing the negatively charged Meisenheimer intermediate.[7,18] Moreover, the effective concentration of the anionic nucleophiles at the cationic interface is higher than in the anionic one.[19] Thus, the reactions are catalyzed relative to the homogeneous solutions, whereas in the anionic micelles the reaction is inhibited.[7,17−19]

Systematic studies using neutral nucleophiles in these kinds of systems are scarce. We have investigated[16] the S_NAr reaction of 1-fluoro-2,4-dinitrobenzene (FDNB) with aliphatic amines in *n*-hexane and *n*-hexane/AOT/water. The results showed that the reactions are faster in the micellar media than in the pure solvent, being base-catalyzed in *n*-hexane but not in the reverse micelles.

The aim of this work is to compare the influence of anionic and cationic interfaces in this type of S_NAr reaction. Therefore, we investigated the S_NAr between FDNB with piperidine (PIP) in the anionic system benzene/AOT/water and in the cationic system benzene/benzyl-*n*-hexadecyldimethylammoniumchloride (BHDC)/water. It must be noted that benzene was elected because is an oil phase where both surfactants can form reverse micelles without the presence of cosurfactants.[20] In *n*-hexane cationic reverse micelles of three components have not been yet characterized. The interface polarity in both systems was studied and compared using 1-methyl-8-oxyquinolinium betaine (QB) as molecular probe. The results show that both interfaces are more polar than the pure organic solvent.[20]

Experimental Section

General. UV−visible spectra were recorded on a Hewlett-Packard HP 8453 spectrophotometer or Hi-Tech Scientific Stopped-Flow SHU SF-51 (SU-40 spectrophotometer unit) for very fast reactions. The HPLC measurements were performed on a Varian 5000 liquid chromatograph equipped with a UV−visible variable λ detector (Varian 2550) operating at 250 nm with a Varian MicroPak SI-5 (150 mm × 4 mm i.d.) column and 1% 2-propanol in *n*-hexane as solvent.

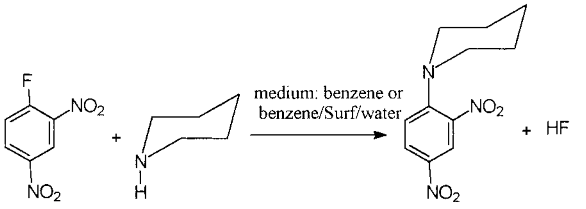
Materials. FDNB from Aldrich and piperidine from Riedel-deHaën were used without further purification. Sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT) from Sigma purified by the procedure described in ref 21 was dried under vacuum over P_2O_5. Benzyl-*n*-hexadecyldimethylamonium chloride (BHDC) from Sigma was recrystallized twice from ethyl acetate and dried under vacuum over P_2O_5.[20] Benzene (Sintorgan, HPLC quality) was used as received. Water was first distilled over potassium permanganate and then bidistilled until a conductivity of 0.3−0.5 $\mu\Omega^{-1}$ M^{-1} at 298 °K was reached.

Procedures. Stock solutions of surfactants reverse micelle were prepared by weighing and dilution in benzene. Stock solutions of 1 M surfactant were agitated in a sonicating bath until the reverse micelle was optically clear. The appropriate amount of stock solution to obtain a given concentration of surfactant in the micellar media was transferred into the cell. The addition of water to the corresponding solution was performed using a calibrated microsyringe. The amount of water present in the system is expressed as the molar ratio between water and the surfactant present in the reverse micelle (W_0 = [H_2O]/[surfactant]). The lowest value of W_0, called $W_0 = 0$, corresponds to a system with no addition of water, and its presence corresponds to the intrinsic humidity of the system ($W_0 \cong 0.3$).

Kinetics. Reactions were followed spectrophotometrically by the increase in the maximum absorption band of the product, *N*-(2,4-dinitrophenyl)piperidine, at 25.0 ± 0.5 °C. To start a kinetic run, a stock solution of FDNB was added (10 μL) into a thermostated cell containing the PIP and the reverse micelle solution. The FDNB concentration in the reaction media was 5×10^{-5} M. The kinetic runs were performed following the increase in the absorbance of the product of the reaction ($\lambda_{max} = 374$ nm). When the reaction was very fast, a High-Tech stopped flow instrument set at the λ_{max} of the product was used. In every case, pseudo-first-order plots were obtained in excess of nucleophile. The pseudo-first-order rate constants (k_{obs}) were obtained by a nonlinear least-squares fit of the experimental data absorbance vs time ($r > 0.999$) by first-order rate equation. The value of the absorbance at infinite reaction time was consistent with the value obtained from authentic samples of the reaction product, within 3%. The pooled standard deviation of the kinetic data, using different prepared samples, was less than 5%.

