Hydrolysis reactions of two benzoyl chlorides as probe to investigate reverse micelles formed by the ionic liquid-surfactant bmim-AOT

Nahir Dib[a]*, R. Dario Falcone[a] and Luis García-Río[b]*

[a] Instituto para el Desarrollo Agroindustrial y de la Salud (IDAS). CONICET. Departamento de Química. Universidad Nacional de Río Cuarto. Agencia Postal # 3. C.P. X5804BYA Río Cuarto. ARGENTINA.

[b] Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Física. Universidade de Santiago de Compostela, 15782 Santiago, SPAIN.

* Corresponding-Authors: Dr. N. Dib. E-mail: ndib@exa.unrc.edu.ar

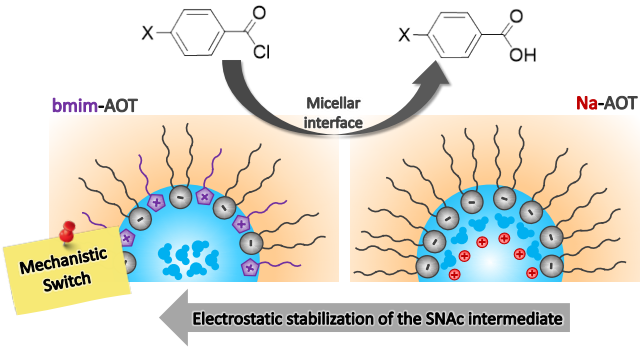
Prof. L. García-Río. E-mail: luis.garcia@usc.es

ABSTRACT

In this work, two hydrolysis reactions were used as probe to investigate the properties of reverse micelles (RMs) formed by the ionic liquid-surfactant 1-butyl-3-methylimidazolium 1,4-bis-2-ethylhexylsulfosuccinate (bmim-AOT). The results were compared with those found for RMs generated with sodium 1,4-bis-2-ethylhexylsulfosuccinate (Na-AOT). As external nonpolar solvents, *n*-heptane (*n*-Hp), isopropyl myristate (IPM) and methyl laurate (ML) were used. Thus, the effect of changing the Na^+ cation by $bmim^+$ was analyzed, as well as the impact of the replacement of a conventional external nonpolar solvent by biocompatible solvents. The kinetics of the hydrolysis reactions of 4-methoxybenzoyl chloride (OMe) and 4-(trifluoromethyl)benzoyl chloride (CF_3) were studied. The results indicate that the replacement of the Na^+ counterion by $bmim^+$ in AOT RMs alters the rates of reactions carried out in them and produces changes in the reaction mechanism. In bmim-AOT RMs, the $bmim^+$ cation is located between the surfactant molecules; this has an important influence on the reaction intermediates' stability and, therefore, in the reaction rates and mechanism. Also, the results indicate that when IPM is used as external solvent instead of ML or *n*-Hp, interfacial water molecules have larger nucleophilicity due to the higher interface penetration of IPM.

KEYWORDS: ionic liquid-like surfactant, reverse micelles, nontoxic solvents, hydrolysis, bmim-AOT, benzoyl chloride.

TABLE OF CONTENTS



1. INTRODUCTION

Reverse Micelles (RMs) are aggregates formed by surfactant molecules in a nonpolar organic medium.[1–4] In these systems, molecules with amphiphilic properties self-assemble so that their polar groups are located towards the interior of the aggregate, while the hydrocarbon chains point outwards, towards the nonpolar solvent. If a third component of polar nature is added, it is encapsulated inside the micellar system. Thus, RMs present three microenvironments: the polar core, the micellar interface, and the external nonpolar phase.[5]

The properties of RMs depend on mainly of the type of external nonpolar solvent, the nature of the surfactant, and the confined polar solvent. Based on the nature of the encapsulated solvent, two types of RMs can be defined: aqueous RMs, in which water is encapsulated,[6–11] and non-aqueous RMs, in which other polar solvents are confined, such as ethylene glycol, dimethylformamide, ionic liquids (ILs), among other.[2,12] The external nonpolar solvent can be a traditional solvent, such as *n*-heptane (*n*-Hp), toluene or benzene,[8,13,14] biocompatible nonpolar solvents, such as isopropyl myristate (IPM) or methyl laurate (ML),[15–17] or hydrophobic ILs.[18] Furthermore, a widely used parameter when studying RMs is W, which is defined as the molar ratio between polar solvent and surfactant; when the polar solvent is water, $W=W_0$ and W_0=[water]/[surfactant].[2]

ILs are salts formed by large and asymmetric ions; many of them are liquid at room temperature since the attractive forces between the anion and the cation are weak compared to conventional salts.[19–25] In general, ILs consist of an organic cation, among the most widely used are 1-alkyl-3-methylimidazolium[26–28], N-alkyl pyridinium[29,30], tetraalkylammonium[31–33] and an inorganic anion, such as halide anions (Cl^-, Br^-, I^-)[34–36], tetrafluoroborate [BF_4^-],[37] bis-(trifluoromethylsulfonyl)imide [NTf_2^-][37] and hexafluorophosphate [PF_6^-].[37,38]

