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Non-aqueous reverse micelles media for the S_NAr reaction between 1-fluoro-2,4-dinitrobenzene and piperidine†

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ABSTRACT: The kinetics of the nucleophilic aromatic substitution (S_NAr) reaction between 1-fluoro-2,4-dinitrobenzene (FDNB) and piperidine (PIP) in ethylene glycol (EG)/ sodium bis (2-ethyl-1-hexyl) sulfosuccinate (AOT)/*n*-heptane and dimethylformamide (DMF)/AOT/*n*-heptane non-aqueous reverse micelle systems is reported. EG and DMF were used as models for hydrogen bond donor (HBD) and non-hydrogen bond donor (non-HBD) polar solvents, respectively. The reaction was found not to be base catalyzed in these media. A mechanism to rationalize the kinetic results is proposed in which both reactants may be distributed between the two environments. The distribution constants of FDNB between the organic and each micellar pseudophases were determined by an independent fluorescence method. These results were used to evaluate the amine distribution constant and the intrinsic second-order rate coefficient of the S_NAr reaction in the interface. The reaction was also studied in the pure solvents EG and DMF for comparison. The results in EG/AOT/*n*-heptane at $W_s = 2$ give similar kinetic profiles than in water/AOT/*n*-hexane at $W = 10$. With these HBD solvents, the interface saturation by the substrate is reached at around the same value of [AOT] and the intrinsic second-order rate coefficient in the interface, k'_b, has comparable values. On the other hand, when DMF is used as a polar non-HBD solvent, the intrinsic second-order rate constant increases by a factor of about 200 as compared to the values obtained using HBD solvents as a polar core. It is concluded that higher catalytic power is obtained when non-HBD solvents are used as polar solvent in the micelle interior. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: reverse micelles; AOT; micellar catalysis; waterless microemulsions; aromatic nucleophilic substitution

INTRODUCTION

In recent years, attempts have been made to prepare and study waterless microemulsions. In this sense, polar solvents having high dielectric constants and low miscibilities with hydrocarbon solvents have been employed to replace water.[1] The most common polar solvents used include formamide (FA), dimethylformamide (DMF), dimethylacetamide (DMA), ethylene glycol (EG), propylene glycol (PG) and glycerol (GY).[2–12] Most of these studies have been focused on phase diagrams,[3] viscosity and conductivity behavior,[4] dynamic light scattering measurements to determine micellar sizes and intermicellar interactions.[5,6,8] Also, dyes absorption or emission spectra,[5,9,10,13-15] and FTIR[6,12,16,17] or ^{1}H-NMR[12,16] spectroscopy have been used to characterize microenvironments.

In principle, reverse micellar system can affect the reaction rates by two main processes.[18] They can rise or diminish the energy of the transition state of the reaction affecting the intrinsic rate constant for bimolecular reactions and, can provide different places where the reactants can be located. Solubilization of the reactant in the same region of the surfactant assembly can lead to significant acceleration of reaction rates due to a 'concentration' effect, while the rates of reactions of segregated reactants are retarded. When both reactants are in the polar core, 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 simple to assess.[19,20] Moreover, reverse micellar systems are of interest as reaction media because they are powerful models for biological systems.[21–24]

In spite of the importance of non-aqueous reverse micellar systems, as potential catalytic media mainly, for reactions that involve reagents that may react with water,[25] systematic studies of aromatic nucleophilic substitution (S_NAr) reactions using neutral nucleophiles in these media have not been previously performed. In previous works, we have been interested in the influence of cationic and anionic reverse micelles on the bimolecular S_NAr reactions between halo nitro substituted aromatic substrates and aliphatic amines. The

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results showed that there is a change in the mechanism and the reaction is faster in the micellar media than in the non-polar pure solvent.[26–29] At this time, we are interested in investigating how the AOT non-aqueous reverse micelles affect the mechanism of the S_NAr reactions.

