

# Hydrolysis of *p*-nitrophenyl perfluorooctanoate in mixed surfactant systems†

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The kinetics of the hydrolysis reaction of *p*-nitrophenyl perfluorooctanoate were studied in the presence of different amphiphilic systems: two hydrocarbon surfactants (sodium dodecyl sulfate, SDS, and polyoxyethylene(23)lauryl ether, Brij-35), a perfluorinated detergent (perfluorononanoic acid, PFNA) and in mixtures of SDS–PFNA and Brij-35–PFNA. The study was performed at different compositions of the mixtures (characterized by the molar fraction of PFNA,  $\alpha_{\text{PFNA}}$ ), and for each  $\alpha_{\text{PFNA}}$  the concentration was varied over a wide range. The kinetic probe *p*-nitrophenyl perfluorooctanoate showed a very strong interaction with the surfactants. In the presence of the mixed surfactants, the behaviour of the probe changed dramatically with the composition of the mixtures, which indicates that this substrate is very sensitive to the effect of the micellar media, being a very good molecule to study these types of surfactant systems. The use of the studied ester allowed us to confirm the presence of two different aggregates in the mixture Brij-35–PFNA as was previously observed with other techniques. The presence of hydrocarbon-rich micelles at low  $\alpha_{\text{PFNA}}$ , as well as perfluorinated rich micelles at high  $\alpha_{\text{PFNA}}$  was also confirmed. The kinetic behaviour of *p*-nitrophenyl perfluorooctanoate in SDS–PFNA mixtures fully agreed with our previous description of the aggregates formed in this system. The presence of a practically pure PFNA micelle at high  $\alpha_{\text{PFNA}}$  could be also demonstrated from the kinetic results.

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## 1. Introduction

The use of water as a solvent for reactions has numerous advantages when compared with organic solvents. Specifically, its non-toxic character and ability to accelerate reactions with polar transition states can bring environmental and kinetic advantages over organic solvents. Yet, its major disadvantage derives from the fact that most organic compounds are insoluble in water, thus co-solvents are generally needed, reducing its benefits. An alternative to co-solvents involves the use of surfactants. They are used in much lower concentrations than organic solvents, are non-volatile and in some cases can be recycled, turning them into environmentally friendly alternatives.<sup>1</sup>

The use of micellar systems as reaction media has been broadly studied due to their ability to modify reaction rates and selectivity, and due to their ability to solubilize organic substrates.<sup>2–4</sup> These systems are widely used in emulsion polymerization reactions,<sup>5</sup> as replacement of volatile organic solvents, as templates in the synthesis of new materials (specially nanoparticles)<sup>6,7</sup> and as enzyme and membrane

models.<sup>8,9</sup> In some cases it has been found that the use of micellar media results in different products from those obtained in homogeneous media.<sup>10</sup> Some reports also show enantioselective reactions in the presence of surfactants.<sup>11</sup>

The ability of micelles to modify reaction rates depends on several factors:<sup>12–14</sup> (a) lower dielectric constant in the micelles than in water, which causes a solvent effect; (b) stabilization/destabilization of the transition state by the head groups of the surfactants; and (c) concentration of the reactants through interactions with the micelle surface or through insertion into the micelle itself. These effects are known as Micellar Media Effects (MME).

Water-catalyzed processes are especially interesting to study MME. The rate of hydrolysis of phenyl chloroformate in cationic micelles was reported to diminish when the polar head size and the affinity of the counterion for the micelle increase.<sup>15</sup> These head-group and counterion effects indicate that depletion of water in the interfacial region complements the charge effect in the control of the reactivity in micelles. One way to assess the importance of the charge effect independently from other MME is to study the same reaction in the presence of ionic and non-ionic micelles.<sup>16</sup>

A systematic kinetic study in micellar systems offers not only information on the amphiphilic system<sup>17</sup> but also on the reactivity and reaction mechanism in these media. It also provides information on the solubilization and location of the substrate in the micelle.<sup>18</sup>

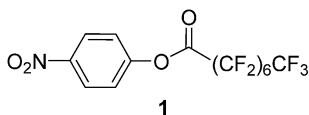
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Base-catalyzed ester hydrolysis has been widely used as a model reaction to evaluate MME in chemical reactions due to its well-known, relatively simple mechanism.<sup>19,20</sup> Its study is also particularly important since it is a key reaction in biological systems.

In the hydrolysis reactions of aryl alkanoates when the leaving group is a substituted phenoxide, the stabilization of the transition state given by the micelle remains nearly constant and is independent of the nature of the surfactant used.<sup>21</sup> This fact indicates that the reaction center and the leaving group are almost completely in an aqueous environment in the transition state. Yet, catalysis plays a major role when the length of the acyl group chain is increased, with the order *p*-nitrophenyldodecanoate > *p*-nitrophenylhexanoate  $\gg$  *p*-nitrophenyl acetate.<sup>12</sup> When the chain length is increased, the substrate associates more strongly with the micelle causing a bigger effect on the reaction.

The hydrolysis of *p*-nitrophenyl perfluorooctanoate (**1**) was previously studied in our laboratory and it was shown that it aggregates in water at very low concentrations.<sup>22</sup> The aggregation and hydrolysis reaction in water occur on a similar time scale. In that work we conducted a detailed study of the effect of several pure surfactants: sodium dodecyl sulphate (SDS), dodecyltrimethylammonium bromide and chloride, polyoxyethylene(23)lauryl ether (Brij-35), and perfluorooctanoic acid on the reactivity of compound **1** in water at pH = 6.00 and ionic strength of 0.3 M.<sup>22</sup> All surfactants were able to associate with **1** at a rate considerably faster than that of the self-association of the substrate, and well above the Critical Micellar Concentration (CMC) the hydrolysis took place in the micellar pseudo-phase at a faster rate than that in the absence of the micelles. However, we found differences in reaction rates when the ionic nature of the surfactant changed. The rates observed in the presence of nonionic surfactant had values ranging between those in cationic and in anionic surfactants, that is,  $k_{\text{cationic}} > k_{\text{nonionic}} > k_{\text{anionic}}$ . The differences observed when the nature of the surfactant changed, indicates that it may be a good sensor of micellar effects. Recently, we characterized two mixed surfactant systems, Brij-35-perfluorononanoic acid (PFNA)<sup>23</sup> and SDS-PFNA.<sup>24</sup> We established that in the Brij-35-PFNA system two non-coexisting aggregates are formed (evidenced by the presence of two CMC).<sup>23</sup> We attributed the first CMC to a mixed aggregate that changes its morphology when reaching the second CMC. In the SDS-PFNA system instead, mixed micelles are formed at low  $\alpha_{\text{PFNA}}$ ; yet, aggregates richer in the fluorinated surfactant are formed at high  $\alpha_{\text{PFNA}}$  but only one CMC is observed.<sup>24</sup>



