The hydrolysis of phenyl trifluoroacetate in AOT/*n*-heptane RMs as a sensor of the

encapsulated water structure.

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**Abstract**

A study was carried out on the hydrolysis of phenyl trifluoroacetate (PTFA) in AOT/*n*-heptane/water reverse micelles. The results obtained have been interpreted by taking into account the distribution of the PTFA using a kinetic model based on the pseudophase model and, it is demonstrated that the reaction takes place in the water pool of the reverse micelles. Moreover, it is established that the water molecules involved in the hydration of the interface do not react with PTFA or they do it at much slower rate comparing with the water molecules that form the pool. The value of the second order rate constant in the water pool, $k_{w-MI}$, is of the same order of magnitude as that in pure water but is greater (500 times) than those obtained in water-acetonitrile mixtures with low water content. We performed kinetic solvent isotopic effect (KSIE) and proton inventories experiments (PI) and we concluded that the water is acting as a general-base catalyst and the water sequestered in the water pool is pre-organized favoring the activation process, in contrast to what happened in water-acetonitrile mixtures.

**Introduction**

Carboxylic esters are among the most important functional groups in organic chemistry and play a central role in biochemistry.[1] The mechanism of hydrolysis has been extensively studied under different reaction conditions and in different media. It is known that in the water-catalyzed hydrolysis of esters, the rate constants have a strong dependence on the water concentration; Neuvonen *et al.* [2,3] demonstrated that the hydrolysis of substituted phenyltrifluoroacetate in water-acetonitrile mixtures with low water content shows exceptionally negative entropies of activation that indicates a mechanism in which a

substantial increase in structuring of the solvent molecules occurs during the activation process, where the ester is preferentially solvated by acetonitrile and the polar transition state by water. 2 On the other hand, Venkatasubban *et al.* have suggested that the hydrolysis of *p*-nitrophenyltrifluoroacetate involves a bifunctional catalysis (or general base catalysis) mechanism with three water molecules in the transition state;[4] these results are in concordance with other obtained from studies of the neutral hydrolysis for p-methylphenyltrichloroacetate[5] and 4-nitrophenylheptafluorobutyrate.[6] Recently it has been demonstrated, using theoretical models that the bifunctional catalysis mechanism probably prevails in a low polarity non aqueous solution.[7]

Reversed micelles (RMs) are spatially ordered macromolecular assembly of surfactants formed in a non-polar solvent, in which the polar head groups of the surfactants point inward and the hydrocarbon chains point toward the non-polar medium.[89] This systems contain aqueous nanodroplets entrapped in a film of surfactant and dispersed in a low polarity bulk solvent and the enclosed water has physical properties, such as polarity and viscosity, that are different from those of bulk water.[10] These nanoscale aggregates are suitable media for processes that involve hydrophobic and hydrophilic reactants in a variety of chemical and biological reactions. 8[,11,12] The surfactant most frequently used is the anionic sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT, Figure 1).[13,14,15,16,17,18]

A unique microenvironment for carrying out a variety of chemical and biochemical reactions is found in the polar cores of RMs which have also been used as model systems for studying various reactions in confinement.[11,19,20,21] Despite their simplicity, they provide an excellent method to study fundamental effects of confinement. Moreover, the unique AOT interfacial properties, such as the "pH",[14,15,18] the ionic strength9[,10,15], micropolarity[10] among others make the interfacial water molecules very interesting to be

studied as reactant. The extensive use of RMs as nanoreactors for aqueous phase reactions requires precise knowledge of the states of the enclosed water. In this way, Garcia-Rios *et al.* studied the solvolytic behavior of substituted benzoyl chlorides and substituted phenyl chloroformates in AOT RMs. [22,23,24] They have shown that benzoyl chlorides with electron-releasing groups react via a dissociative mechanism giving an acylium intermediate; by contrast, electron-withdrawing groups favor an associative mechanism involving a tetrahedral intermediate, similar to the solvolytic mechanism of substituted phenyl chloroformates, with the water addition step being rate determining. Depending on the water content in the RMs, they showed that the hydration of the anionic headgroups of the surfactants increases the electron density on the hydrogen atoms in the water molecule, with the consequent breakage of the hydrogen bonds of the normal water. This type of interaction causes a reduction on the electrophilic character of the water and, consequently, an increase in its nucleophilic character.