In this paper, we report for the first time data on the kinetics of the S_NAr reactions between 1-fluoro-2,4-dinitrobenzene (FDNB) and piperidine (PIP) in EG/sodium bis (2-ethyl-1-hexyl)sulfosuccinate (AOT)/*n*-heptane and DMF/AOT/*n*-heptane in non-aqueous reverse micelle systems. EG and DMF were used as models for hydrogen bond donor (HBD) and non-hydrogen bond donor (non-HBD) polar solvents, respectively. The distribution constant of FDNB between the organic and the micellar pseudophases were determined by an independent fluorescence method and used to evaluate the amine distribution constant and the intrinsic second-order rate coefficient of the S_NAr reaction in the interface. A mechanism to rationalize the kinetic results is proposed.

Experimental general

UV-visible spectra were recorded on a Shimadzu UV-2401PC using 1 cm path length quartz cells. The kinetics were recorded on a Hi-Tech Scientific Stopped-Flow SHU SF-51 (SU-40 spectrophotometer Unit) thermostatized at $32.0 \pm 0.5^{\circ}C$. 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 PIP from Riedel-de Haen were used without further purification. Sodium bis (2-ethyl-1-hexyl) sulfosuccinate (AOT) from Sigma (more than 99%) was dried under reduced pressure and was kept under vacuum over P_2O_5 until it was used. The UV-visible of 1-methyl-8-oxyquinolinium betaine in the presence of AOT reverse aggregates in *n*-heptane showed that the surfactant is free of acidic impurities.[30] *n*-Heptane (Sintorgan, HPLC quality), DMF and EG, from Aldrich (more than 99% purity), were used as received. Ultrapure water was obtained from Labconco equipment Model 90901-01.

Procedures

Stock solutions of reverse micelles were prepared by weighing and dilution in *n*-heptane. Stock solution of 0.5 M surfactant was agitated in a sonicating bath until the reverse micelle was optically clear. The appropriate amount of the stock solution to obtain a given concentration of surfactant in the micellar solution was transferred into the cell. The addition of the polar solvent to the corresponding solution was performed using a calibrated microsyringe. The amount of EG or DMF present in the system is expressed as the molar ratio between these polar solvents and the surfactant present in the reverse micellar solution (W_s = [polar solvent]/[surfactant]).

Kinetics

Reactions were followed spectrophotometrically by the increase in the maximum absorption band of the product, N-(2,4-dinitrophenyl) PIP, at $32.0 \pm 0.5\,^{\circ}C$. To start a kinetic run, a stock solution of FDNB was added (10 μl) into a thermostatized cell containing the PIP and the reverse micellar solution. The FDNB concentration in the reaction media was 1×10^{-4} M. The kinetic runs were performed following the increase in the absorbance of the reaction product ($\lambda_{max} = 385$ nm). In every case, pseudo-first-order plots were obtained in excess of PIP. The pseudo-first-order rate constants (k_{obs}) were obtained by a non-linear least-squares fit of the experimental data absorbance versus 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%.

Determination of the partition constant (K_s) of FDNB in the micellar systems

The binding constant of FDNB to the reverse micellar pseudophase was evaluated using the Encinas–Lissi's fluorescence quenching method.[31,32] Tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{+2}$) which is quenched by nitroaromatic compounds was used as the fluorescence probe.[33]

RESULTS

As it was previously found in other reverse micellar systems,[26,27] the reactions of FDNB with PIP in EG and DMF homogeneous solutions and in reverse micelles, EG/AOT/*n*-heptane and DMF/AOT/*n*-heptane, produce the corresponding *ipso*-fluorine substitution product in quantitative yields as shown by UV-visible spectroscopic and HPLC analysis of the reaction mixture.

In every case a large excess of PIP was used and the reactions follow pseudo-first-order kinetic reaction. The spectra at different reaction progresses show a clear isosbestic point evidencing the cleanness of the reactions.

Table 1. Kinetic and solvents parameters for the reaction of FDNB with PIP in homogeneous media at 32 °C

Solvent	k' ($s^{-1}M^{-1}$)[a]	k'' ($s^{-1}M^{-2}$)[a]	π^{*}[b]	α[b]	β[b]
EG	13.8 ± 0.7	—	0.92	0.9	0.75
DMF	256 ± 13	—	0.88	0	0.73
Water	2.5 ± 0.1	—	1.09	1.17	0.47
n-Hexane[c]	—	171 ± 8	−0.08	0	0

[a] See Eqn (4).
[b] from Ref. 40.
[c] from Ref. 26.