Taking into account the results mentioned above regarding the effect of surfactants on the hydrolysis of **1**, we carried out a study of the kinetic of the reaction in the presence of mixed surfactants since we considered that it might give information

about the nature of the mixture at the molecular level. We found that the changes in the observed rate constants are in good agreement with the results previously published regarding the properties of the surfactant mixtures and the results are reported here.

## 2. Results and discussion

The effect of the mixtures of Brij-35-PFNA and SDS-PFNA was evaluated on the kinetic behaviour of **1**. The study was performed by varying the composition of the mixture, characterized by the molar fraction of the fluorinated surfactant ( $\alpha_{\text{PFNA}}$ ). The hydrolysis reaction of ester **1** in water and in the presence of different surfactants or mixtures was followed by UV-Visible absorption spectroscopy, measuring the appearance of *p*-nitrophenol at 319 nm or the disappearance of the substrate at 260 nm. As the total change in optical density measured at the higher wavelength was larger, resulting in more accurate rate constant values, we only report the data obtained at this wavelength. However, it should be noted that at 260 nm the observed rate constants showed similar trends as those measured at 319 nm and the analysis of the data obtained led to the same general conclusions.

The reaction was evaluated in the absence of buffer or additional electrolytes to avoid complications in the interpretation of the results associated with the exchange of additional ions at the interface. In previous work<sup>25</sup> we have demonstrated that the reaction of aryl trifluoroacetates is independent of the pH below pH = 7, therefore it is reasonable to assume that the kinetic of **1** is also pH independent in acidic solution.

### 2.1. Hydrolysis of **1** in water

Although this substrate was previously studied in water at pH 6 and controlled ionic strength, we re-analyzed the reaction of **1** in water without any additives to have the same conditions that in the following studies in the presence of surfactants.

At all substrate concentrations, using water as solvent, good isosbestic points are observed in the absorbance vs. wavelength plot (Fig. 1A is representative). However, the absorbance vs. time data fits to a double exponential equation implying the presence of two kinetic processes (see Fig. 1B). Table 1 summarizes the variation of the observed rate constant with the substrate concentration in water. It can be seen that there is a tendency for the rate constant  $k_2$  to decrease when concentration increases. This behavior is usually found in compounds that self-aggregate in solution: when aggregation increases, reactivity decreases, especially in fluorinated reactants.<sup>26</sup>

Fluorocarbon surfactants are known to have a slow aggregation rate.<sup>27</sup> In substrate **1** the slow aggregation manifests itself in the fact that aggregation and hydrolysis occur at similar time scales, which means that aggregation competes with hydrolysis. However, this is not the case with hydrocarbon-derived esters, thus only one kinetic process (corresponding to the hydrolysis of the aggregated substrate) is observed. It is important to note that neither  $k_1$  nor  $k_2$  represent rate constants of elementary reactions. They are a combination of several elementary

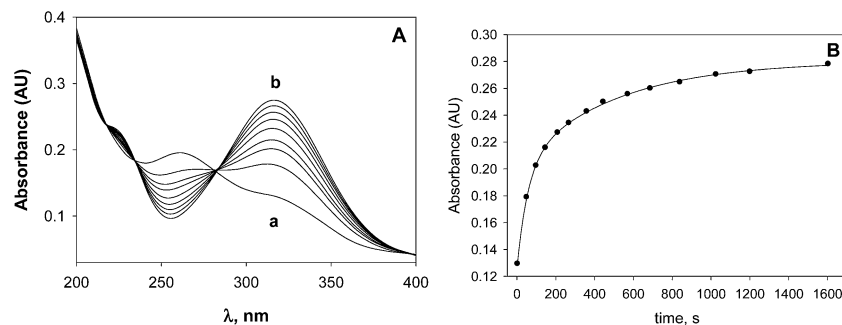


Fig. 1 (A) Hydrolysis of **1** in water. Time elapsed between a and b: 30 minutes.  $T = (25.0 \pm 0.1) ^\circ\text{C}$ , MeCN = 3.8%,  $[\mathbf{1}] = 2.5 \times 10^{-5} \text{ M}$ . (B) Absorbance at 319 nm vs. time data for the spectra in (A). Data were fitted to a double exponential equation.

Table 1 Observed rate constants for the hydrolysis of **1** in water as a function of substrate concentration<sup>a</sup>

$[\mathbf{1}]$ , $10^{-5} \text{ M}$	$k_2$ , $10^{-2} \text{ s}^{-1}$	$k_1$ , $10^{-2} \text{ s}^{-1}$	$[\mathbf{1}]^b$ , $10^{-5} \text{ M}$	$k_2^b$ , $10^{-2} \text{ s}^{-1}$	$k_1^b$ , $10^{-2} \text{ s}^{-1}$
1.00	$0.18 \pm 0.01$	$2.04 \pm 0.03$	1.08	0.191	1.03
2.50	$0.150 \pm 0.002$	$2.1 \pm 0.1$	2.47	0.212	0.89
3.36	$0.149 \pm 0.004$	$1.6 \pm 0.1$	3.45	0.118	0.469

<sup>a</sup>  $T = (25.0 \pm 0.1) ^\circ\text{C}$ ; solvent contains MeCN = 3.8%;  $\lambda = 319 \text{ nm}$ . The values of the rate constants were obtained by fitting the absorbance *versus* time data to the following equation:  $A = A_\infty + a_1 e^{-k_1 t} + a_2 e^{-k_2 t}$ . Each value corresponds to the average of at least three determinations; the errors are standard deviations from the fit. <sup>b</sup> Data taken from ref. 22, ionic strength 0.3 M; pH 6.00; [buffer] = 0.096 M ( $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ ).

reactions. To find the relationship between the values of the observed  $k_1$  and  $k_2$  and every step of the mechanism it would be necessary to know it in detail, which is not possible with the available data.