As noted above, ILs can be used in the formation of RMs systems, constituting the external nonpolar phase or the polar core, depending on their properties. Furthermore, there are

ILs with amphiphilic properties that can be used as surfactants in the generation of RMs.[39–44] In these IL-surfactants, at least one of the ions that form it has amphiphilic properties.[19,45–48]

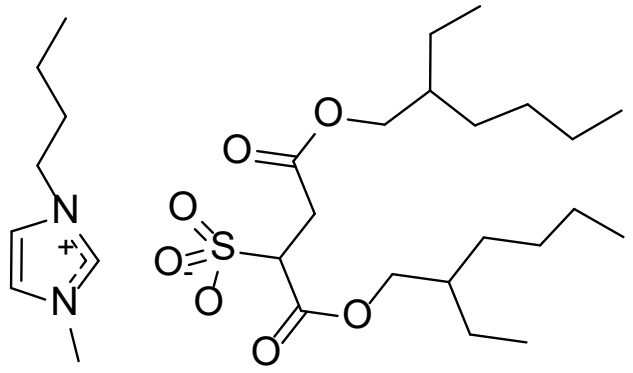
In our group, RMs have been generated using different ILs in their composition, either as the polar component or as the surfactant.[7,8,11,49] One of the IL-surfactants that we have used in the formation of aqueous RMs is 1-butyl-3-methylimidazolium 1,4-bis-2-ethylhexylsulfosuccinate (bmim-AOT, **Scheme 1**).[7,8,10,11] Traditional nonpolar solvents such as toluene, benzene, chlorobenzene and *n*-Hp were initially used. However, the formation of bmim-AOT RMs using biocompatible nonpolar solvents (IPM and ML) was recently reported,[11] with the aim of developing less toxic and more environmentally friendly reverse micellar systems.

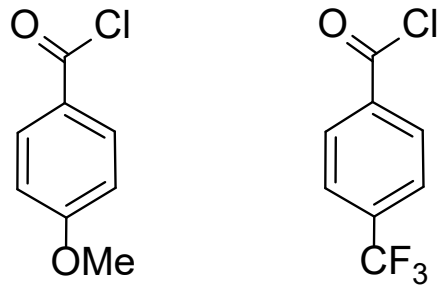
In the present work, we continue with the study of the properties of bmim-AOT RMs in *n*-Hp, IPM and ML, and its comparison with the micellar systems formed by the traditional surfactant sodium 1,4-bis-2-ethylhexylsulfosuccinate (Na-AOT), using two reactions as probe. The objective is to obtain more information about the interfacial composition and properties of bmim-AOT and Na-AOT RMs, and at the same time, analyze the effect that these systems have when they are used as nanoreactors.

Two substrates were used for this study: 4-methoxybenzoyl chloride (OMe) and 4-(trifluoromethyl) benzoyl chloride (CF_3) (**Scheme 1**). This choice is based on the fact that the hydrolysis reaction of these benzoyl chlorides (**Scheme 2**) is very sensitive to the properties of the reaction medium.[50] Furthermore, the solvolysis of these substrates has been studied in different supramolecular systems, such as direct micelles,[51,52] vesicles,[50] and reverse micelles[53–55] with very interesting results. In particular, studies in RMs show interesting aspects since both the rate and the mechanism of the reaction are modified.[53,55–57]

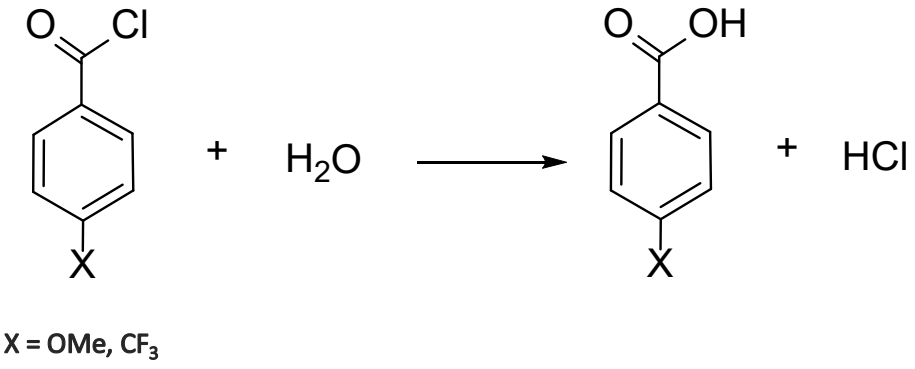
Both OMe and CF_3 are very poorly soluble in water, thus it can be assumed that in RMs they are only located in the external nonpolar solvent and/or the micellar interface.[55] Thus, the

hydrolysis reaction only occurs at the interface, where both the substrate and the water are present, allowing to obtain information about the properties of the micellar interface and interfacial water.





Scheme 1. Molecular structure of bmim-AOT and the benzoyl chlorides OMe and CF_3.



Scheme 2. Hydrolysis reaction of benzoyl chlorides OMe and CF_3.