When it is attempted to elucidate how the microheterogeneous media affect the S_NAr reaction several variables were investigated as follows.

Reaction in neat EG and DMF

The reaction between FDNB and PIP was first studied in homogeneous solutions of EG and DMF. In both solvents there is a linear dependence on k_{obs} with the PIP concentration (See supplementary material, Fig. 1S for EG). The kinetic results in both solvents are gathered in Table 1, where k' values are the second-order rate constants. Also, for comparison the results previously obtained for the same reaction in water and *n*-heptane are included in Table 1.[26] The reaction is faster in DMF than EG and water.

Reaction in the non-aqueous AOT/*n*-heptane microemulsions

Effects of AOT concentration. The kinetics of the reaction was studied varying AOT concentrations between 0 and 0.5 M, keeping the other experimental conditions, W_s, and [PIP] constant. Figure 1A and B shows the kinetic results at $W_s = 2$, for EG/AOT/*n*-heptane and DMF/AOT/*n*-heptane, respectively. As can be observed from Fig. 1A for EG sequestrated inside the aggregate, k_{obs} increases on increasing AOT concentration until approximately 0.1 M and, the plots show a downward curvature. After this AOT concentration value, k_{obs} change very little with the surfactant concentration. On the other hand, when DMF is used as the polar solvent (Fig. 1B) k_{obs} increases on increasing AOT concentration in the whole range studied. These results are reflecting that the saturation by FDNB of the micellar interface is achieved for EG reverse micelles while this is not reached in the DMF ones at least in the surfactant concentration range used.

Effect of amine concentration. To study the effect of PIP concentration, the reaction was carried out using 0.3 M of AOT at $W_s = 2$. Figure 2A and B shows the results for EG/AOT/*n*-heptane and DMF/AOT/*n*-heptane,

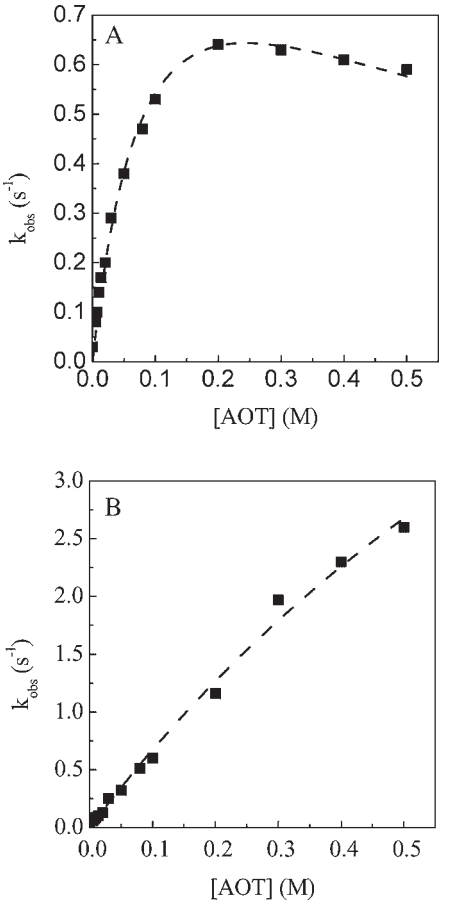


Figure 1. Dependence of k_{obs} with the AOT concentration, for the reaction between FDNB and PIP in: (A) EG/AOT/*n*-heptane and (B) DMF/AOT/*n*-heptane. [FDNB] = 1.0×10^{-4} M, [PIP] = 0.015 M, $W_s = 2$. The dashed line shows the fitting by Eqn (11)

respectively. In both cases, k_{obs} increases linearly with the [PIP].

Effect of polar solvent dispersed. The effects of changing the value of W_s on k_{obs} keeping AOT and PIP concentrations constant, is shown in Fig. 3A and B for EG/AOT/*n*-heptane and DMF/AOT/*n*-heptane, respectively. As it can be observed from Fig. 4A and B, the value of k_{obs} increases almost linearly with W_s in the whole range measured. It must be pointed that the maximum W_s that can be reached is around 4 for DMF and 2.4 for EG at 32°C.[13,14]