Our group have studied the hydrolysis of substituted phenyltrifluoroacetates and demonstrated that the reaction is concerted and does not involve an intermediate, although the position of the transition state may be closer to the tetrahedral intermediate.[25,26] Besides the reaction is general base catalyzed therefore in the absence of added bases, the transition state may contain more than one water molecule therefore we consider that this ester could be a good probe as a sensor for the water structure in confined systems as are the water droplet in RM. We selected phenyltrifluroacetate (PTFA, Figure 1) as substrate and AOT/*n*-heptane RMs and from the study under different conditions together with results of kinetic isotopic effect and a proton inventory study we could demonstrate that the reaction is much faster in the water pool than in the interface. Moreover, we show that the water molecules encapsulated inside AOT RMs at $W = 1$ ($W = [H_2O]/[surfactant]$) are not involved in the

basic catalysis that the hydration reaction require, because they are strongly bounded to the

AOT molecules at the interface.
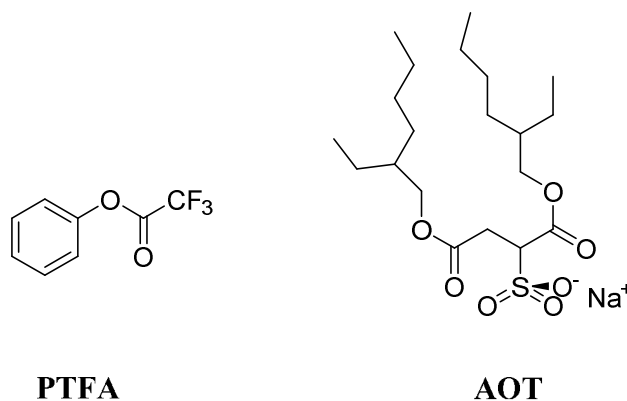


**Figure 1**: Chemical structures of molecules used in this study

**Experimental Section**

**General Methods.**

UV-vis spectra were recorded on a spectrophotometer equipped with a temperature

controlled cell holder at 25.0º C. Control experiments of neutral hydrolysis of phenyl

trifluoroacetate (Scheme 1) in the reverse micelle media showed that the final spectrum of

the phenol of the reaction coincided with another obtained dissolving the expected amount

of phenol in a similar reverse micelle solution prepared independently.

**Materials**

The substrate PTFA was prepared by the reaction of phenol with trifluoroacetic anhydride

following literature methods.[26] The product was distilled under reduced pressure and

collected after distillation of the remaining trifluoroacetic anhydride, and trifluoroacetic

acid. The IR spectrum matched that of literature.[27] The purity was controlled by

comparison of the spectrum of a completely hydrolyzed solution with a stock solution of the phenol.

Sodium bis(2-ethylhexyl) sulfosuccinate (>99%) was dried under reduced pressure and was kept under vacuum over $P_2O_5$ until it was used. *n*-heptane HPLC grade and water was ultrapure. $D_2O$ (99.9%) was used for the study of kinetic solvent isotope effects.

**Procedures:** A $2x10^{-4}$ M stock solution of PTFA was prepared by dissolving the necessary amount of PTFA in *n*-heptane. The AOT solution at the desired concentration  was prepared by dissolving the necessary amount of surfactant with the PTFA/*n*-heptane solution. To start the reaction, the surfactant solution was transferred into a volumetric flask containing a volume of the desired water (the water was previously added with a calibrated microsyringe) and the amount of water present in the system is expressed as the molar ratio between water and the surfactant ($W = [H_2O]/[\text{surfactant}]$). Experiments were performed in which the surfactant concentration was varied between 0.1 and 0.5 M while keeping constant *W*, for *W* values between 5 and 30. Under this experimental conditions the ratio $[H_2O]/[PTFA]$ was always higher than 770 since at [AOT] = 0.1M and W=5 the reactions were too slow (the half-life of the reactions, $t_{1/2}$, were greater than 9.5 hours) we did not attempt to do measurements below this concentration of AOT.