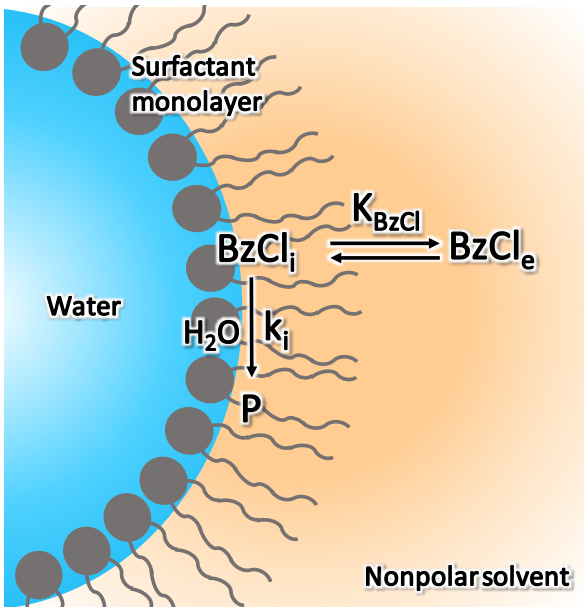
The obtained results provide kinetic evidence of the different interfacial properties of Na-AOT and bmim-AOT RMs, and the influence of the replacement of the external nonpolar solvent *n*-Hp by the biocompatible IPM and ML. The present work shows that when studying reactions in reverse micellar systems, it is not only important to take into account the effect of the counterion on the properties of interfacial water, but also the location of the counterion in the RM and the impact of this on the stabilization of the reaction intermediate. In some cases, as in the hydrolysis of benzoyl chloride OMe in bmim-AOT RMs, this factor is very important, not only produces changes in the reaction rates but also in the mechanism.

Furthermore, the results found evidenced the different penetration of biocompatible external solvents in bmim-AOT RMs, which had not been possible to detect previously by ^{1}H NMR. Therefore, the present work also shows that the study of the kinetics of the hydrolysis reactions in RMs is an interesting alternative to techniques more commonly used in investigating these micellar systems, such as the ^{1}H NMR technique.

2. RESULTS AND DISCUSSION

To determine the kinetic parameters from the experimental data, a model developed in previous works based on the formalism of the micellar pseudophase was used. The pseudophase model was originally developed for direct micelles[58–61], however, it can be applied to other supramolecular systems such as RMs with satisfactory results. According to this model, the reverse micellar system consists of an aqueous phase, the interface and the continuous nonpolar medium.[56,62] When a substrate is added to the system, it is located in one or more of the micellar pseudophases according to its solubility. Thus, the overall reaction rate of the substrate is given by the sum of the reaction rates in each pseudophase and will depend on the reagent concentrations in the aqueous phase, the interface and the continuous medium. As noted before,

both OMe and CF_3 are poorly soluble in water,[55] thus it can be assumed that in RMs they are only present in the external nonpolar solvent and/or the micellar interface. Accordingly, the hydrolysis reaction only occurs at the interface, where both the substrate and the water are present (**Scheme 3**).



Scheme 3. Benzoyl chloride (BzCl) distribution processes in the reverse micellar system and location of the reaction. K_{BzCl} is the partition constant of BzCl; k_i is the hydrolysis rate constant at the micellar interface; $BzCl_e$ and $BzCl_i$ are the substrate located at the external phase and interface, respectively.

According to **Scheme 3**, the relationship between the composition of the micellar system and the pseudo first-order rate constant, k_{obs}, for the hydrolysis of benzoyl chloride is given by the equation 1 [56,62]:

$$k_{obs} = \frac{k_i K_{BzCl}}{K_{BzCl}+Z} \quad (1)$$

where k_i is the rate constant of hydrolysis at the micellar interface and K_{BzCl} is the partition constant of benzoil chloride between the external nonpolar solvent ($BzCl_e$) and the interface ($BzCl_i$):

$$K_{BzCl} = \frac{[BzCl]_i}{[BzCl]_e} Z \quad (2)$$

In equation 2, the concentrations refer to the total volume of the system and Z is defined as Z = [nonpolar solvent]/[surfactant].

Reordering **Equation 1** the following expression is obtained:

$$\frac{1}{k_{obs}} = \frac{1}{k_i} + \frac{Z}{k_i K_{BzCl}} \quad (3)$$

according to which, if $1/k_{obs}$ is plotted as a function of Z parameter, a straight line is obtained whose slope is equal to $1/k_iK_{BzCl}$ and the intercept $1/k_i$; the K_{BzCl} value can be obtained from the relationship between the intercept and the slope. Then, once the K_{BzCl} value is known, the rate constant k_i is obtained through **Equation 1**.

Experimentally, the hydrolysis reactions of OMe and CF_3 were followed by monitoring the UV-vis absorbance of the substrate as a function of time and the pseudo first-order rate constant, k_{obs}, was obtained by nonlinear regression of the absorbance-time data, by the integrated first-order rate equation 4:

$$A_t = A_0 + (A_\infty - A_0) \exp(-k_{obs}\, t) \quad (4)$$

where A_0, A_t, and A_∞ are the absorbances at times 0, t and infinity, respectively.