Determination of the partition constant (K_s) of FDNB in the micellar systems. A question can be raised regarding if polar solvents relatively soluble in *n*-heptane such as DMF are preferably associated to the micellar pseudophase under all the conditions employed.[5] However, there are studies that support the assumption that the sequestrated polar solvent/AOT ratio is independent of the AOT concentration at a fixed analytical W_s value. Previously[9] we have shown that the spectra of a probe totally associated to the reverse micelles, change

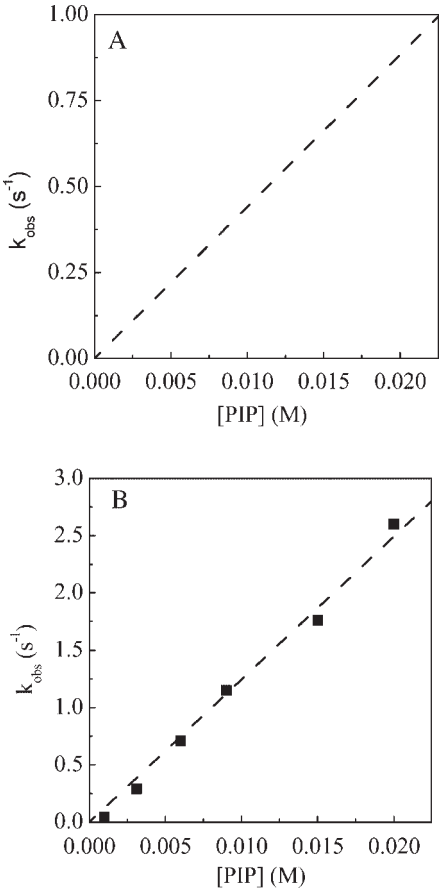


Figure 2. Dependence of k_{obs} with the PIP concentration, for the reaction between FDNB and PIP in: (A) EG/AOT/*n*-heptane and (B) DMF/AOT/*n*-heptane. [FDNB] = 1.0×10^{-4} M, [AOT] = 0.3 M, $W_s = 2$. The dashed line shows the fitting by Eqn (11)

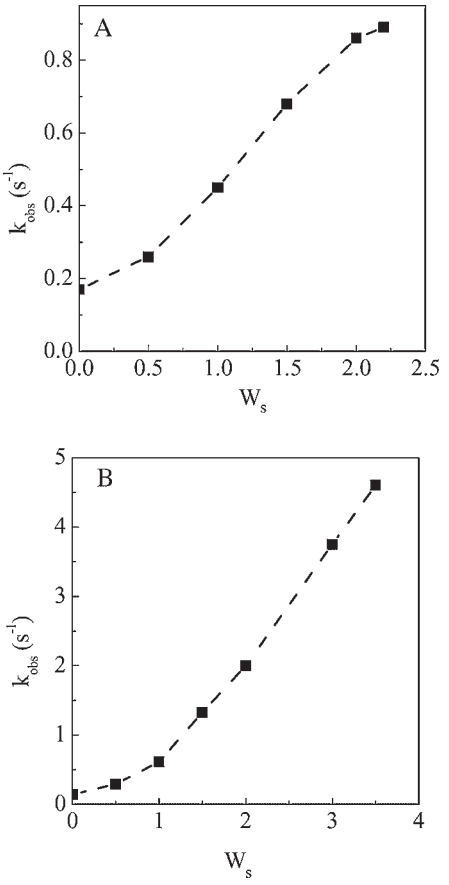


Figure 3. Variation of k_{obs} with W_s, for the reaction between FDNB and PIP in: (A) EG/AOT/*n*-heptane and (B) DMF/AOT/*n*-heptane. [FDNB] = 1.0×10^{-4} M, [PIP] = 0.015 M, [AOT] = 0.3 M

with W_s but not with the AOT concentration (at fixed W_s) for every solvent considered in the present work. This indicates that the properties of the micelles, at a given analytical W_s value, are not dependent upon the AOT concentration, implying that most of the polar solvent must be associated to the micellar pseudophase. Moreover, as Riter *et al*.[5] have concluded, at small values of W_s the polar solvent appears to remain preferentially inside the micelles, even when they are relatively soluble in *n*-heptane such as DMF.