Results

The reactions of FDNB with piperidine in benzene, benzene/AOT/water, and benzene/BHDC/water reverse micelles produce *ipso*-fluorine substitution, giving the *N*-(2,4-dinitrophenyl)piperidine (eq 1) in quantitative yields as shown by UV−visible spectroscopic analysis of the reaction mixture.



(1)

In every run, the UV−visible spectra taken at different times show a clear isosbestic point, evidencing the cleanness of the reaction and the fact that the rising absorption is due to the absorbance of the product. Moreover, considering that hydroxide ion may result from amine hydrolysis in the water pool (see below), the possibility of the reaction between FDNB and this ion was searched. However, no reaction was detected under the experimental condition. TLC and HPLC chromatography analysis also show only one product at all times of reaction. In every case a large excess of nucleophile was used and the reactions follow pseudo-first-order kinetic. Trying to elucidate the mechanism of the S_NAr reaction in reverse micelles, influences of several variables were investigated as follows.

Effects of AOT Concentration. Reaction in Benzene/AOT/Water Reverse Micelles. The kinetics of the reaction was studied varying AOT concentrations between 0 and 0.5 M, keeping the other experimental conditions fixed. At $W_0 = 0$, no micellar effect was observed. The kinetics results, at any AOT concentration, were the same as that in benzene. A value of $k_{obs} = 0.0148$

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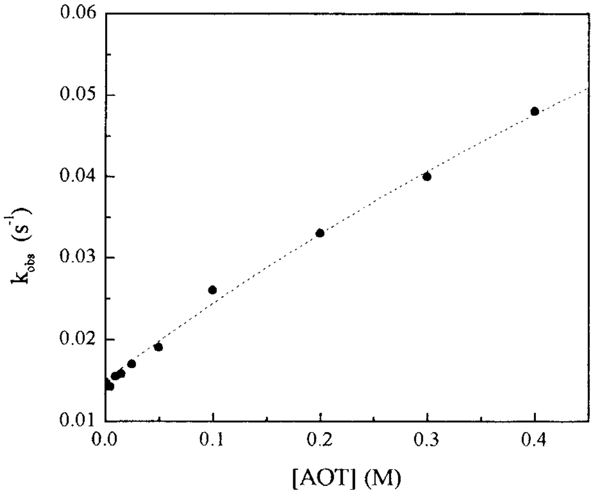

Figure 1. Dependence of the pseudo-first-order rate constant (k_{obs}) with the AOT concentration for the reaction between FDNB and PIP in water/AOT/benzene reverse micelles at $W_0 = 10$. [FDNB] = 5.0×10^{-5} M, [PIP] = 5.0×10^{-3} M. The dotted lines show the fitting by eq 10.

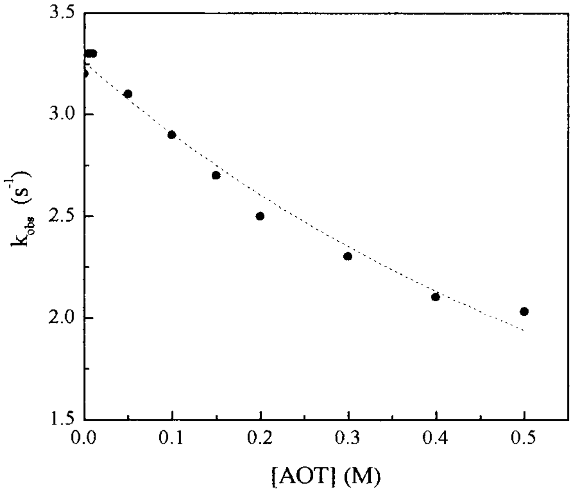

Figure 2. Variation of the pseudo-first-order rate constant (k_{obs}) with the AOT concentration for the reaction between FDNB and PIP in water/AOT/benzene reverse micelles at $W_0 = 10$. [FDNB] = 5.0×10^{-4} M, [PIP] = 0.1 M. The dotted line shows the fitting by eq 11.

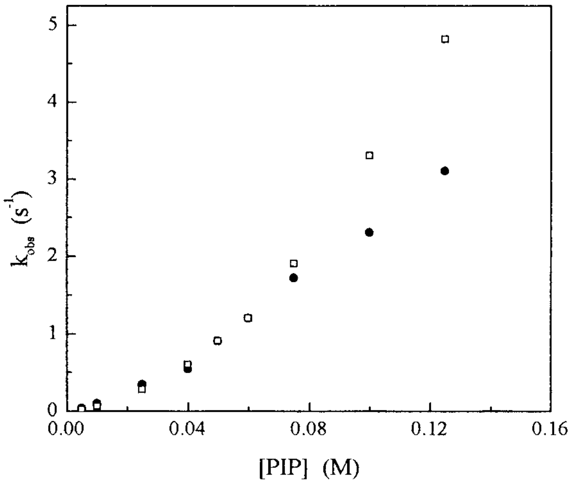

Figure 3. Variation of pseudo-first-order rate constant (k_{obs}) with PIP concentration for the reaction of FDNB with PIP (□) in benzene and (●) water/AOT/benzene reverse micelles at $W_0 = 10$. [FDNB] = 5.0×10^{-5} M, [AOT] = 0.3 M.