First, the hydrolysis reaction rates of OMe and CF_3 were obtained in bmim-AOT and Na-AOT RMs, varying the surfactant concentration and keeping the water content constant (W_0). Then, K_{BzCl} values for OMe (K_{OMe}) and CF_3 (K_{CF3}) in each micellar system were determined from the experimental data and applying **Equation 3**.

Furthermore, a series of experiments were carried out in which the water content (W_0) was varied in order to analyze the influence of the degree of hydration of the micellar interface and the interfacial composition on the reaction rate. The k_{obs} values were obtained under the different experimental conditions and then, with the K_{BzCl} values and **Equation 1**, the k_i values were calculated.

The results obtained from the study of the hydrolysis reactions of OMe and CF_3 in bmim-AOT and Na-AOT RMs using *n*-Hp, IPM and ML as nonpolar solvent, following the procedure described, are presented below.

2.1. Hydrolysis of OMe

The absorption spectra of a typical run corresponding to the hydrolysis of OMe in Na-AOT/*n*-Hp RMs are shown in **Figure S1**. In Na-AOT/biocompatible solvent, bmim-AOT/*n*-Hp and bmim-AOT/biocompatible solvent RMs the absorption behaviors were similar. Initially, a single band corresponding to the absorption of OMe is observed in the spectrum; then, the absorbance of this band decreases with time and a new band develops at a shorter wavelength that corresponds to the product of the reaction. An isosbestic point between these bands can be observed. The OMe hydrolysis reaction in the RMs was followed by monitoring the disappearance of the reagent at 280-295 nm depending on the micellar system (see pages S11-S201 and S275-S751 of the Supporting Information).

As mentioned before, a series of experiments were performed in which the reaction rates of OMe in the RMs were determined at different concentrations of surfactant keeping the water content constant, to calculate the K_{OMe} values (see the Supporting Information).

Then, OMe reaction rates in the different micellar systems were determined by varying the water content. From the k_{obs} values obtained in these experiments and the partition constants (**Table S1**), the values of the rate constant of hydrolysis at the micellar interface, k_i, were calculated using **Equation 1**. **Figure 1** shows the results obtained for the hydrolysis of OMe in Na-AOT/*n*-Hp and bmim-AOT/*n*-Hp RMs. Similar tendencies were found when using IPM and ML as nonpolar external solvents (**Figure S4** and **S5**).

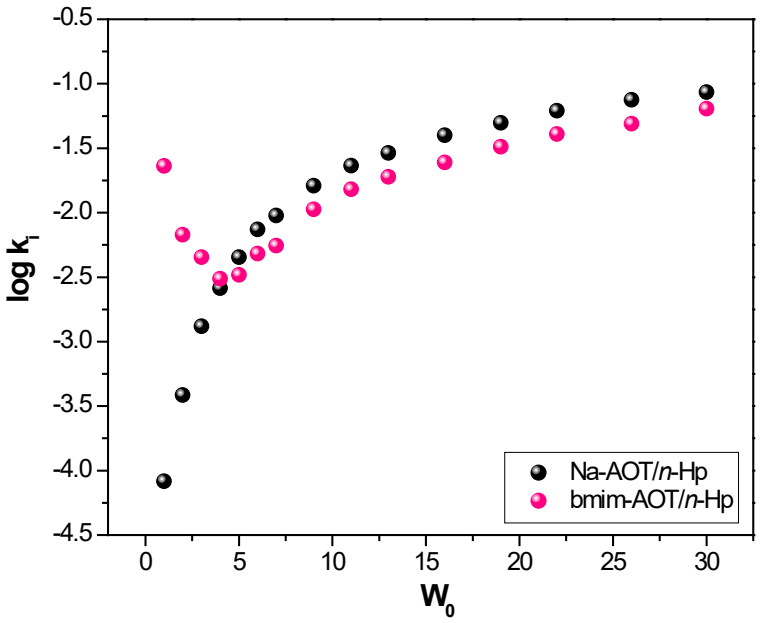


Figure 1. Log k_i as a function of the water content (W_0) for OMe hydrolysis reaction in Na-AOT/*n*-Hp and bmim-AOT/*n*-Hp RMs. T = 25°C.

As can be seen in **Figures 1**, **S4** and **S5**, in Na-AOT RMs a gradual increase in the hydrolysis reaction rate occurs with increasing W_0. Interestingly in bmim-AOT RMs, the observed trend depends on the W_0 range analyzed. At $W_0 > 5$, the reaction rate increases with

increasing water content as for Na-AOT systems; however, at W_0<5 a decrease in the reaction rate is observed when increasing the amount of water confined in the micellar system.