**Kinetics:** The hydrolysis reaction of PTFA (Scheme 1) was followed spectrophotometrically by monitoring the increase in the absorbance of phenol at 272 nm ($A_t$) versus time and representative absorption spectra are shown in Figure S1 (supporting

information). Pseudo-first-order rate constants, $k_{obs}$, were calculated from linear plots of

$\ln(A_\infty-A_t)$ vs. time, where $A_\infty$ is the final absorbance of the reaction at 272 nm.

The kinetic data always fitted the first-order integrated rate equation satisfactorily ($r >$

0.999). The standard deviation of the kinetic data, using different samples, was less than

5%.
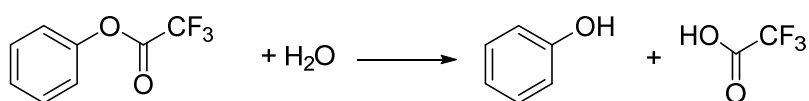


Scheme 1: Hydrolysis reaction of PTFA

**Results**

We expected that the changes in reactivity of the hydrolysis of PTFA should be

strongly related to changes in the physical properties of the confined water, which turns out

to be dependent on $W$.[11] Thus two types of experiments were carried out in the kinetic

study (*i*) the surfactant concentration was varied maintaining the $W$ parameter constant,

hence water properties are not altered. Under these conditions the effect that the RMs have

on the substrate distribution and therefore on the reactivity can be analyzed, (*ii*) the $W$

parameter was varied at constant surfactant concentration in order to study the effect of the

water structure on the chemical reactivity.

*i*) **Effects of AOT concentration.**

The surfactant concentration was varied between 0.1 and 0.5 M while keeping

constant $W$, for $W$ values between 5 and 30. Figure 2 shows the influence of the AOT

concentration on $k_{obs}$ for $W$=10 and 23. It can be seen that $k_{obs}$ increases linearly with the

AOT concentration and depend on the water content. Similar behavior was obtained for

W= 5, 15, 30, as shown in Figure S2, (supplementary information).
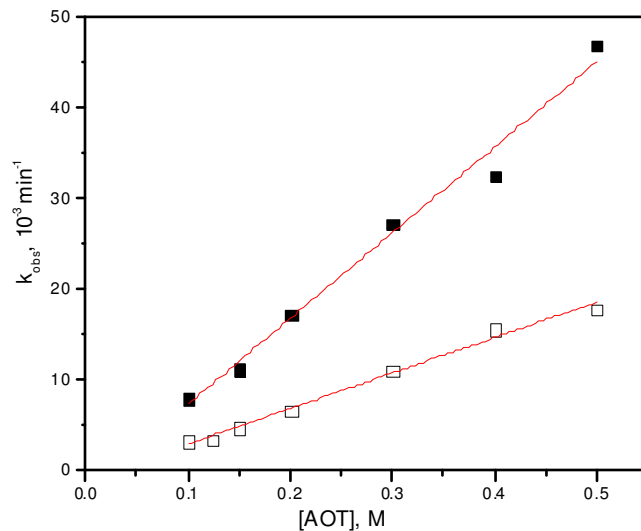


**Figure 2.** Influence of the concentration of AOT on $k_{obs}$ in

the hydrolysis of PTFA at $W = 10$ (open squares) and 23 (fill

squares) at 25.0 °C. The data were fitted to a linear equation

($r^2$=0.997).

*ii)* **Effect of *W*.**

The effect of changing *W* on $k_{obs}$ keeping AOT concentrations constant are shown in

Figure 3, for values of [AOT] between 0.1M and 0.5 M. It is remarkable that the $k_{obs}$ values