Comparing the values of  $k_1$  and  $k_2$  with those previously published in the presence of buffer (pH = 6) and 0.3 M ionic strength we can see (Table 1) that  $k_2$  have similar values whereas  $k_1$  are significantly different. It was suggested that  $k_1$  have high contribution of the hydrolysis rate while  $k_2$  is mainly related to the rate of self-aggregation of **1**. This may indicate that the change in ionic strength modify the water structure in the proximity of the reacting ester.

## 2.2. Hydrolysis of **1** in the presence of pure surfactants

The kinetic behaviour shown in the presence of pure surfactants varies according to the surfactant employed. Table 2 depict the observed rate constants for the hydrolysis of **1** at concentration  $2.5 \times 10^{-5} \text{ M}$  in the presence of variable concentrations of Brij-35 and SDS.

At concentrations below the surfactant CMC, two kinetic processes are observed in a similar way to what happens in the absence of surfactants, although the rate constants are different. This observation shows that, below their CMC, these surfactants are not efficient enough to disaggregate the substrate. Once the surfactant concentration is well above the CMC, only one kinetic process is detected. This fact indicates that **1** is incorporated into the micelle faster than it self-aggregates. In the case of Brij-35 the maximum value of the rate constant observed ( $45\text{--}48 \times 10^{-2} \text{ s}^{-1}$ ) is higher than the value obtained for SDS ( $\approx 1 \times 10^{-2} \text{ s}^{-1}$ ). The behaviour of SDS is quite

different to what is usually observed in other reactions. As it can be seen in Table 2 the observed rate constant first decreases and then suddenly increases to reach an almost constant value. This result might indicate that at low micellar concentration more than one molecule of **1** (pre-associated) interacts with the

Table 2 Effect of single hydrocarbon surfactants on the observed rate of hydrolysis of **1**<sup>a</sup>

[Surf], $10^{-3} \text{ M}$	SDS ( $8.25 \times 10^{-3} \text{ M}$ )		Brij-35 ( $0.09 \times 10^{-3} \text{ M}$ )
	$k_2$ , $10^{-2} \text{ s}^{-1}$	$k_1$ , $10^{-2} \text{ s}^{-1}$	$k$ , $10^{-2} \text{ s}^{-1}$
0.20			$4.7 \pm 0.3$
0.50	$0.29 \pm 0.01$	$0.7 \pm 0.2$	
0.75	$0.21 \pm 0.02$	$0.60 \pm 0.02$	
2.00			$38 \pm 6$
3.00		$0.52 \pm 0.07$	
5.00		$0.30 \pm 0.02$	
7.00		$0.259 \pm 0.002$	$45 \pm 1$
10.00		$1.04 \pm 0.07$	
15.00		$1.07 \pm 0.01$	
20.00			$43 \pm 1$
35.00		$0.99 \pm 0.03$	
50.00			$48 \pm 5$

<sup>a</sup>  $[\mathbf{1}] = 2.5 \times 10^{-5} \text{ M}$ ;  $T = (25.0 \pm 0.1) ^\circ\text{C}$ ; solvent contains MeCN = 3.8%;  $\lambda = 319 \text{ nm}$ . If only one value of rate constant is informed, it means that the data fit to a single-exponential equation. When two values are informed, they were obtained by fitting the absorbance *versus* time data to the following equation:  $A = A_\infty + a_1 e^{-k_1 t} + a_2 e^{-k_2 t}$ . Each value corresponds to the average of at least three determinations; the errors are standard deviations from the fit. The values in brackets correspond to the previously determined CMC of the pure surfactants (see ESI, Table S1† and ref. 23 and 24).

micelle but when the micelle concentration increases, is the monomer the one that interacts with the micelle.

On the other hand, **1** shows only one kinetic process at all concentrations of PFNA even at concentrations below its CMC (Table 3). This result indicates that PFNA interacts with **1** even at very low concentration and prevents its self aggregation. The rate constants determined for this process are somewhere between the values of the two kinetic processes observed for the substrate in pure water, and it decreases with the increase in surfactant concentration reaching a value approximately constant above the CMC of PFNA. These results are similar to those previously reported for the kinetic of **1** in the presence of perfluorooctanoic acid.<sup>22</sup>

The effect of the surfactants on the rate constants depends on their nature, and may result from a combination of factors such as localization of the substrate in the micelle and the transition state of the reaction. It is well known that fluorinated chains are highly hydrophobic, so it can be expected that the substrate chain is associated with the micelle. However, the aromatic ring moiety is less lipophilic, so this part of the molecule can be located in a more aqueous region. The interfacial region is less polar and "less aqueous" than water, so the reaction is expected to be inhibited when compared to pure water as was observed for several different systems. For instance, the spontaneous hydrolysis of phenyl chloroformate in water–ethylene glycol was studied in presence of alkyl-trimethylammonium surfactants. The hydrolysis was retarded in the presence of micelles. This was expected since deacylations are inhibited by a decrease in solvent polarity and water content, which occurs in micellar interfacial regions.<sup>28</sup>

With PFNA two other factors have to be considered to explain the observed behaviour: (i) PFNA has a very low  $pK_a^{12,29}$  so, when dissolved in water, it can be considered an anionic surfactant. As mentioned above, the presence of anionic surfactants destabilizes the transition state thus inhibiting the reaction. (ii) As both, surfactant and substrate, have perfluorinated hydrophobic chains, they associate strongly and the substrate is disaggregated even at low surfactant concentrations (only one kinetic process is observed). This substrate–surfactant association has two opposite effects: on one hand, the disaggregation

of the substrate increases the reaction rate; on the other hand, the strong interaction of the substrate with the surfactant makes the ester less available to react with water.