Benzoyl chlorides can react with nucleophiles via nucleophilic acyl substitution which involves the formation of a tetrahedral anion intermediate (SNAc), or through a dissociative mechanism (S_N1), in which an acyl carbocation is formed.[50,53,55,56] The latter predominates in benzoyl chlorides with electron-donating substituents since they stabilize the carbocation; while the SNAc mechanism is favored for benzoyl chlorides with electron-withdrawing groups because they stabilize the anionic intermediate.[50,54]

The hydrolysis of OMe generally occurs through a dissociative mechanism (S_N1).[50,55] In this case, the reaction rate is strongly affected by the polarity of the medium and the ability to stabilize the leaving group.[50,54–56] Water encapsulated within a reverse micellar system is less polar and less available compared to a continuous aqueous phase;[62] therefore, the hydrolysis of OMe in the micellar medium is slower than in pure water. Furthermore, the lower the water content in the RMs, greater will be the reduction in the polarity of the encapsulated water. Therefore, in Na-AOT RMs the increase in the hydrolysis rate of OMe with increasing water content (**Figures 1**, **S4** and **S5**) can be attributed to the increasing polarity of the medium. Similar results have been found for water/Na-AOT/isooctane, water/H-AOT/isooctane,[56] and water/ammonium bis(2-ethylhexyl)phosphate/isooctane[57].

Previous studies of Na-AOT RMs in *n*-Hp, IPM, and ML, using ^{1}H NMR spectroscopy,[10,11] reveal that interfacial water molecules interact with the anionic head group of AOT. At low water contents, practically all water molecules are involved in the hydration of the surfactant, through the formation of hydrogen bonds between the hydrogen of the water and the oxygen of the sulfonate group of AOT. Therefore, in addition to the decreasing polarity of the medium, at low W_0 the water molecules are not available for the solvation of the leaving

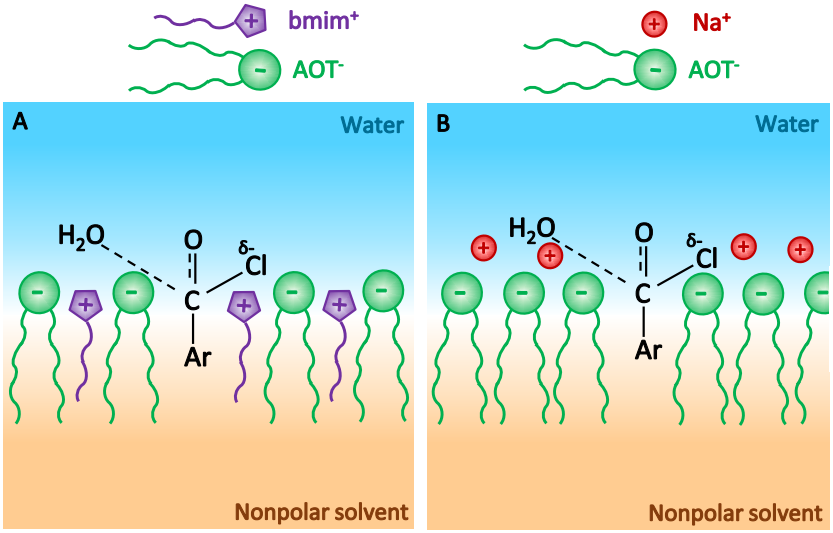
group (Cl^-), which makes the reaction less favorable. Because of this, in Na-AOT RMs, the hydrolysis reaction is slower at low water content.

In bmim-AOT RMs, the increase in the reaction rate of OMe when the water content is increased for W_0=5-30 can also be explained based on the increasing polarity of the encapsulated water and the higher ability to stabilize the Cl^- ion. However, to explain the observed trend at low W_0 values (W_0<5), other factors must be considered.

Unlike the dissociative mechanism, the rate of the hydrolysis reaction that proceeds through SNAc mechanism is highly dependent on the nucleophilicity of water.[50,54–56] In both Na-AOT and bmim-AOT RMs, interfacial water molecules have larger nucleophilicity than bulk water as a result of the interaction with the AOT polar head. As W_0 decreases, the proportion of interfacial AOT-interacting water increases, which could favor water nucleophilicity and thus SNAc reaction mechanism. In Na-AOT RMs, even at low water contents, the S_N1 mechanism predominates, which is in agreement with the increase in the hydrolysis rate observed when W_0 increases (**Figures 1**, **S4** and **S5**). However, the results suggest that in bmim-AOT RMs, at low W_0 (W_0<5) the SNAc mechanism is more favorable, finding a decrease in the reaction rate when the water content increases. These differences found for Na-AOT and bmim-AOT RMs at low W_0 can be explained taking into account the chemical nature of the surfactant counterion and how this influences the stabilization of the reaction intermediate.