increase linearly with *W* but never reach the value measured in water ($k_{obs}^{H2O}$=117 min$^{-1}$).[28]
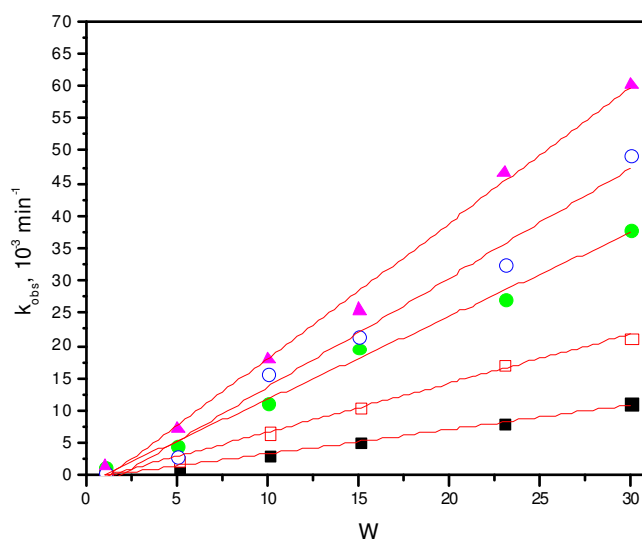
**Figure 3.** Variation of $k_{obs}$ with respect to $W$ for the hydrolysis of PTFA in water/AOT/*n*-heptane RMs. [AOT] = 0.1 M (fill square), 0.2 M (open square), 0.3M (fill circle), 0.4 M (open circle) and 0.5M (fill triangle). The data were fitted using Eq. 7 ($r^2$=0.994).

It is worth to mention that for W=1 there were no changes on $k_{obs}$ with surfactant concentration, and only we could determine a mean value of $k_{obs} = (8 \pm 5) \times 10^{-4}$ min$^{-1}$. It is known that at $W < 2$, water molecules are strongly bound to the AOT sulfonate group and under these conditions the AOT molecules form compact, polymorphic assemblies with low aggregation numbers and only adding more water but maintaining $W < 2$ leads to micellization.[29]

**Discussion**

The kinetic data for reactions in RMs can only be interpreted in terms of reactivity if the local reactant concentrations and the intrinsic rate constants for the different pseudophases in the RMs media can be obtained from apparent rate constants. We applied a kinetic model based on the pseudophase model which is generally used in studies of reactivity in micellar solutions.[11,20,21,22,24] The model assumes that RMs consists of three different pseudophases: an aqueous phase ($w$), a medium essentially consisting of $n$-heptane ($o$), and an interface consisting primarily of surfactant ($i$).

PTFA is stable in $n$-heptane and AOT /$n$-heptane RMs (in the absence of water) for a period of some days (phenol was not formed) therefore the hydrolysis reactions must take place in the aqueous pseudophase and/or at the interface, depending on the distribution of the ester. Although PTFA is a hydrophobic substrate it can be dissolved in water,[30] thus there is a chance that a small quantity of PTFA in the aqueous pseudophase could react with a rate constant greater than at the interface.

In a first approximation, we can consider that the PTFA is distributed within the three pseudophases of the RMs (Scheme 2), but the hydrolysis process takes place simultaneously at the interface and the aqueous pseudophase.
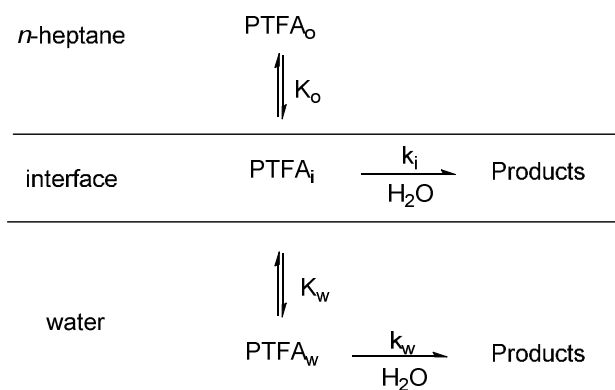
**Scheme 2**: The pseudophase model for the hydrolysis

of PTFA in AOT/*n*-heptane RMs

The global reaction rate (*r*) will be the sum of the rates in both pseudophases

$$r \; = \; k_i.\,[\text{PTFA}]_i + k_w.\,[\text{PTFA}]_w \tag{1}$$

where $k_i$ and $k_w$ are the pseudo first order rate constants of hydrolysis at the interface and aqueous phase of the RMs respectively.