Consequently the distribution of the reactants between the micelle and the non-polar organic solvent is defined using the pseudophase model.[34] This model considers the microaggregates as a distinct pseudophase whose properties is independent of the AOT concentration and is only determined by the value of the characteristic parameter W_s. In this model, only two solubilization sites are considered, that is, the external non-polar solvent and the micellar interface (i.e., all the surfactant molecules). In this way, the distribution of FDNB between the micelles and the external solvent pseudophase defined in Eqn (1) is expressed in terms of the partition constant K_s shown in Eqn (2):

$$\mathrm{FNDB_f} + \mathrm{AOT} \overset{K_s}{\rightleftharpoons} \mathrm{FNDB_b} \tag{1}$$

$$K_s = \frac{[\mathrm{FDNB_b}]}{[\mathrm{FDNB_f}][\mathrm{AOT}]} \tag{2}$$

Where $[\mathrm{FDNB}]_b$ is the analytical concentration of the substrate incorporated to the micelles, $[\mathrm{FDNB}]_f$ is the concentration of the substrate in the non-polar organic solvent, and [AOT] is the micellized surfactant (total surfactant concentration minus the critical micellar concentration $\cong 10^{-4}$ M). This equation applies at a fixed value of W and when $[\mathrm{FDNB}]_T \ll [\mathrm{AOT}]$.

According to the Encinas–Lissi's fluorescence quenching method[31,32] the distribution constant can be straightforwardly obtained by measuring the quenching of a fluorophore anchored at the AOT interface. $Ru(bpy)_3^{+2}$ belongs to this kind of fluorophores[35,36] and is quenched by FDNB as it was previously found.[33] The intensity of the $Ru(bpy)_3^{+2}$ emission is not affected with the addition of EG and DMF to the reverse micellar solution (results not shown). This method was used to determine K_s for the micellar systems used at $W_s = 2$ as it was previously

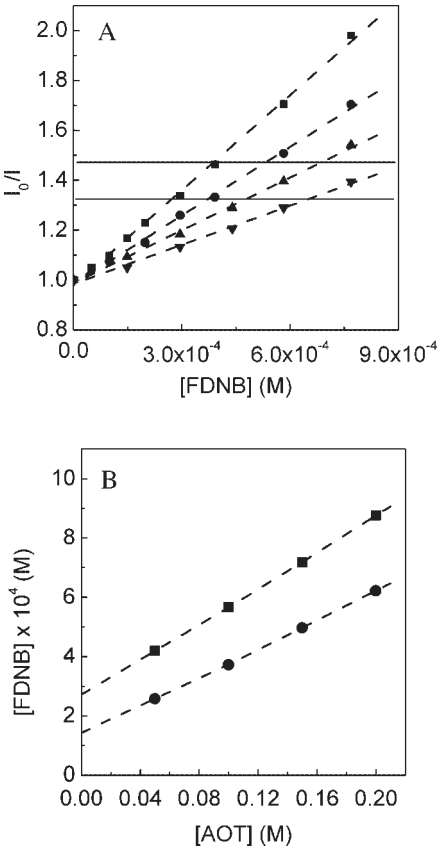


Figure 4. (A) Effect of FDNB addition upon the fluorescence intensity from $Ru(bpy)_3^{+2}$ in EG/AOT/*n*-heptane reverse micelles at $W_S = 2$. $[Ru(bpy)_3^{+2}] = 6.85 \times 10^{-6}$ M. $\lambda_{exc} =$ 412 nm. $\lambda_{em} = 616$ nm. [AOT]/M: ■ 0.05, ● 0.10, ▲ 0.15, ▼ 0.20. (B) Analytical concentration of FDNB needed to give different I_0/I values as a function of the AOT concentration. I_0/I values: 1.47 and 1.33

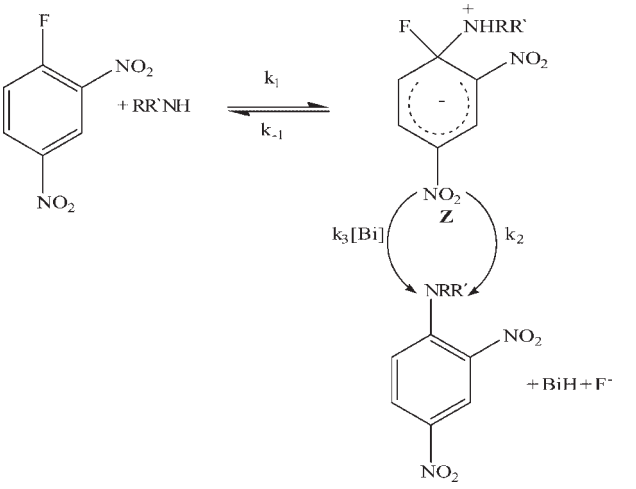
reported for the distribution constant of 9-anthracenemethanol in the same non-aqueous reverse micelles systems.[14]