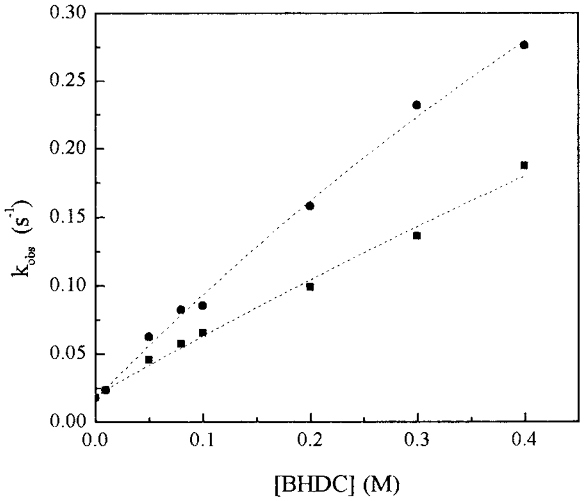

Figure 4. Variation of pseudo-first-order rate constant (k_{obs}) with BHDC concentration for the reaction of FDNB with PIP in water/BHDC/benzene reverse micelles at (●) $W_0 = 0$ and (■) $W_0 = 10$. [FDNB] = 5.0×10^{-5} M, [PIP] = 5.0×10^{-3} M. The dotted lines show the fitting by eq 10.

± 0.0005 s^{-1} was obtained for [PIP] = 5×10^{-3} M, which coincides with a value previously reported.[25]

Two different types of profiles were obtained at $W_0 = 10$ depending on the amine concentration. A slight increment on k_{obs} was found on increasing AOT concentration at [PIP] lower than 0.07 M. A typical plot of k_{obs} vs [AOT] at [PIP] = 5×10^{-3} M shows a downward curvature (Figure 1). On the other hand, at higher PIP concentration (i.e., ≥0.07 M), a decrease on k_{obs} was obtained as shown for [PIP] = 0.1 M in Figure 2. Moreover, at [PIP] ≤ 0.07 M, k_{obs} increases with W_0, while at higher PIP concentration the reaction rate diminishes with the amount of water dispersed.

Effect of Amine Concentration. To study the effect of amine concentration, the reaction was carried using 0.3 M AOT at $W_0 = 0$ and 10. As can be expected, at $W_0 = 0$ the kinetic behavior was the same than the measured in benzene. The results at $W_0 = 10$ are shown in Figure 3. As can be seen, the k_{obs} values are slightly higher or very similar to the observed reaction rate in benzene at low nucleophile concentration (<0.07 M). At higher amine concentration the values of k_{obs} decrease in comparison with the one found in the organic solvent. Because, as will be discussed below, the reaction is occurring in both benzene and interface pseudophases, it must be noted that k_{obs} has the contribution of both rate constants.

Effect of BHDC Concentration. Reaction in Benzene/BHDC/Water Reverse Micelles. Typical kinetic results with varying BHDC concentration are shown in Figure 4 at $W_0 = 0$ and 10. As can be observed k_{obs} increases on increasing BHDC concentration in the whole

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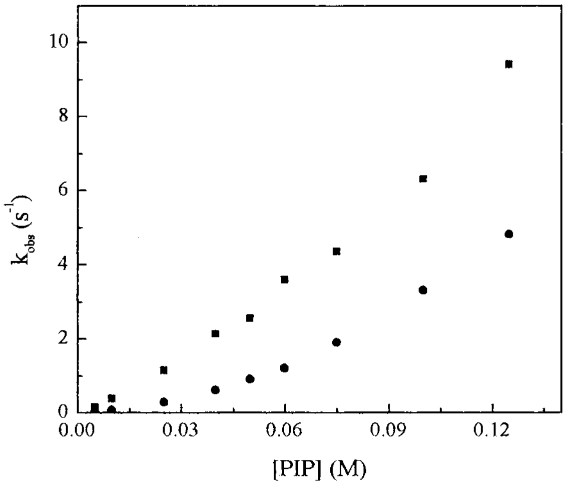


Figure 5. Variation of pseudo-first-order coefficient (k_{obs}) with PIP concentration for the reaction of FDNB with PIP in water/BHDC/benzene reverse micelles at (■) $W_0 = 0$ and (●) $W_0 = 10$. [FDNB] = 5.0×10^{-5} M, [BHDC] = 0.3 M.