The distribution equilibria of the ester between the pseudophases can be defined in terms of molar ratio as

$$K_o \; = \frac{[\text{PTFA}]_i}{[\text{PTFA}]_o.[\text{AOT}]} \tag{2}$$

$$K_w \; = \frac{[\text{PTFA}]_w.[\text{AOT}]}{[\text{PTFA}]_i.[\text{H}_2\text{O}]} \tag{3}$$

where subscripts *o*, *i* and *w* refer to the *n*-heptane, interface and aqueous phase, respectively, and the concentrations are referred to the total volume of the system.

Considering that the total concentration of the ester is the sum of the concentrations in the three pseudophases, we can obtain Eq. 4 (deduction of equation is shown in the supplementary information)

$$k_{obs} = \frac{[AOT].(k_i.K_o + k_w.W.K_w.K_o)}{1 + K_o.[AOT] + W.K_w.K_o.[AOT]} \tag{4}$$

It must be noted that the PTFA partition coefficient, $K_o$ and $K_w$ cannot be obtained experimentally because in the absence of water the UV-vis absorption of the PTFA is hidden by the tail of AOT and in presence of water the ester is susceptible toward hydrolysis (Figure S1 in supporting information).

The value of the partition coefficient between water/$n$-heptane, $K_o^w$, can be written in terms of $K_o$ and $K_w$ using Eq. 5:[31]

$$K_o^w = K_o.K_w \tag{5}$$

A possible way to estimate de value of $K_o^w$ is using the values of log P, where log P=log ([solute]$_{octanol}$/[solute]$_{water}$) = log(1/$K_{octanol}^{water}$) and on the assumption that $K_o^w \sim K_{octanol}^{water}$. The value of Log P = 2.76 was calculated theoretically[32] and gives $K_o^w \cong 0.0017$.

Considering the relationship ([AOT].$K_o$ +W. $K_w$. $K_o$. [AOT]) $\ll$ 1,[33] Eq.4 can be simplified into Eq. 6

$$k_{obs} = [AOT](k_i.K_o + k_w.K_w.K_o.W) \tag{6}$$

Replacing $K_w.K_o$ in Eq. 6 by $K_o^w$, Eq. 7 is obtained

$$k_{obs}=[AOT].(\ k_i.K_o+k_w.\ K_o^w.\ W) \tag{7}$$

This equation predicts the existence of a linear relationship between $k_{obs}$ and [AOT] at constant $W$ as well as a linear dependence of $k_{obs}$ with $W$ at constant [AOT], Figures 2 and 3 show that the results fit to Eq. 7.

Table 1 shows the values of the slopes (*slope* $_{k-AOT}$) and intercepts obtained from plots of $k_{obs}$vs. [AOT] (Figure 2) at different W and it can be seen that in all cases the intercepts are zero within experimental error and the slope increases with values of $W$.

**Table 1.** Values of the slope and intercept obtained from plots $k_{obs}$ vs. [AOT] at different W values (Figure 2) according to Eq. 7 for hydrolysis of PTFA in AOT/*n*-heptane RMs at 25 °C.

| W | *slope* $_{k-AOT}$, $10^{-3}\,M^{-1}.min^{-1}$ | Intercept, $10^{-3}min^{-1}$ |
|---|---|---|
| 5 | 15.2 | -(0.2±0.2) |
| 10 | 39 | -(0.9±0.4) |
| 15 | 52 | (0.1±0.5) |
| 23 | 94 | -(2±2) |
| 30 | 119 | -(2±3) |

The Eq. 7 predicts a linear relationship between *slope $_{k\text{-}AOT}$* vs. *W* (Figure 4) with an intercept and slope of the straight line given by $k_i.K_o$ and $k_w$. $K_o^w$ respectively. In regard to Figure 4, the intercept obtained is practically zero within experimental error (intercept= $-(6\pm4)\ x10^{-3}\ min^{-1}$) which implies a a null value of $k_i$ and therefore that there is no detectable hydrolysis coming from the interface. This fact is reinforced by the results obtained at $W = 1$ where the reaction rate is negligible in comparison with the one coming from the water pool.