The hydrolysis of OMe via nucleophilic acyl substitution involves the formation of an anionic intermediate, therefore, this reaction pathway would be favored in an environment in which the negative charge of the intermediate is stabilized. Considering the more hydrophobic character of $bmim^+$ compared to Na^+, in bmim-AOT RMs the $bmim^+$ cation is part of the surfactant layer. Therefore, the presence of the $bmim^+$ cation at the micellar interface, which is where the hydrolysis reaction occurs, stabilizes the intermediate with a partial negative charge

277 of the SNAc mechanism. In contrast, since the Na^+ counterion is located in the aqueous
278 pseudophase in Na-AOT RMs, the negative charge density at the interface is larger than in the
279 system formed by bmim-AOT (**Scheme 4**); therefore, the increased electrostatic repulsion with
280 the anionic intermediate of the SNAc mechanism makes the OMe hydrolysis reaction less
281 favorable in Na-AOT RMs.
282



283

284 **Scheme 4.** The $bmim^+$ cation at the micellar interface of bmim-AOT RMs stabilizes the
285 intermediate with a partial negative charge of the SNAc mechanism (A); in Na-AOT RMs, the
286 Na^+ counterion is located in the aqueous phase therefore the greater negative charge at the
287 interface destabilizes the intermediate (B).
288

289 In summary, for the hydrolysis of OMe in Na-AOT RMs, the dissociative mechanism
290 predominates in all the range of W_0 analyzed; however, in the micellar systems formed by
291 bmim-AOT, both reaction mechanisms compete, being more favorable the SNAc mechanism
292 at low water contents and the S_N1 for $W_0 > 5$. Therefore, the replacement of the Na^+ counterion
293 by $bmim^+$ in AOT RMs not only alters the interfacial properties and the reaction rates carried
294 out in them but also produces changes in the reaction mechanism.

Previous works have reported a similar mechanistic switch for the hydrolysis of benzoyl chlorides in RMs. In particular, studies of the hydrolysis of benzoyl chloride and 4-methylbenzoyl chloride in water/ammonium bis(2-ethylhexyl) phosphate/isooctane[57], isooctane/Brij 30/water[53] and isooctane/Na-AOT/water[56] RMs show changes in the reaction mechanism when the water content is varied. Unlike the present work, in these previous reports, the change of mechanism is due to interfacial water properties and the surfactant charge.

It is important to note that at $W_0 > 5$, where the S_N1 mechanism predominates in both Na-AOT and bmim-AOT RMs, the reaction rates are slightly larger in the micellar systems formed by the traditional surfactant Na-AOT (**Figure 1**, **S4** and **S5**). This can be attributed to the higher stability of the carbocationic intermediate in Na-AOT RMs, as a result of a larger negative charge density of the micellar interface compared to bmim-AOT RMs, as previously commented.

Figure 2A shows the log k_i as a function of water content for the hydrolysis of OMe in Na-AOT RMs in *n*-Hp, IPM and ML, while **Figure 2B** shows the results corresponding to the bmim-AOT systems.

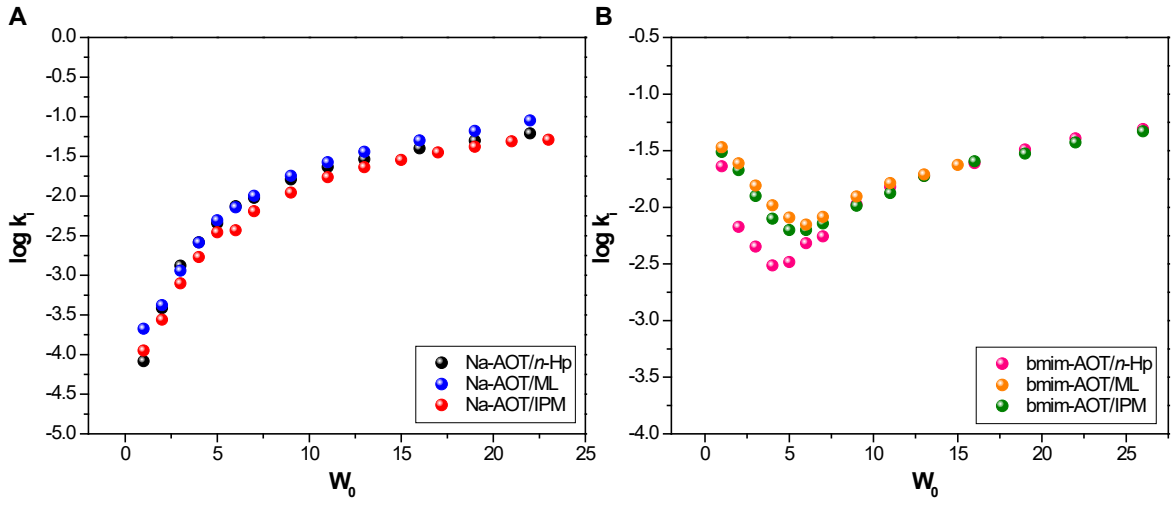


Figure 2. Log k_i as a function of the water content (W_0) for OMe hydrolysis reaction in (A) Na-AOT and (B) bmim-AOT RMs, using *n*-Hp, IPM and ML as nonpolar external solvent.

Figure 2A shows that the hydrolysis reaction rate of OMe in Na-AOT RMs practically does not vary when changing the external solvent. In bmim-AOT RMs, there are no differences for $W_0>5$ either; however, at low water content ($W_0 < 5$), it is evident that the type of external solvent affects the reaction rate (**Figure 2B**). To explain these results, first, it is necessary to consider the reaction mechanism that predominates in each case.