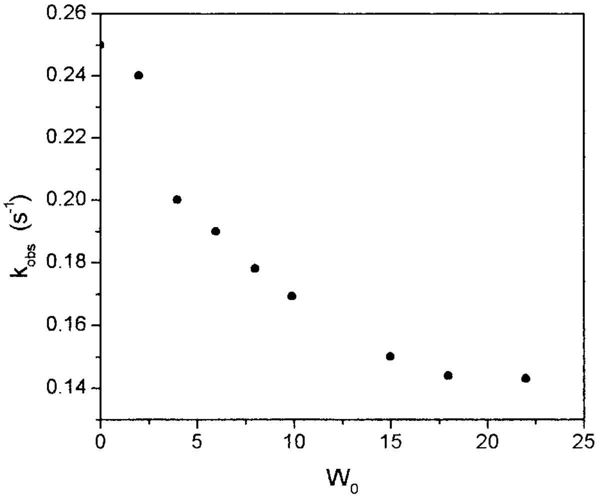


Figure 6. Variation of pseudo-first-order rate constant (k_{obs}) with W_0 in water/BHDC/benzene reverse micelles for the reaction of FDNB with PIP. [FDNB] = 5.0×10^{-5} M, [PIP] = 5.0×10^{-3} M, [BHDC] = 0.3 M.

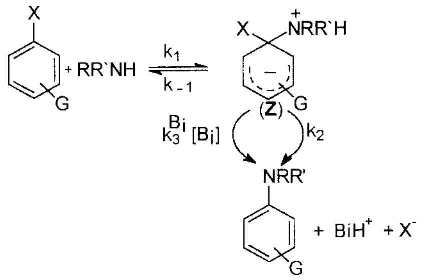
range. These results suggest that the saturation of the substrate molecules in the micellar interface is not reached in the range of surfactant concentrations used. Moreover, from Figure 4 it can be inferred that the reaction is slower at $W_0 = 10$ than $W_0 = 0$.

Effect of the Amine Concentration. Figure 5 shows the variation of the k_{obs} with the PIP concentration in the micelle at [BHDC] = 0.3 M, $W_0 = 10$ and in pure benzene. Similar profiles were obtained at $W_0 = 0$. As can be seen, the rate of reaction is higher in the reverse micelle than in the pure solvent, at any PIP concentration.

Effect of the Water Dispersed. The effects of changing the value of W_0 on k_{obs}, keeping BHDC and PIP concentrations constant, is shown in Figure 6. As can be observed, the value of k_{obs} decreases with W_0.

Discussion

Mechanism of Reaction. For primary or secondary amines as nucleophiles the general mechanism accepted[22–24] for S_NAr reactions involving halogen or nitrite as leaving groups can be represented by eq 2, where R′



(2)

could be H or an alkyl group, X is the leaving group ,and G stands for electron-withdrawing substituents. B_i is the nucleophile or any other base added to the reaction medium. With application of the steady-state hypothesis to this mechanism and in the limiting situation when $k_{-1} \gg k_2 + k_3^{B_i}[B_i]$, eq 3 is obtained, where k_A is the second-

$$k_A = k' + k''[B_i] \qquad (3)$$

order rate constant, $k' = k_1k_2/k_{-1}$, and $k'' = k_1k_3^{B_i}/k_{-1}$. In this case the decomposition of **Z** is rate-limiting, and base catalysis may be expected. A linear response to base concentration such as depicted in eq 3 is characteristic of the majority of base-catalyzed reactions. On the other hand, if $k_{-1} \ll k_2 + k_3^{B_i}[B_i]$, or more precisely $k_2 \gg k_{-1}$, the formation of the intermediate **Z** is rate-limiting and consequently $k_A = k_1$. There are intermediate situations where curvilinear dependence of k_A with amine concentration may be found.[22–24]