This is expected considering that at this *W* there are no free water molecules to act as base catalyst as the hydrolysis reaction requires. Also, they are water molecules so structured that cannot act as catalyst in the reaction that need the help of other water molecules. It has been observed that the neutral hydrolysis of PTFA in aqueous solution of sodium dodecyl sulfate (SDS), shows a distribution between the two phases (aqueous medium and micelle) but the rate of reaction at the interface is negligible compared with that in water. [34] It is remarkable that these results contrast with those obtained previously by other authors for the hydrolysis of benzoyl chlorides[22,23,29] and we will discuss this later in the paper.

From the value of the slope of the straight line shown in Figure 4, namely $(4.1 \pm 0.1)\ x10^{-3}\ min^{-1}$, and using Eq. 7 with $K_o^w=0.0017$, we estimated the value of $k_w= (2.47 \pm0.07)min^{-1}$.
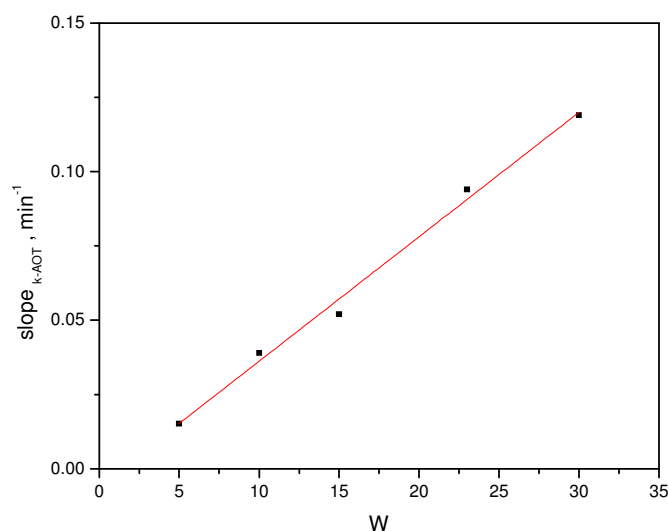
**Figure 4.** Plot of *slope* $_{k\text{-}AOT}$ vs. W for hydrolysis PTFA in AOT/*n*-heptane RMs at 25 °C using Eq.7 ($r^2$=0.991).

The values of the slope (*slope* $_{k\text{-}W}$) and intercept obtained from plots of $k_{obs}$ vs. *W* at different [AOT] (Figure 3) are summarized in Table S1 (supplementary information) and it can be observed that in all cases the intercept is practically zero and the *slope* $_{k\text{-}W}$ increases with the AOT concentration. The plot of *slopes* $_{k\text{-}W}$ vs. [AOT] is linear as shown in Figure S3 (supplementary information), with slope (4.5 ± 0.1) x $10^{-3}$ $min^{-1}$. Using Eq. 7 and the value of $K_o^w$, we estimated the value of $k_w$= (2.70 ±0.08) $min^{-1}$ in close agreement with the value obtained from the data collected at variable AOT concentration (see above).

To obtain the micellar second-order rate constants $k_{w\text{-}MI}$ for absolute comparison of reactivity in different media, the water concentration should be known.

Since we cannot calculate which is the molarity of free water (reactant) in the AOT/ *n*-heptane RMs, we calculated a range for [$H_2O$] using the highest and the lowest water

amount added during preparation of the RMs, this is 0.5 M (at W=5, [AOT]=0.1M) to 15 M

(at W=30, [AOT]=0.5M). Using these values and that obtained for $k_w$, we estimated a range

for the $k_{w-MI}$ values within 4.97 min$^{-1}$M$^{-1}$ to 0.16 min$^{-1}$M$^{-1}$ for water concentration of 0.5M

and 15M respectively. The values are in the order of magnitude of that determined for

water ($k_{w-H2O}$=2.11 min$^{-1}$M$^{-1}$)[26] but are significantly greater than that obtained in water-

acetonitrile mixture at [$H_2O$]=3.89 M (a water concentration similar to those used in the

preparation of the RMs)[2], namely $k_{w-ACN/H2O}$=3.41x10$^{-3}$ min$^{-1}$M$^{-1}$. We can affirm that the

values for $k_{w-MI}$ are not due to a higher water content in the RMs, hence a possible

interpretation for the higher value of $k_{w-MI}$ in AOT RMs in comparison with the value found

in water-acetonitrile mixtures, could be that the surfactant acts as a basic catalyst of the

nucleophilic addition of water. With regard to properties of the AOT RMs, it has been

shown that the charge density on the AOT headgroup increases as the water content of the

RMs decreases and this increase in the charge density could be responsible of its capacity

to act as a basic catalyst.[24] However we have seen that at low water content (W=1) the

reaction is very slow which indicate that the sulfonate group is not acting as general base

catalyst.