Brij-35 is a non-ionic surfactant so it would not affect the transition state of the hydrolysis reaction through electrostatic interactions, but it does affect the aggregation of **1**. Hence, when the substrate associates with Brij-35 micelles its hydrolysis rate is increased (Table 2) partly due to the fact that **1** is disaggregated. The strong association of Brij-35 with perfluorinated compounds was previously attributed to interactions between the  $-C^{\delta+}-F^{\delta-}$  dipoles of the substrate and the corresponding  $-C^{\delta+}-O^{\delta-}$  of the oxyethylene units of the surfactant.<sup>30,31</sup> Also, it is known that ether groups of polyoxyethylene surfactants interact with interfacial water.<sup>32</sup> El Eini *et al.* reported that polyoxyethylene surfactants have water molecules trapped in the polyoxyethylene headgroup with 5.2 to 10.5 water molecules per ethylene oxide unit as the hydrophilic chain length increases.<sup>33</sup> In the case of the microemulsions of an analogous surfactant, Brij-30 (shorter headgroup), enhancement of the nucleophilic character of the interfacial water at low interface hydration was confirmed by NMR studies and correlated with the catalysis shown for solvolysis of 4-nitrobenzoyl chloride.<sup>32</sup> A similar effect was proposed to explain the increase in the solvolysis constants found for 4-nitrobenzoyl chloride in Brij-35 micelles.<sup>34</sup> The authors suggest that Brij-35 micelles offer an environment with a concentration of water significantly lower than that in the aqueous phase<sup>35</sup> but that can be compared with a highly hydrated nonionic microemulsion. The increment seen in the hydrolysis rate constants for compound **1** in the presence of Brij-35 may result from two effects: the interaction of the ester with the micelles, that disaggregate it, plus the particular water environment present in Brij-35 micelles. However, the rate constants obtained at the maximum Brij-35 concentration (almost  $0.5 \text{ s}^{-1}$ ) is still 10 times smaller than the estimated rate constant for the neutral hydrolysis of monomeric ester **1**, that is  $5 \text{ s}^{-1}$ .<sup>22</sup> The results can be rationalized in terms of the partitioning of the reactant between water and micelles whose interfacial regions are less polar than pure water and similar to mixed organic solvents as reaction media.<sup>14</sup>

Finally, in the presence of SDS, two kinetic processes are observed below its CMC, with a decrease in the observed rate constant ( $k$ ). This is similar to the behaviour shown in PFNA, although SDS below its CMC is not efficient enough to disaggregate the substrate, thus only the effect of the negative head group is observed. When the CMC of SDS is reached, only one kinetic process is observed, indicating that **1** associates with the micelle and  $k$  increases up to  $0.01 \text{ s}^{-1}$ . This increment can be attributed to substrate disaggregation. Despite this, the values reached are lower than those in Brij-35 and pure water since SDS is an anionic surfactant and, as already mentioned, ionic strength and negative charge affect hydrolysis rate, in addition to lesser accessibility to water when the substrate associates to a micelle. The negatively charged interface in anionic surfactants can also contribute to producing a decrease in the rate values observed due to the destabilization of the transition state. This behaviour was exhibited in several systems: the rate constant for

Table 3 Effect of PFNA on the observed hydrolysis rate of **1**<sup>a</sup>

[Surf], $10^{-3} \text{ M}$	PFNA ( $2.11 \times 10^{-3} \text{ M}$ ) $k$ , $10^{-2} \text{ s}^{-1}$
0.05	$0.8 \pm 0.2$
0.25	$0.49 \pm 0.02$
0.50	$0.480 \pm 0.001$
1.00	$0.3183 \pm 0.0006$
2.00	$0.28 \pm 0.02$
4.00	$0.116 \pm 0.001$
5.00	$0.106 \pm 0.003$
6.00	$0.1017 \pm 0.0008$
7.00	$0.103 \pm 0.001$

<sup>a</sup> [**1**] =  $2.5 \times 10^{-5} \text{ M}$ ;  $T = (25.0 \pm 0.1) \text{ }^\circ\text{C}$ ; solvent contains MeCN = 3.8%;  $\lambda = 319 \text{ nm}$ .

the hydrolysis of 4-nitrophenyl chloroformate decreases in the presence of anionic and non-ionic micelles, and it is more sensitive to the structure of the head group than to the length of the surfactant hydrophobic tail. In this case the effects are not ascribed either to sizeable differences in the micelle-ester association constants nor to entirely different average solubilization/reaction sites in the micellar pseudophases. They arise mainly from the medium effect, the interaction of the reactant state with the anionic surfactant and the destabilization of the transition state by the charged interface.<sup>36</sup>

In summary, there are different effects that can influence the reaction rate of a compound in the presence of micellar media. It is not easy to determine their contribution to the effect observed, or which one is more important to predict substrate behaviour.

### 2.3. Hydrolysis of 1 in the mixed system Brij-35-PFNA

The results of the hydrolysis of 1 in mixtures of Brij-35-PFNA are summarized in Table 4. Under all conditions the absorbance values vs. time fit to a simple exponential equation, indicating that only one kinetic process takes place.

From the analysis of the data in Table 4 it can be seen that for a constant total surfactant concentration higher than  $1 \times 10^{-4}$  M, the observed rate constant decreases with the increase in molar fraction of PFNA. For instance, at a total surfactant concentration of  $5 \times 10^{-3}$  M, the observed rate constants vary from  $25.9 \times 10^{-2} \text{ s}^{-1}$  to  $0.45 \times 10^{-2} \text{ s}^{-1}$  for  $\alpha_{\text{PFNA}} = 0.1$  and 0.9 respectively (Fig. 2). When the molar fraction of PFNA increases, its content in the mixture also rises, and the observed rate constant at  $\alpha_{\text{PFNA}} = 0.9$  decreases to a similar value to that obtained in the presence of a 10 times lower concentration of pure PFNA (Table 3,  $[\text{PFNA}] = 0.5 \times 10^{-3}$  M,  $k = 0.48 \times 10^{-2} \text{ s}^{-1}$ ).