According to the results shown before and considering that two pseudophases are mainly present at $W_0 \leq 10$, the interface and the bulk organic solvent,[2,16,28] and both reactants may be distributed between the two environments, a mechanism summarized as follows can be

$$\begin{tikzcd}
\mathrm{FDNB_f} \arrow[d, shift left, "K_S"] \arrow[d, shift right, leftarrow, "\mathrm{Surf}"'] & + & \mathrm{PIP_f} \arrow[d, shift left, "K_A"] \arrow[d, shift right, leftarrow, "\mathrm{Surf}"'] \arrow[r, shift left, "k_1^f"] & Z_f \arrow[l, shift left, "k_{-1}^f"] \arrow[r, "k_3^f\ \mathrm{PIP}"] & P \\
\mathrm{FDNB_b} & + & \mathrm{PIP_b} \arrow[r, shift left, "k_1^b"] & Z_b \arrow[l, shift left, "k_{-1}^b"] \arrow[r, "k_2^b"] & P
\end{tikzcd}$$

proposed, where subscripts f and b indicate the organic phase and the micellar pseudophase, respectively. Surf represents the micellized surfactant molecules. The rate coefficients of the reaction k_1, k_{-1}, k_2, and k_3 were defined above (eq 1). K_s and K_A are the distribution constants for FDNB and PIP between the organic phase and micellar pseudophase, respectively.

It is known that this reaction is wholly base-catalyzed in benzene and the decomposition of the intermediate Z_b is rate-limiting.[25] However, these S_NAr reactions are not base-catalyzed in polar solvents.[24] The micropolarity of the interface in reversed micelles of benzene/AOT or BHDC/water is always higher than in benzene.[20,26] Thus, it can be assumed that the reactions of FDNB with PIP are not base-catalyzed in the anionic micellar interface

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or in the cationic one. Consequently, the formation of the intermediate $\mathbf{Z}_b$ is assumed to be rate-limiting.

The rate of the reaction can be expressed by eq 4 where

$$\frac{d[P]}{dt} = k_f[Am_f][FDNB_f] + k'_b\frac{[Am_b][FDNB_b]}{\bar{v}[Surf]} \quad (4)$$

k_f represents the second-order rate constant in the organic solvent ($k_f = k''[Am_f]$). For absolute comparison of reactivity in different media, the molar reaction volume at the interface, $\bar{v}$, should be known. This can be estimated from the molar volume of AOT and BHDC in the reverse micelles, which can be taken as $\bar{v}$.[19,27] Thus, k'_b is the conventional second-order rate constant in the interface. The concentrations in square brackets refer to the total volume of reverse micelle.

The distribution constant of FDNB can be expressed by eq 5:[28]

$$K_s = \frac{[FDNB_b]}{[FDNB_f][Surf]} \quad (5)$$

A simple mass balance using the distribution constant K_s and the analytical concentration of FDNB, $[FDNB_T]$, allows one to calculate the $[FDNB_b]$ (eq 6):

$$[FDNB_b] = \frac{K_s[Surf][FDNB_T]}{(1 + K_s[Surf])} \quad (6)$$

In the same way, using the distribution constant defined by eq 7, $[PIP_b]$ can be expressed by eq 8:

$$K_A = \frac{[PIP_b]}{([PIP_f][Surf])} \quad (7)$$

$$[PIP_b] = \frac{K_A[Surf][PIP_T]}{(1 + K_A[Surf])} \quad (8)$$

If $[PIP_T] \gg [FDNB_T]$ a pseudo-first-order behavior for the kinetics of the reaction is assumed. Then, replacing $[FDNB_b]$ and $[PIP_b]$ in eq 4, we can obtain the final expression for the rate (eq 9) and the observed pseudo-first-order rate constant k_{obs} (eq 10). with

$$\frac{d[P]}{dt} = k_{obs}[FDNB_T] \quad (9)$$

$$k_{obs} = \frac{k_f + (k_b'K_SK_A[PIP_T][Surf]/\bar{v})}{(1 + K_S[Surf])(1 + K_A[Surf])} \quad (10)$$

The variation of k_{obs} with the [Surf] can now be explained from eq 10. It shows that when the values of the products between the distribution constants and [Surf] are not negligible with respect to unity, k_{obs} would exhibit a nonlinear relationship with the surfactant concentration.[16] However, if K_A and K_S are small enough, this product are almost negligible with respect to unity and micellar interface saturation is not reached. The second-order rate constant of the reaction in the organic solvent, k_f, is known from the studies of these reactions in benzene.[25] The molar volume of BHDC and AOT to be taken as $\bar{v}$ was estimated in values of 0.44 M^{-1} and 0.38 M^{-1}.[19,27,29]

Reaction in the AOT/Benzene System. Considering that the kinetic response of the system at PIP concentration <0.07 M is different than at higher amine concentrations, the possibility of PIP protonation at this micellar interface was analyzed.

The importance of the hydrolysis basic-equilibrium of PIP in water was demonstrated for nitrosation reactions involving PIP in anionic direct micelles, albeit this effect was not important in cationic micellar systems.[30] Also, it was found[31] that the absorption and emission behavior of β-carbolines in cyclohexane/AOT/water reverse micelles is highly influenced by protonation at the interface.