The studies carried out to evaluate the kinetic solvent isotopic effect (KSIE) in an

aqueous medium[26] or in water-acetonitrile mixtures[4] have shown that the $k_{H2O}/k_{D2O}$ = 2-3,

suggesting that water is involved in a general-base-catalyzed pathway, where one water

molecule acts as general base, removing a proton from other water molecule (nucleophile)

in the transition state. To test whether the reaction of water in the RM are general-base-

catalyzed we performed KSIE experiments in AOT/ $n$-heptane RMs at W=5 and W=30.

At W=5 the reaction is 2.24 times slower in $D_2O$ than in $H_2O$ ($k_{H2O}/k_{D2O}$ =2.24), and the

measured KSIE is similar at W=30 ($k_{H2O}/k_{D2O}$ =2.52). Since the values for $k_{H2O}/k_{D2O}$ are

practically independent of *W* and similar to that observed in pure water or water-acetonitrile mixtures, we conclude that the water is acting as a general-base catalyst.

In order to get insights into the transition state (TS) structure upon increasing the water content, we conducted proton inventories experiments (PI) 6 at W= 5 and 30. The use of PI to probe the structures of TS is documented[4,5,6,35] so that only a brief account will be given here. The observed rate constant, $k_n$, in the presence of $H_2O$–$D_2O$ mixtures is related to the observed rate constant in pure $H_2O$, $k_o$, by Eq. 8

$$\frac{k_n}{k_o} = \frac{\prod_i^{TS} (1\text{-}n\text{+}n.\varphi_i)^{\neq}}{\prod_j^{RS} (1\text{-}n\text{+}n.\varphi_j)} \tag{8}$$

where (*n*) is the atom fraction of deuterium in the solvent and (RS) refers to the reagent state. All TS hydrogens (i) and all RS hydrogens (j) that contribute to the isotope effect possess a term in the numerator and denominator, respectively. Each hydrogen site is associated with a fractionation factor, $\varphi$, that expresses the preference of deuterium for the site relative to that of bulk solvent. Analysis of the present reaction is simplified by the following: PTFA carry no exchangeable hydrogens; $\varphi$ of the other reactant, water, is unity by definition. Consequently, the denominator of Eq. (8) is unity, and we need consider only the hydrogens of the TS.

If more than a single proton undergo significant changes in bonding in passing from reactant to transition state,[35] then the plot of $k_n$ /$k_o$ versus *n* will be non linear but bowl shaped. Such a bowl-shaped plot implies a rate-determining transition state where multiple proton transfers are occurring. Figure 5 is a plot of $k_n$ /$k_o$ vs *n* for the hydrolysis of PTFA in RMs AOT at W=30 (similar behavior was observed at W=5)
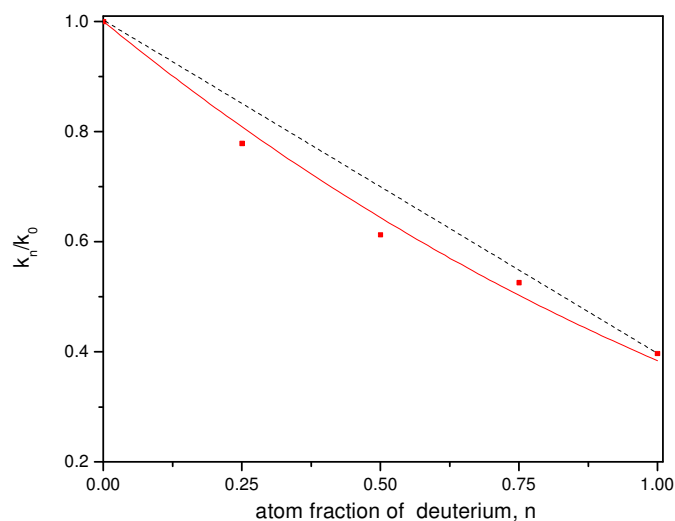
**Figure 5.** Plots of $k_n/k_o$ vs $n$ in AOT RMs at W=30. The solid line is adjusted to Eq. 9 ($r^2=0.988$) The broken line is drawn to emphasize the nonlinearity of the solid line.