Furthermore, in previous works, it was found that in bmim-AOT RMs, IPM and ML penetrate the micellar interface, unlike *n*-Hp, whereby the ester group of the biocompatible solvent interacts with the $bmim^+$ cation which is part of the surfactant monolayer.[11] This decreases the $bmim^+$-AOT^- interaction and increases the negative charge density at the polar head of the surfactant. Consequently, the nucleophilicity of water molecules that interact through hydrogen bonding with AOT also increases. This has a great effect on the reaction rate of the hydrolysis that occurs through SNAc mechanism. Therefore, this explains why in bmim-AOT RMs, when the predominant mechanism is SNAc ($W_0< 5$), higher reaction rates are observed when using IPM and ML instead of *n*-Hp as the external solvent.

2.2. Hydrolysis of CF_3

In the absorption spectra recorded for the hydrolysis of CF_3 in Na-AOT/*n*-Hp RMs (**Figure S6**), a single band corresponding to the absorption of the substrate is initially observed. The absorbance of this band decreases with time and a new band develops at a shorter wavelength that corresponds to the absorption of the product. The hydrolysis of CF_3 in Na-AOT/biocompatible solvent, bmim-AOT/*n*-Hp and bmim-AOT/biocompatible solvent RMs showed similar tendencies on the spectra. In all cases, the hydrolysis reaction was followed by

monitoring the disappearance of the substrate at a wavelength between 293-295 nm depending on the micellar system (see pages S201-S275 and S752-S869 of the Supporting Information).

CF_3 hydrolysis rates in the studied micellar systems were determined by varying the surfactant concentration, at constant W_0, in order to determine K_{CF3} values (see the Supporting Information). A series of experiments in which the hydrolysis rate was determined at different values of W_0 were also performed. Then the values of k_i were calculated from the experimental data (k_{obs} and K_{CF3}) and **Equation 1**. The results obtained for the hydrolysis of CF_3 in Na-AOT and bmim-AOT RMs are shown in **Figure 3**.

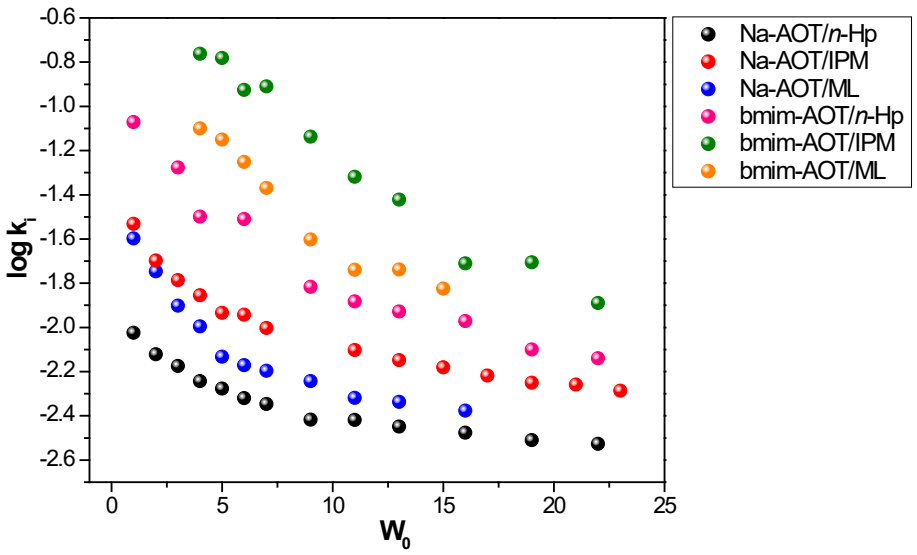


Figure 3. Log k_i as a function of the water content (W_0) for CF_3 hydrolysis reaction in Na-AOT and bmim-AOT RMs, using *n*-Hp, IPM and ML as nonpolar external solvent.

It can be seen from **Figure 3** that, in all the micellar systems, the reaction rate decreases with increasing water content. This can be understood taking into account that the hydrolysis of benzoyl chlorides with electron-withdrawing substituents, such as CF_3, generally occurs through an SNAc mechanism.[50,55] Therefore, the reaction rate is strongly influenced by the

nucleophilic character of the water. In the studied micellar systems, the interfacial water molecules interact with the sulfonate groups of AOT, resulting in an increase in the nucleophilicity of water compared to pure water. At low W_0, practically all the encapsulated water interacts with the surfactant, therefore, the reaction is faster than at high water contents. As W_0 increases and the hydration of the interface is completed, the amount of free water increases and it begins to recover its hydrogen-bond network structure, thereby decreasing the nucleophilicity of the water molecules. Consequently, increasing the water content decreases the hydrolysis reaction rate of CF_3.