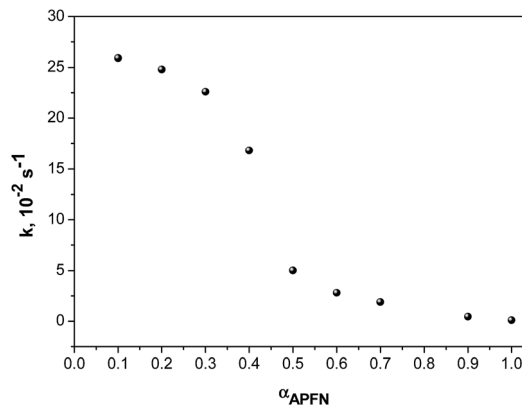


Fig. 2 Observed rate constant for the hydrolysis of 1 as a function of PFNA molar fraction at  $[S]_{\text{total}} = 5 \times 10^{-3}$  M for the mixture Brij-35-PFNA.  $[1] = 2.5 \times 10^{-5}$  M;  $T = (25.0 \pm 0.1) \text{ }^\circ\text{C}$ ; the solvent contains MeCN = 3.8%;  $\lambda = 319$  nm.

Fig. 2 shows that the largest decrease occurs before  $\alpha_{\text{PFNA}} = 0.5$  is reached. From  $\alpha_{\text{PFNA}} = 0.5$  to  $\alpha_{\text{PFNA}} = 1$ , the rate decrease is less significant, probably indicating that the composition change in the micelle is less important. Compound 1, strongly associated with the perfluorinated surfactant, may be sensing an intramicellar demixing, *i.e.*, a region in the micelle enriched with PFNA, due to the enrichment of the aggregate in the perfluorinated surfactant. That could be the reason for the lesser dependence of the observed rate constant with  $\alpha_{\text{PFNA}}$ . A similar behaviour is evidenced at other constant concentrations of the mixture analysed.

As it was reported before,<sup>23</sup> mixtures of PFNA with Brij-35 have two critical micellar concentrations (ESI, Table S1†) which have been attributed to a change in morphology of the micelle when the concentration increases.

Table 4 Observed rate constants ( $10^{-2} \text{ s}^{-1}$ ) for the hydrolysis of 1 in Brij-35-PFNA mixtures<sup>a</sup>

[Surf], $10^{-3}$ M	$\alpha_{\text{PFNA}}$							
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.9
0.01	2.13 ± 0.01	3.6 ± 0.9	2.9 ± 0.5		3.4 ± 0.3	2.1 ± 0.1	3.5 ± 0.2	
0.05	4 ± 2	3.51 ± 0.09	2.48 ± 0.07	2.6 ± 0.1	2.9 ± 0.1	1.64 ± 0.05	2.4 ± 0.3	3.1 ± 0.2
0.1		6 ± 2	2.38 ± 0.07	2.35 ± 0.01	2.18 ± 0.08	1.22 ± 0.04	2.0 ± 0.2	2.9 ± 0.2
0.2		4.0 ± 0.2	3.5 ± 0.4	3.4 ± 0.1	2.4 ± 0.2	2.3 ± 0.5	1.26 ± 0.08	1.58 ± 0.03
0.5	8.3 ± 0.7	11.9 ± 0.8	8.9 ± 0.6	7.7 ± 0.3	5.18 ± 0.09	2.8 ± 0.1	2.9 ± 0.4	1.3 ± 0.1
0.7		12.5 ± 0.8	16.1 ± 0.6		7.8 ± 0.2		4.55 ± 0.03	
1	14 ± 1		21.8 ± 0.4	16.5 ± 0.4	9.9 ± 0.4	7.9 ± 0.2	5.9 ± 0.2	1.7 ± 0.1
2	22 ± 1	19.9 ± 0.8	16.9 ± 0.6	19.7 ± 0.2	8.3 ± 0.3	5.1 ± 0.6	3.6 ± 0.2	2.5 ± 0.1
3.5					6.8 ± 0.6		1.89 ± 0.05	1.6 ± 0.1
5	25.9 ± 0.6	24.8 ± 0.9	22.6 ± 0.4	16.8 ± 0.2	5.01 ± 0.07	2.8 ± 0.1	1.9 ± 0.1	0.447 ± 0.008
7					4.21 ± 0.08	2.7 ± 0.3	1.61 ± 0.01	
10			18.3 ± 0.3	6.17 ± 0.08	3.73 ± 0.03	2.5 ± 0.2		
15	28.9 ± 0.5	15.8 ± 0.4	13.8 ± 0.2	5.48 ± 0.09				
20		16.6 ± 0.7	9.3 ± 0.3					
30	27.2 ± 0.9							
50	25.6 ± 0.4							

<sup>a</sup>  $[1] = 2.5 \times 10^{-5}$  M;  $T = (25.0 \pm 0.1) \text{ }^\circ\text{C}$ ; the solvent contains MeCN = 3.8%;  $\lambda = 319$  nm. The data fit to single-exponential equation. Each value corresponds to the average of at least six determinations and the errors are standard deviations of the fit. The CMCs previously obtained for different compositions of this mixed system are summarized in ESI, Table S1† and ref. 23.



The analysis of the data at each molar fraction (Table 4 and Fig. 3) has three regions: (i) a region under the first CMC of the mixtures, where the observed rate constants do not change or decrease slightly; (ii) a region between both CMC, where the observed rate constants increase; (iii) a third region, at high  $[S]_{\text{total}}$ , where the rate constants diminish sharply. This behaviour is common to all the solutions with PFNA molar fraction higher than 0.1. For the solution with  $\alpha_{\text{PFNA}} = 0.1$  the decrease in rate after the second CMC is less marked.