Typical results are shown for FDNB in Fig. 4A for EG/AOT/*n*-heptane. The observed effect decreases as the AOT concentration is increased as expected for the distribution of the molecule between the micellar pseudophase and the organic bulk. Similar data were obtained in DMF/AOT/*n*-heptane (not shown). Figure 4B shows the plots of the analytical FDNB concentration needed to reach a given value of I_o/I ratio (where I_o and I are the $Ru(bpy)_3^{+2}$ fluorescence intensity, in the absence and in the presence of FDNB, respectively) against the AOT concentration. The intercepts of these plots correspond to the FDNB remaining in *n*-heptane ($[FDNB_f]$, while the slope is the FDNB incorporated into the micellar pseudophase per mole of surfactant ($[FDNB_b]$). In this way, the value of the distribution constant could be calculated as $K_s =$ slope/intercept.[31,32] The values of K_s obtained at $W_s = 2$ where of $10 \pm 1\ M^{-1}$ for EG/AOT/*n*-heptane and $0.8 \pm 0.1\ M^{-1}$ for DMF/AOT/*n*-heptane.

DISCUSSION

Mechanism of reaction

For secondary (and primary) amines as nucleophiles the general mechanism accepted[37–39] for S_NAr reactions involving halogen as leaving groups can be represented by Eqn (3).



(3)

Where B_i is the nucleophile or any other base added to the reaction medium. Application of the steady state hypothesis to this mechanism, and in the limiting situation when $k_{-1} \gg k_2 + k_3\ [B_i]$ Eqn (4) is obtained,

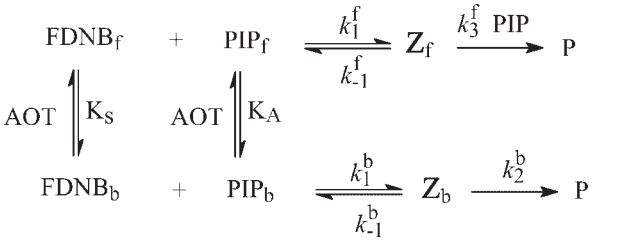
$$k_{obs}/[B_i] = k_A = k' + k''[B_i] \quad (4)$$

Where k_{obs} is the observed pseudo-first-order constant, k_A is the second-order rate constant, $k' = k_1k_2/k_{-1}$ and $k'' = k_1k_3/k_{-1}$. 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 Eqn (4) is characteristic of the majority of base-catalyzed reactions. On the other hand, if $k_{-1} \ll k_2 + k_3\ [B_i]$ or more precisely $k_2 \gg k_{-1}$, the formation of the intermediate **Z** is rate limiting and consequently $k_A = k_1$ and a plot of k_{obs} versus $[B_i]$ gives a linear response. There are intermediate situations where curvilinear dependence of k_A with amine concentration may be found.[37–39] In other words, the intermediate **Z** stabilization by the medium is crucial for the reaction pathway. In non-polar solvents where the **Z** zwitterionic intermediate is less stabilized than in polar organic solvents, large value of k_{-1} is expected with the consequent base catalysis observe in this media.[39]

In homogeneous media, as it was previously showed,[26] the decomposition of **Z** is rate limiting for the reaction in the non-polar solvent (Table 1). On the other hand, the mechanism of S_NAr reactions can change when polar solvents are used the formation of **Z** being the rate-determining step.[26,39] From Table 1, it can be seen that the reaction in water, EG, and DMF which are highly polar

(as measured its high values of π^*)[40] are not base catalyzed. Moreover, the reaction rates are considerable faster in non-HBD (with $\alpha = 0$) solvents than in HBD ones such as water and EG. This can be explained considering that in HBD solvents amines are highly solvated through hydrogen bonding. In non-HBD solvents, this interaction is not longer present with the corresponding increase in the amine nucleophilicity. These results are consistent with the fact that the reaction in water, which has the higher value of α, is slower than in the other polar solvents.