On the other hand, for nitrosation reactions carried out in isooctane/AOT/water microemulsions,[27] the effect of the protonation of aliphatic amines was not detected. Likewise, when the charge-transfer interaction between hexylamine and 7,7,8,8-tetracyanoquinodimethane in cyclohexane/AOT/water reverse micelles was studied, there was no evidence of the amine protonation even at $W_0 = 10$.[32]

Previous studies of S_NAr reaction between FDNB and PIP performed in *n*-hexane/AOT/water reverse micelles[16] showed no PIP hydrolysis. The effect of the amine concentration on k_{obs} at [AOT] = 0.2 M, $W_0 = 0$ and 10, shows a linear relationship expected for a non-base-catalyzed reaction, while an upward curvature would be obtained if the hydrolysis equilibrium of the PIP is present.[30] Moreover, the reaction is faster at $W_0 = 10$ than $W_0 = 0$, indicating that, even when the water pool is formed, the protonation of the amine is not detected.

From the results in the present work, it seems that the protonation effect, if any, is negligible. When the [PIP] is low (Figure 1) there is micellar catalytic effect, while at higher PIP concentration there is not (Figure 2). Considering that PIP's $pK_a = 2.88$ in pure water[30] it could be expected that the percentage of molecules ionized at $[PIP] = 5 \times 10^{-3}$ M would be nearly 40% of the total PIP concentration and that in the presence of AOT this percentage increase significantly as found for aqueous micelles.[30] In addition at [PIP] = 0.1 M, the concentration of protonated amine would be just 10% of the total concentration, i.e., it is negligible. Therefore, if PIP would be protonated at the micellar interface k_{obs} should decrease with [AOT] preferentially at low amine concentration. Quite the opposite, this trend was found at high PIP concentration (compare Figures 1 and 2). Moreover no evidence was found of hydroxide ion in the media, an ion that will react with FDNB giving the corresponding phenol derivative.[19] These results could be indicating that in the AOT reverse micellar systems studied the proton concentration at the interface is actually much lower than could be expected by comparing with direct micelles. In fact in previous studies[20] working with QB as molecular probe, which is a very sensitive molecule to acids, no evidence of acidic interface in the benzene/AOT/water reverse micelles was found. Finally it must be noted that PIP has low affinity for the microemulsion aqueous phase[16,27] (see Table 1), a fact that may contribute to preventing protonation.

The lack of micellar effect observed at $W_0 = 0$ working with different concentrations of AOT shows that the

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Table 1. Kinetic Parameters and Distribution Constants for the Reaction between FDNB and PIP in Different Media

	k' (M^{-1} s^{-1})	k'' (M^{-2} s^{-1})	k'_b (M^{-1} s^{-1})	K_S (M^{-1})	K_A (M^{-1})
benzene[a]	0.72	609			
AOT−benzene[b] $W_0 = 10$			113 ± 10	1.0 ± 0.2	0.09 ± 0.04
AOT−benzene[c] $W_0 = 10$				0.90 ± 0.20	0.10 ± 0.04
BHDC−benzene[d] $W_0 = 0$			1670 ± 200	0.10 ± 0.04	0.30 ± 0.10
BHDC−benzene[d] $W_0 = 10$			1060 ± 200	0.11 ± 0.05	0.30 ± 0.10
BHDC−benzene[e] $W_0 = 0$			1950 ± 300		
BHDC−benzene[e] $W_0 = 10$			1100 ± 300		

[a] From ref 25. [b] From fitting Figure 1 by eq 10. [c] From fitting Figure 2 by eq 11. [d] From fitting Figure 4 by eq 10. [e] From fitting Figure 7 by eq 10. Parameter values calculated using 0.995 confidence level in nonlinear regression.

reaction takes place mainly in the organic pseudophase, probably as a result of the very low values of K_S. In fact, in the micellar system it is not kinetically distinguishable. Also, the attempts to calculate the value of K_S using Encinas-Lissi's[33] fluorescence quenching method varying AOT concentration between 0.05 and 0.3 M failed, probably because the value is in the limit of sensitivity of the method. Thus, it is assumed that FDNB resides mainly in the organic phase of the micellar solution, which seems quite reasonable as a result of the aromatic character of both the solute and the organic solvent.