It is worth noting that, at a surfactant concentration lower than the first CMC, only one kinetic process is observed, with a rate constant value similar to that of the fastest process for the reaction in water ( $k_1$  in Table 1). As mentioned earlier, the fastest kinetic process is mainly associated with the hydrolysis reaction. This behaviour is similar to that found in pure PFNA.

The second region seen in the plots of Fig. 3 occurs at surfactant concentrations above the first CMC value. The rate increase detected after the first CMC is similar to that found in pure Brij-35; however, the maximum rate constant value obtained was 1.5 to 2 times lower than the value observed at the same concentration of pure Brij-35, even at low  $\alpha_{\text{PFNA}}$ . Besides, the maximum is considerably higher than the value obtained at the corresponding concentration of pure PFNA. This result may indicate that within this concentration range (between  $\text{CMC}_1$

and  $\text{CMC}_2$ ) hydrocarbon-rich mixed micelles are formed and the presence of some fluorinated compound in the aggregates is responsible for the decrease in rate compared with pure Brij-35 micelles. On the other hand the micelles formed after  $\text{CMC}_2$  are fluorocarbon-rich micelles, therefore the hydrolysis of **1**, especially at high  $\alpha_{\text{PFNA}}$ , has a rate constant similar but not equal to that found in the pure fluorocarbon surfactant. We suggest that the presence of some Brij-35 in the micelle is responsible for the small acceleration of the rate compared with the value in pure perfluorinated surfactant. The picture of the system from the kinetic data is in good agreement with our previous results on the characterization of this mixture using other techniques.<sup>23</sup>

#### 2.4. Hydrolysis of **1** in the mixed system SDS–PFNA

Contrary to the observed behaviour of the mixtures Brij-35–PFNA, SDS–PFNA mixtures show only one CMC.<sup>24</sup> However nuclear magnetic resonance results indicate that there are intramolecular demixing at high  $\alpha_{\text{PFNA}}$ .

Table 5 summarizes the results of the hydrolysis of **1** in SDS–PFNA mixtures. It can be seen that the behaviour of **1** depends, again, on the composition of the mixture. At low surfactant concentrations two kinetic processes are observed, but for  $\alpha_{\text{PFNA}} = 0.2$  already at  $7 \times 10^{-4}$  M of total surfactant concentration, only one kinetic process is observed indicating that the

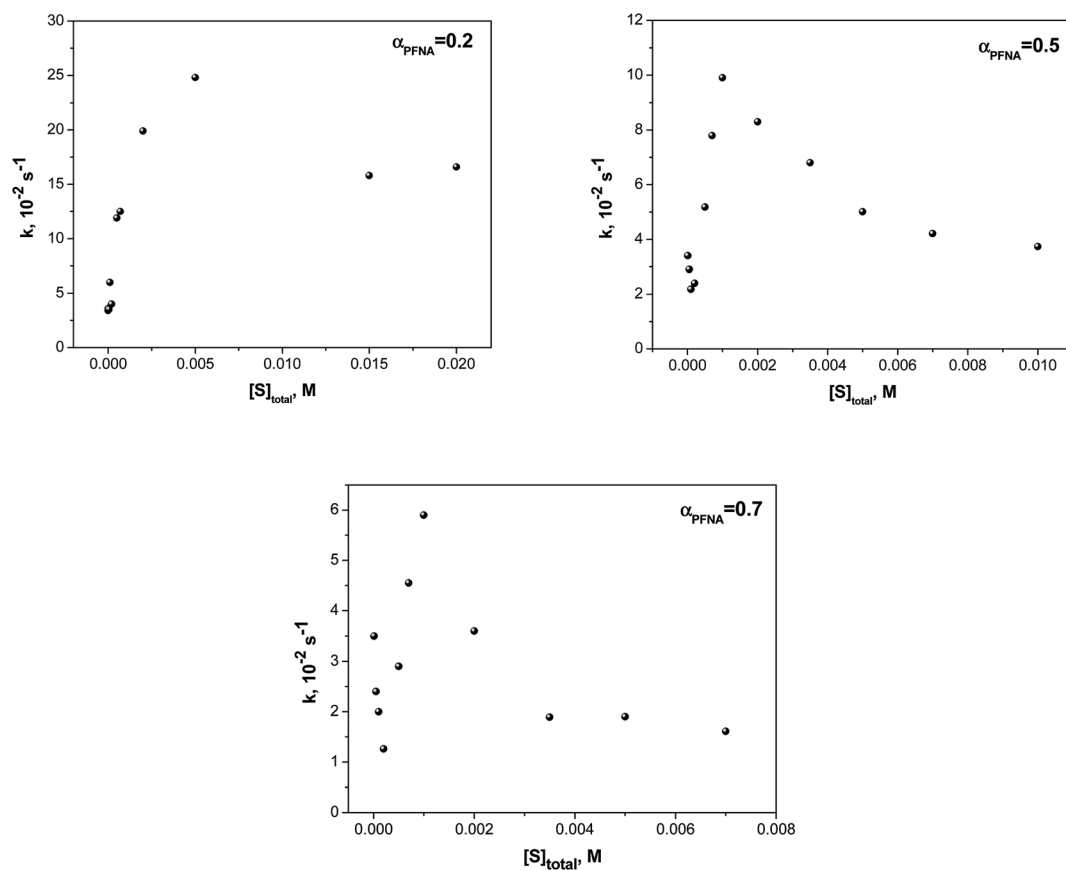


Fig. 3 Observed rate constants for the hydrolysis of **1** as a function of total surfactant concentration for Brij-35–PFNA mixture ( $[S]_{\text{total}}$ ).  $\alpha_{\text{PFNA}} = 0.2$ ,  $\text{CMC}_1 = 1.1 \times 10^{-4}$  M,  $\text{CMC}_2 = 5.7 \times 10^{-4}$  M;  $\alpha_{\text{PFNA}} = 0.5$ ,  $\text{CMC}_1 = 1.6 \times 10^{-4}$  M,  $\text{CMC}_2 = 7.4 \times 10^{-4}$  M;  $\alpha_{\text{PFNA}} = 0.7$ ,  $\text{CMC}_1 = 2.4 \times 10^{-4}$  M,  $\text{CMC}_2 = 1.0 \times 10^{-3}$  M.  $[\mathbf{1}] = 2.5 \times 10^{-5}$  M;  $T = (25.0 \pm 0.1)^\circ\text{C}$ ; the solvent contains MeCN = 3.8%;  $\lambda = 319$  nm.