According to the results showed before and since both reactants may be distributed between the two environments, the interface and the bulk organic solvent, a mechanism summarized Eqn (5) can be proposed.



(5)

Where the subscripts and superscripts f and b indicate the non-polar organic phase and the micellar pseudophase, respectively. AOT represents the micellized surfactant molecules. The rate coefficients for the reaction k_1, k_{-1}, k_2, and k_3 were defined above [Eqn (3)]. K_S and K_A are the distribution constant for FDNB and PIP between the organic phase and micellar pseudophase, respectively.

As it was previously discussed, the reaction is wholly base catalyzed in *n*-heptane while is not in polar solvents. The micropolarity of the interface in non-aqueous reversed micelles of EG/AOT/*n*-heptane and DMF/AOT/*n*-heptane is always higher than in the organic solvent.[13] Thus, it can be assumed that the reactions of FDNB with PIP are not base catalyzed in the non-aqueous reverse micelles systems. Consequently, the formation of the intermediate $\mathbf{Z}_b$ is assumed to be rate limiting.

The rate of the reaction can be expressed by Eqn (6).

$$\frac{d[P]}{dt} = k_f[PIP_f][FDNB_f] + k'_b \frac{[PIP_b][FDNB_b]}{\overline{v}[AOT]} \qquad (6)$$

Where k_f represents the intrinsic second-order rate constant in the non-polar organic solvent ($k_f = k''[PIP_f]$). For absolute comparison of reactivity in different media, the molar reaction volume at the interface, $\overline{v}$, should be known. This can be estimated from the molar volume of AOT in the reverse micelles, which can be taken as $\overline{v} = 0.38\,M^{-1}$.[41,42] Thus, k'_b is the conventional intrinsic second order rate constant in the interface. The concentrations in square brackets correspond to the analytical concentration referred to the total volume of reverse micelle solution.

A simple mass balance using the distribution constant K_S defined in Eqn (2) and the analytical concentration of FDNB, [FNDB$_T$], allows to calculate the [FDNB$_b$] [Eqn (7)].

$$[FDNB_b] = \frac{K_S[AOT][FDNB_T]}{(1+K_S[AOT])} \qquad (7)$$

In the same way, using the distribution constant defined by Eqn (8), [PIP$_b$] can be expressed by Eqn (9)

$$K_A = \frac{[PIP_b]}{[PIP_f][AOT]} \qquad (8)$$

$$[PIP_b] = \frac{K_A[AOT][PIP_T]}{(1+K_A[AOT])} \qquad (9)$$

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 Eqn (6), we can obtain the final expression for the rate [Eqn (10)] and the observed pseudo-first-order rate constant k_{obs} [Eqn (11)].

$$\frac{d[P]}{dt} = k_{obs}[FDNB_T] \qquad (10)$$

with

$$k_{obs} = \frac{k_f + (k'_b K_S K_A [PIP_T][AOT]/\overline{v})}{(1+K_S[AOT])(1+K_A[AOT])} \qquad (11)$$

The variation of k_{obs} with the [AOT] can now be explained from Eqn (11). As can be observed when the values of the products between the distribution constants and [AOT] are not negligible respect to unity, k_{obs} would exhibit a non-linear relationship with the surfactant concentration being a value of [AOT] where the saturation of the interface is reached.[26] This is the case of EG/AOT/*n*-heptane (Fig. 1A) where $K_S = 10\,M^{-1}$. On the other hand, if K_A and K_S are small enough, this product are almost negligible respect to unity and micellar interface saturation is not reached as found for DMF/AOT/*n*-heptane (Fig. 1B) were $K_S = 0.8\,M^{-1}$.

The intrinsic second-order rate constant of the reaction in the organic solvent, k_f, is known from the studies of these reactions in *n*-hexane,[26] assuming similar characteristics of this solvent with *n*-heptane. By fitting the experimental data with Eqn (11) (Fig. 1A and B) the values of k'_b and K_A can be obtained and the results are gathered in the Table 2.