At $W_0 = 10$ and [PIP] ≤ 0.07 M acceleration of the reaction rate is observed. In this case the increased polarity of the interface[16,20] may favor the reaction by stabilizing the $\mathbf{Z_b}$ intermediate, increasing $k_1{}^b$. The characteristic base catalysis observed in benzene is lost. By fitting the experimental data with eq 10, the value of k'_b and the distribution constants were calculated (see Table 1). As can be seen, the reaction in the micellar medium is more than 2 orders of magnitude faster than in benzene. This can be observed in Figure 3 at low amine concentration where k_{obs} is higher in the micelle system than in the organic solvent. It must be noted that k'_b in this system is 1 order of magnitude faster than in *n*-hexane/AOT/water reverse micelles at the same W_0.[16] Considering the studies with zwitterionic probes,[20] one can assume that the **Z** intermediate should be located in the "oil side" of the micellar interface in the benzene/AOT/water system. On the other hand, in the *n*-hexane/AOT/water system **Z** may be forced to reside more in the aqueous side of the interface. The later would be a hydrogen bond donor environment, which decreases the rate constant, as is observed when this reaction takes place in protic solvents.[24,34]

On the other hand, at [PIP] > 0.07 M, the reaction rates are retarded in the micellar medium with a typical behavior of segregated reactants. A possible explanation could be that, at high [PIP] the reaction in the organic pseudophase, where it is strongly base-catalyzed, predominates.

In this condition the second term of eq 4 is negligible and k_{obs} has the expression given in eq 11. This equation

$$k_{obs} = \frac{k''[PIP_T]^2}{(1 + K_A[AOT])^2(1 + K_S[AOT])} \qquad (11)$$

predicts the results observed in Figure 2. Since most of the reaction occurs in the organic phase, k_{obs} diminishes with [AOT] as a result of the reactants' distribution between the organic phase and the micellar interface. These reactant distributions also explain the decrease of k_{obs} in the micelles compared to the organic medium, shown in Figure 3 at high PIP concentration. By fitting Figure 2 by eq 11 the values of K_A and K_s are obtained and gathered in the Table. It must be pointed out that the small deviation observed in this fitting (Figure 2) could be due to the fact that the contribution to k_{obs} coming from the micelle interface was not taken into account in eq 11; however, similar values for K_A and K_s, within experimental error, as those calculated by eq 10 are found. The K_A value in this system is smaller than that obtained in *n*-hexane/AOT/water.[16] This seems quite reasonable because benzene, a more polar and polarizable solvent,[35] will better solubilize the amine. Moreover, the hydrogen bond interactions between AOT and PIP are weaker in benzene. Similar effects were observed in the interaction of aromatic amines with AOT in which a solvent more polar than *n*-hexane, such as carbon tetrachloride, increases the solubility of the amine and weakens the interaction with the surfactant.[36]

Reactions in BHDC/Benzene System. The increase of k_{obs} values while increasing BHDC concentration (Figure 4) at both W_0 studied could be due to the gradual incorporation of the reactants into the micellar aggregates. However, the micellar interface saturation observed in the *n*-hexane/AOT/water system[16] is never reached. By fitting Figure 4 by eq 10, the values of K_S, K_A, and k'_b can be obtained (Table 1). As can be inferred, k'_b is several orders of magnitude faster than that observed in pure benzene. Also, as was shown in Figure 6, the value of k'_b is lower at $W_0 = 10$ than at $W_0 = 0$. This result suggests a decrease in the PIP nucleophilicity due to the hydration of the amine, as has been observed for other systems where the reaction takes place at the interface.[16]

The greater catalytic effects of cationic interfaces over the anionic ones have been previously detected with anionic nucleophiles[7,17−19] and are explained by the cationic surfactant's stabilization of the amines **Z** intermediate. In this reaction, which involves a neutral nucleophile and no neat charge is expected for **Z**, a similar effect is found. Thus, at $W_0 = 10$ the rate of reaction in BHDC is about 10 times faster than in AOT, while at $W_0 = 0$ in the last system there is no micellar catalytic effect. A possible explanation for the cationic micellar catalysis is that it could be due to specific interaction between the ammonium head of BHDC and the zwitterionic intermediate $\mathbf{Z}_b$.[20,37] This effect could be responsible for the additional stabilization of $\mathbf{Z}_b$ with the

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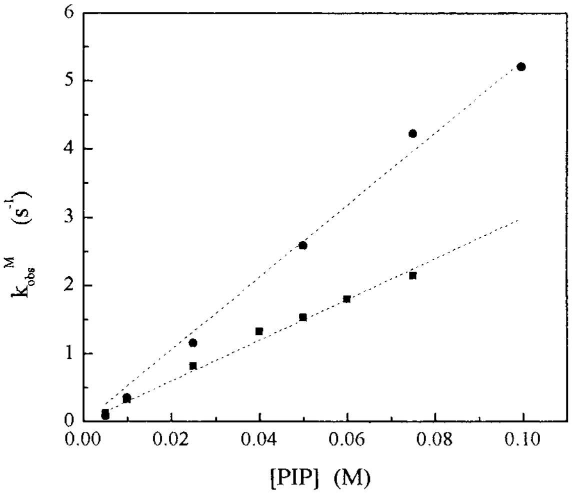