Table 5 Observed rate constants ( $10^{-2} \text{ s}^{-1}$ ) for the hydrolysis of **1** in SDS–PFNA mixtures<sup>a</sup>

[Surf], $10^{-3} \text{ M}$	$\alpha_{\text{PFNA}}$ (CMC)							
	0.2 (8.26 mM)		0.5 (5.53 mM)		0.7 (4.03 mM)		0.9 (3.10 mM)	
	$k$	$k_2$	$k_1$	$k_2$	$k_1$	$k$		
0.70	0.64 ± 0.05	0.0227 ± 0.0006	0.25 ± 0.03	0.102 ± 0.002	0.77 ± 0.02			
0.75		0.039 ± 0.001	0.37 ± 0.06					
1.00	0.170 ± 0.004	0.028 ± 0.005	0.365 ± 0.007		0.092 ± 0.001			
2.00	0.24 ± 0.02						0.21 ± 0.01	
2.50			0.134 ± 0.002		0.105 ± 0.009			
3.00			0.1314 ± 0.0003				0.1445 ± 0.0005	
4.00	0.134 ± 0.001						0.112 ± 0.001	
5.00					0.117 ± 0.001		0.136 ± 0.002	
6.00			0.110 ± 0.001				0.105 ± 0.003	
7.00	0.35 ± 0.02		0.1037 ± 0.0008				0.103 ± 0.002	
7.50			0.102 ± 0.001		0.120 ± 0.001		0.130 ± 0.002	
10.00			0.0989 ± 0.0009		0.122 ± 0.002		0.099 ± 0.002	
15.00	2.1 ± 0.1							
20.00	4.6 ± 0.1							
30.00	5.1 ± 0.4							
35.00	4.5 ± 0.1							

<sup>a</sup> [**1**] =  $2.5 \times 10^{-5} \text{ M}$ ;  $T = (25.0 \pm 0.1) ^\circ\text{C}$ ; the solvent contains MeCN = 3.8%;  $\lambda = 319 \text{ nm}$ . If only one value of rate constant is informed, it means that the data fit to a single-exponential equation. When two values are informed, they were obtained by fitting the absorbance vs. time data to  $A = A_\infty + a_1 e^{-k_1 t} + a_2 e^{-k_2 t}$ . Each value corresponds to the average of at least two determinations and the errors are standard deviations of the fit. The values in brackets correspond to the CMC of the mixture at the corresponding  $\alpha_{\text{PFNA}}$  (ESI, Table S1† and ref. 24).

association of the substrate with the present perfluorinated surfactant inhibits the self-association of **1**. At this molar fraction the maximum value of the observed rate constant obtained is higher than in pure SDS and in pure PFNA. This result might indicate that the interphase in this mixed micelle has the water less structured and more available for the reaction. At higher molar fraction the rate constants measured after the CMC have about the same value as that in pure perfluorinated surfactant which may indicate same intramolecular demixing and association of the probe with the fluorinated reach region of the micelle. This is consistent with the fact that at low  $\alpha_{\text{PFNA}}$  the micelles are mixed while at high  $\alpha_{\text{PFNA}}$  the aggregates become almost of pure PFNA, as reported elsewhere.<sup>24</sup>

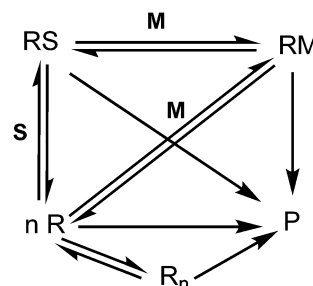
### 2.5. Comparison between the different systems under study

The behaviour of **1** in the presence of surfactants can be represented by Scheme 1, where R is the substrate, S is the monomeric surfactant, M represents the micelles and P represents the products of the reaction. Each step has its rate and/or equilibrium constants, which are not shown in the scheme for clarity reasons. A detailed kinetic analysis is not possible due to the many reaction paths involved. Depending on the surfactant or mixtures of surfactant employed, different regions in Scheme 1 gain relevance. When the reaction takes place in SDS or Brij-35, we observe two kinetic processes at concentrations below the respective CMCs indicating that these monomeric surfactants are not able to completely disaggregate the substrate; thus, the reaction still occurs, partly, from the aggregated substrate. On the other hand, PFNA can disaggregate the ester **1** even at concentrations lower than its CMC. In addition, PFNA

can modify the offered environment to the reaction when it is mixed with hydrocarbon surfactants. This is reasonable considering that perfluorinated chain have more affinity among themselves than towards hydrocarbon chains.

Although we cannot determine quantitatively the association constants of ester **1** with the mixed surfactant systems, we can make some qualitative estimates of the interaction. Due to the presence of PFNA in mixtures with Brij-35, only one kinetic event occurs even at lower concentrations than the first CMC of the system. Only one kinetic process was found in all compositions of the mixture, indicating that the interaction of **1** with these aggregates is stronger than with pure Brij-35 micelles.

In mixtures of PFNA with SDS instead, at concentrations lower than the CMC, two processes are still present. The mixture is not able to completely disaggregate the substrate when micelles are not present. This could indicate a weaker interaction of substrate **1** with this mixed system.



Scheme 1 Representation of the hydrolysis of **1** in the presence of surfactants.