On the other hand, linear relationships of k_{obs} with the nucleophile concentration as shown in Fig. 2A and B, are indicating the lack of base catalysis at both non-aqueous micellar pseudophase. These are expected results considering that the micellar interfaces are more polar than the organic medium with the corresponding **Z** stabilization.[13] By introduction of the proper values of K_A, the values of k'_b were recalculated for each system at $W_s = 2$ by fitting a different set of experimental data (Fig. 2A and B) by Eqn (11). The results are compared in the Table 2.

Table 2. Kinetic parameters and distribution constants for the reaction of FDNB with PIP in different non-aqueous reverse micelles media at 32°C

Medium	k'_b ($s^{-1} M^{-1}$)	K_A (M^{-1})
EG/AOT/*n*-heptane $W_s = 2$	20 ± 1[a] 19 ± 1[b]	1.6 ± 0.3[a]
DMF/AOT/*n*-heptane $W_s = 2$	3314 ± 100[c] 3562 ± 100[d]	0.10 ± 0.02[c]
Water/AOT/*n*-hexane $W_0 = 10$[e]	14.3 ± 0.6	5.4 ± 0.3

[a] From fitting Fig. 1A by Eqn (11).
[b] from fitting Fig. 2A by Eqn (11).
[c] from fitting Fig. 1B by Eqn (11).
[d] from fitting Fig. 2B by Eqn (11). Parameter values calculated using 0.995 confidence level in non-linear regression.
[e] From Ref. 26.

As can be seen good estimates for k'_b within experimental error are obtained by two independent methods.

The results show similar kinetic profiles in EG/AOT/*n*-heptane at $W_s = 2$ than in water/AOT/*n*-hexane at $W = 10$.[26] With these HBD solvents, the interface saturation by the substrate is reached at around the same value of [AOT] and k'_b has comparable values. These are probably reflecting the fact that EG/AOT/*n*-heptane at $W_s = 2$ has similar properties than the reverse micelles made of water/AOT/*n*-heptane at $W = 10$ as observed with optical probes.[13]

On the other hand, when DMF is used as polar solvent, there is an increase of around 200 times on k'_b in comparison with the values obtained using HBD solvents as polar core (Table 2). Moreover, the rate of reaction rates in neat EG (Table 1) and in its microemulsions is very similar while with DMF there is an increase of about 15 times in the microheterogeneous medium. The hydrogen bond specific interaction between PIP and HBD solvents may reduce the amine nucleophilicity. On the contrary, the solvation of the amine through that kind of interaction is not possible when DMF is used as polar solvent, thus it is expected that an increase its nucleophilicity. Moreover, previous studies using 1-methyl-8-oxyquinolinium betaine (QB) as molecular probe showed that it senses a more polar environment in DMF/AOT/*n*-heptane reverse micelle than in the pure solvent even at the maximum W_s reached. This indicated that the solvent constrained in the droplet is peculiarly structured probably by strong dipolar interactions.[13] All these facts are consistent with the considerable rise in the rate reaction found in the DMF microemulsions.

In addition higher reaction rates are observed increasing W_s, (Fig. 3A and B), showing the increase in the reactivity of the micellar media as can be expected for the increase in polarity of the interface.

The distribution constants K_A and K_S, are higher when HBD solvents are used probably reflecting the importance of hydrogen bond interaction with the polar solvent in the partition to the reactants between the interface and the bulk non-polar organic pseudophase. Similar behavior was recently found for the partition of 9-anthracenemethanol and acridine orange base in different non-aqueous AOT reverse micelles system using polar solvents such as EG and DMF.[14,15]

The value of the solvatochromic parameters for PIP, $\alpha = 0.10$ and $\beta = 1.04$[40] show that this amine is a very good hydrogen bond acceptor (HBA). Recently it has been shown that the main driving force in the partition of amines in aqueous reverse micelles[43] is the HBD ability of the solute. Consequently, a larger value of K_A is expected when HBD solvents such as water and EG are used in the polar core of the aggregates as is actually found.

In summary, the work shows the possibility of using non-aqueous reverse micelles as catalytic media for S_NAr reactions when amines are use as nucleophiles. It is concluded that higher catalytic power is obtained when non-HBD solvents are used as polar solvent in the micelle interior.

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