Thus, the proton inventory data for W=5 y W=30 are described by Eq. 9, which is based on a three-proton model and is adequate for reactions where the number of protons participating in the rate-limiting step of the reaction is 3.4[,]5[,]6

$$\frac{k_n}{k_o}=(1\text{-}n+n.\varphi)^3 \qquad (9)$$

This equation reproduces the data satisfactorily, as can be seen from the fitting of the experimental proton inventory data in Figure 5, the values of $\varphi$ calculated are 0.74±0.01 and 0.73±0.01 for W=5 and 30 respectively. Thus, the transition state structure is independent of the content of water in the RMs and appears to be the same in both cases.

It is worth noting that the average φ for PTFA , $\varphi_{mean}$=0.735, is similar to those calculated for the pH-independent hydrolyses in aqueous acetonitrile of 4-nitrophenyl trifluoroacetate (0.697±0.005)[4], and 4-methylphenyl trichloroacetate (0.707±0.003)[5] for which cyclic TS as represented in Figure 6 were proposed.
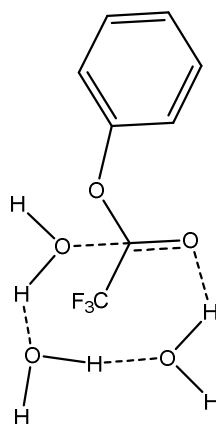


**Figure 6**: The transition state model for hydrolysis of PTFA in AOT RMs

As it was mentioned before the reaction is very sensitive to the structure of water. In water-acetonitrile mixtures with low water content, the reaction shows exceptionally negative entropies of activation which indicates a substantial increase in structuring of the solvent molecules during the activation process.[2] Hence, the catalysis observed in AOT RMs could be explained considering the reagent state. It seems to us that the water molecules reorganization process that happens on going from the initial state to the transition state during the activation process is favored if the water shows a degree of organization in the reagent state. It is known that in the AOT RMs, water interacts with the surfactant polar head through hydrogen-bond interactions at the interface, the bulk hydrogen bond network is destroyed,[36] as a consequence no reaction coming from the RMs interface even at $W = 1$ is detected. On the other hand, our results indicate that the water in

the water pool is ordered as reflected by the higher rate constant compared with that in water-acetonitrile mixtures where the water is disordered.2 Also, we are confident that variables such as pH or the ionic strength have not effect on the reaction because they are dramatically different for the interfacial water and not for the water pool, which resembles the values of the bulk water.[14,15]Thus, we show how confinement dramatically affect the water structure and its reactivity in ester hydrolysis.

### Conclusion

Applying the pseudophase model it was demonstrated that the hydrolysis of the PTFA takes place only in the water pool and there is no detectable reaction neither in the organic phase or the interface. A range for the second order rate constant in the aqueous nanodroplet, $k_{w-MI}$, was estimated and it is in the order of magnitude of that determined in pure water but much higher than the values reported in water-acetonitrile with low water content.

Kinetic solvent isotopic effect experiments (KSIE) demonstrate that free water in the water pool is acting as a general-base catalyst and using proton inventories techniques (PI) we have shown that the transition state structure is independent of the water content in AOT RMs.

The results obtained lead us to suggest that the water pool of the AOT RMs is pre-organized in a way that favor the formation of the transition state were water is acting as a nucleophile and a general base catalyst. On the other hand, the interfacial water pool is so involved in the interface solvation that cannot act as reactant for the hydrolysis reaction.

**Supporting Information Available:**

The absorption spectrum of a reaction at different times, plot $k_{obs}$ vs. [AOT], the deduction of Eq. 4, the values of slope and the intercept obtained from plots of $k_{obs}$ vs. W at different [AOT] and the plot *slope $_{k-W}$* vs. [AOT].

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