The effect of the different systems on the hydrolysis rate of **1** was mainly attributed to (i) destabilization of the transition state in anionic systems; (ii) different content of water or different polarity of the micellar interfaces in the mixed systems. We determined the polarity of the aggregate interfaces at different compositions of each system using pyrene as micropolarity probe<sup>37</sup> (ESI, Table S2†). The ratio between the vibronic bands of the fluorescence spectra of pyrene in SDS–PFNA, ( $I_1/I_3$ ), changes from 0.82 at  $\alpha_{\text{PFNA}} = 0.1$  to 1 at  $\alpha_{\text{PFNA}} = 0.5$ . The value of the same ratio, ( $I_1/I_3$ ), for pure PFNA is also 1, indicating that after  $\alpha_{\text{PFNA}} = 0.5$  the probe senses a similar polarity to that of an aggregate formed only by PFNA, reinforcing the concept that the micelles at high  $\alpha_{\text{PFNA}}$  in this mixture are mainly formed by PFNA as we previously established.<sup>24</sup> On the other hand, the same analysis for Brij-35–PFNA mixtures shows changes in polarity from 1.08 to 1.31 for  $\alpha_{\text{PFNA}}$  0.1 to 0.9 respectively, *i.e.*, an increase in the ratio with the increase in  $\alpha_{\text{PFNA}}$ . Considering that the value of the ( $I_1/I_3$ ) ratio is 1.59 in water,<sup>37</sup> the polarity of the Brij-35–PFNA interface is higher than that corresponding to SDS–PFNA. This fact is also in good agreement with the higher hydrolysis rate observed in the first mixtures. The difference in the polarity of the micellar interface could partly explain the difference evidenced in the rate constants, as another factor influencing micellar effects on organic reactions.

By using mixtures of surfactants we aim to find synergism, it means, better properties in the mixture compared with pure surfactants. In this case, although the micellar system formed by Brij-35–PFNA is more efficient than that of SDS–PFNA, since the disaggregation of the substrate is performed at lower surfactant concentrations with higher hydrolysis rate constants, pure Brij-35 is still much better as the rate constants are higher than those in the Brij-35–PFNA system.

The study of this hydrolysis reaction in these mixed surfactant systems was, however, valuable to gain further knowledge of these complex mixtures. These results are in very good agreement with those obtained with other techniques dealing specifically with the characterization of the mixtures at a molecular level.

### 3. Conclusion

The behavior of **1** was markedly different in both systems studied, showing that this substrate is very sensitive to the environment and to the effect of micellar media.

The differences in the kinetic behavior of **1** in the mixed Brij-35–PFNA system when the total surfactant concentration changed, allowed us to confirm the presence of two different aggregates in this mixture as was previously observed with other techniques.<sup>23</sup> The presence of hydrocarbon-rich micelles at low  $\alpha_{\text{PFNA}}$ , as well as perfluorinated rich micelles at high  $\alpha_{\text{PFNA}}$  was also confirmed.

The SDS–PFNA system was also evaluated. The sensitivity of the substrate is quite amazing since the kinetic behavior fully agrees with our previous description of the system obtained *via* the application of different techniques to characterize the aggregates formed. The presence of a practically pure PFNA micelle at high  $\alpha_{\text{PFNA}}$  could also be demonstrated from the kinetic results.<sup>24</sup>

As **1** has a long fluorinated chain, it can be incorporated into the micelles. Its behavior is strongly dependent on the characteristics of the aggregates and it can sense slight differences. It can clearly distinguish variations in the ionic nature of the polar head as well as in the chain. It is a substrate which can be used effectively as a kinetic molecular probe in these systems.

The differences noted in substrate **1** when the micellar system changes show the importance of the nature of the surfactant polar head when dealing with reactions carried out in colloidal systems.

## 4. Experimental

### 4.1. Materials and methods

Aqueous solutions were made up from water purified in a Millipore apparatus. Acetonitrile HPLC grade (Mallinckrodt) was used as received.

Ester **1** was prepared by the reaction of perfluorooctanoic acid chloride with *p*-nitrophenol following literature methods.<sup>38</sup> The product was obtained after distillation of the remaining acid chloride and phenol, and it was characterized by IR and UV-Visible spectroscopy.

PFNA (Fluka, GC grade), SDS (Sigma-Aldrich, 99%) and Brij-35 (Riedel de Haën, 98%) were used as received. All surfactant solutions in water were prepared at least 24 hours before use to ensure that the aggregation equilibrium was reached. Pyrene (Aldrich, 98%) was used without purification.

### 4.2. Reaction kinetics

The reactions were followed measuring the change in absorbance with time for the appearance of *p*-nitrophenol at 319 nm or the disappearance of **1** at 260 nm. The reactions of **1** in the presence of Brij-35 or in the Brij-35–PFNA mixtures were carried out in a stopped flow apparatus with unequal mixing. The substrate was dissolved in dry acetonitrile and placed in the small syringe (0.1 mL). The larger syringe (2.5 mL) was filled with a water solution containing the surfactants. The reactions of the substrate in water, with pure PFNA or SDS or in the SDS–PFNA mixtures were measured in a conventional UV-visible spectrophotometer. For these kinetic runs, 0.12 mL of a stock solution of **1** in acetonitrile were injected into a 1 cm optical path length quartz cuvette containing 3 mL of water or an aqueous solution of surfactant. In all cases the total acetonitrile concentration was 3.8%, and the reactions were carried out at  $(25.0 \pm 0.1)^\circ\text{C}$ .

As the reactions in PFNA have a pH around 3, we carried out some of the reactions in Brij-35 using  $\text{HCl } 1 \times 10^{-3} \text{ M}$  as solvent to check that the pH did not affect the rate constants. The values of *k* in the presence and absence of HCl were the same within the experimental error so we continued the experiments using water as solvent.

### 4.3. Micropolarity determinations

Studies were carried out by adding a very small volume of a stock solution of pyrene in acetonitrile to a volumetric flask. The corresponding surfactant or mixture of surfactants was then



added. The dilutions prepared in this way contained 0.08% acetonitrile in water. The concentration of pyrene in the solutions was  $1 \times 10^{-6}$  M. The ratio of the bands ( $I_1/I_3$ ) was determined after measuring the fluorescence intensity of pyrene at 374.5 and 384.0 nm. The excitation wavelength was 334 nm.

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