Figure 7. Variation of pseudo-first-order coefficient in the micelle ($k_{obs}{}^{M}$) with PIP concentration for the reaction of FDNB with PIP in water/BHDC/benzene reverse micelles at (●) $W_0 = 0$ and (■) $W_0 = 10$. [FDNB] = 5.0×10^{-5} M, [BHDC] = 0.3 M. The dotted lines show the fitting by eq 10.

corresponding increase on $k_2{}^{b}$. Moreover, although $\mathbf{Z}_b$ is a dipolar compound, Coulombic attraction between the cationic surfactant and the negative pole of the intermediate could be stronger than the attraction between the positive pole and anionic surfactant; consequently $\mathbf{Z}_b$ resides more in the oil side of the benzene/BHDC reverse micelle interface. In the anionic interface, the intermediate resides in a more hydrogen bond donor environment because it is located in the aqueous side of the interface. In this way, in the last medium the rate constants are slower than in the cationic ones, as was observed when the same reaction takes place in protic solvents.[24,34] In fact, that type of interactions seems to be responsible for the anomalous behavior of the zwitterionic compound QB with BHDC in benzene/BHDC/water system.[20]

The values of the pseudo-first-order coefficient in the micelles ($k_{obs}{}^{M}$) were estimated from Figure 5 at different PIP concentration, taking into account eq 12 where $k_{obs}{}^{bz}$

$$k_{obs} = k_{obs}{}^{M} + k_{obs}{}^{bz} \qquad (12)$$

is the pseudo-first-order coefficient in the benzene pseudophase. The $k_{obs}{}^{bz}$ values can be calculated from the kinetic law in benzene[25] and the value of K_A (Table 1). Figure 7 shows the variation of $k_{obs}{}^{M}$ with the PIP concentration at [BHDC] = 0.3 M at $W_0 = 0$ and 10. Linear relationships between $k_{obs}{}^{M}$ and the nucleophile concentration are always obtained. By introduction of the proper values of K_A and K_S obtained in the experiments with varying [BHDC], the values of k'_b were recalculated at $W_0 = 0$ and 10 by fitting the new set of experimental data (Figure 7) by eq 10. The results are shown in the table. As can be seen, good estimates for k'_b within experimental error are obtained by two independent methods. Thus, the kinetic results are consistent with the assumption that in benzene/BHDC/water reverse micelles the reaction is not base-catalyzed ($k_A = k'_b = k_1$) and the formation of **Z** intermediate is rate-determining. Hence, it can be concluded that the reactions takes place mainly in the interface, which is more polar than the organic medium.[20] The values of K_S and K_A are low and very similar to those calculated for the anionic system, showing that the solubilization of the reactants in the organic phase prevails. Nevertheless, the stabilization of the intermediate achieved at the cationic interface overcomes this effect, and neat micellar catalysis is observed.

Conclusions

In benzene/AOT/water reverse micelle medium at $W_0 = 0$, the reaction between FDNB and PIP takes place mainly in the organic pseudophase. In this system, the reactants' distribution toward the micelle interface is negligible and kinetically undetectable. However, at $W_0 = 10$, a slight catalytic micellar effect is observed when [PIP] $\leq$ 0.03 M is used, probably as a result of the increase in the interface micropolarity. At higher amine concentration ($\geq$0.07 M), the base-catalyzed reaction in the benzene pseudophase predominates over the interface reaction, producing a very large increment on k_f. Thus, k_{obs} decreases with [AOT] because of the reactant distributions. The fact that the overall rate of the reaction is accelerated at least 3 orders of magnitude in benzene/BHDC/water reverse micelle medium with respect to the pure solvent suggests that the reactions occur in the micelle interface. A change in mechanism for the S_NAr reaction is observed. The reactions, which are wholly base-catalyzed in benzene, in the reverse micelles are not. The formation of the **Z** intermediate is rate-determining as a result of the higher polarity in the micelle interface as compared with the bulk solvent. The kinetic behavior can be quantitatively explained taking into account the distribution of the substrate and amines. For both media, the interface micellar saturation is never reached probably due to the small K_A and K_S values. Comparisons between anionic and cationic interfaces shows that even nonionic nucleophile the cationic ones exert a greater catalytic effect. A possible specific interaction between the ammonium head of BHDC and the zwitterionic intermediate ($\mathbf{Z}_b$) could be responsible for the additional stabilization of $\mathbf{Z}_b$, with the corresponding increase on $k_b{}^{2}$. The results in this study can be used as a good model to predict micellar catalysis for reaction between nonionic substrates, which give a zwitterionic-type intermediate.

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