Although a decrease in log k_i is found in all micellar systems with increasing water content, CF_3 hydrolysis rates vary significantly depending on whether Na-AOT or bmim-AOT RMs are used. For example, at $W_0 = 4$, in bmim-AOT/IPM $k_i = 1.7x10^{-1}$ s^{-1}, while in Na-AOT/IPM $k_i = 1.4x10^{-2}$ s^{-1}; in bmim-AOT RMs the reaction rate is more than 10 times larger than in the Na-AOT system. Similar tendencies were found when using *n*-Hp or ML as the external solvent. It is important to note that in bmim-AOT RMs, the nucleophilicity of interfacial water is lower than in Na-AOT.[8,10,11] Therefore, if only this factor is taken into account, a SNAc reaction would be expected to be more favorable in Na-AOT than in bmim-AOT RMs. However, this is not what is observed experimentally, as there is another factor that must be taken into account: the counterion $bmim^+$ location compared to Na^+ and the effect of this on stabilizing the reaction intermediate, as previously mentioned.

Furthermore, it can be seen that not only the chemical nature of the surfactant affects the reaction rate of CF_3, but also the identity of the external nonpolar solvent used in the formulation of the RMs. In both bmim-AOT and Na-AOT RMs, hydrolysis reaction rates are larger in biocompatible solvents than in *n*-Hp. This can be explained taking into account the higher biocompatible solvents interface penetration compared to *n*-Hp, and the effect of this on the nucleophilicity of water, as discussed before.

Also, from **Figure 3**, it is evident that when using IPM instead of ML, the hydrolysis of CF_3 is faster, both in bmim-AOT and Na-AOT RMs. Previous studies reveal that IPM penetrates more into the interface of reverse micelles than ML, due to its higher viscosity and polarity.[11,15] This suggests that the interaction of the biocompatible solvent with the counterion of the surfactant is more effective in the case of IPM; thus, the increase in the negative charge density on AOT, and therefore, the increase in nucleophilicity of the water molecules that interact with the surfactant is higher when using IPM instead of ML as the external solvent. Consequently, the reaction rates are higher when using IPM to formulate the RMs.

Previously bmim-AOT and Na-AOT RMs were studied through ^{1}H NMR spectroscopy;[11] In these studies, the different penetration of IPM and ML in Na-AOT RMs was evidenced, obtaining different chemical shifts when using each biocompatible solvent. However, in bmim-AOT RMs, chemical shifts were very similar when using IPM and ML; therefore, these ^{1}H NMR studies did not allow to differentiate the penetration of biocompatible solvents into bmim-AOT systems. Taking into account all the results exposed in the present work, the use of the hydrolysis reaction of CF_3 as a probe allows detecting the different penetration of IPM and ML not only in Na-AOT RMs but also in bmim-AOT RMs.

3. CONCLUSIONS

The results indicated that the hydrolysis of OMe in Na-AOT RMs occurs through a dissociative mechanism in all the range of W_0 analyzed. However, in the micellar systems formed by bmim-AOT only at W_0>5 the S_N1 pathway predominates; at low water contents (W_0 <5) the SNAc mechanism is more favorable, leads to a change of mechanism. These differences between bmim-AOT and Na-AOT are directly related to the chemical nature of the surfactant counter ion and its role in the stabilization of the SNAc reaction intermediate.

In systems formed by Na-AOT, the Na^+ counterion is located in the aqueous pseudophase, while in bmim-AOT, the $bmim^+$ cation is located at the micellar interface, between the AOT molecules, due to its more hydrophobic character. The presence of $bmim^+$ at the interface, which is where the hydrolysis reaction occurs, allows stabilizing the anionic intermediate of the SNAc pathway. Thus, in bmim-AOT RMs at low water contents, where the S_N1 pathway is less favorable, OMe hydrolysis occurs through the SNAc mechanism. Therefore, the replacement of the Na^+ counterion by $bmim^+$ in Na-AOT RMs, not only alters the rates of reactions carried out in them but also produces changes in the reaction mechanism.

The hydrolysis of CF_3 occurs through an SNAc mechanism in all the studied micellar systems, showing an increase in reaction rate with decreasing water content. These results were consistent with the fact that, both in Na-AOT and in bmim-AOT RMs, at low W_0, practically all the water interacts with the polar head of AOT, thus its nucleophilicity is higher compared to pure water. Furthermore, the hydrolysis reactions were faster in bmim-AOT RMs compared to Na-AOT, because the presence of the $bmim^+$ cation at the interface stabilizes the anionic intermediate.

Moreover, when the SNAc mechanism for the hydrolysis of benzoyl chlorides predominates, the reaction rates are higher when using IPM and ML instead of *n*-Hp as the external solvent. In Na-AOT and bmim-AOT RMs, IPM and ML penetrate the micellar interface, unlike *n*-Hp, whereby the ester group of the biocompatible solvent interacts with the $bmim^+$ cation that is part of the surfactant monolayer. Consequently, the cation-AOT interaction decreases, and the negative charge density at the polar head of the surfactant increases, thereby increasing the nucleophilicity of the water molecules that interact with AOT. This has a great effect on the rate of hydrolysis reaction that proceeds through an SNAc mechanism since it strongly depends on the nucleophilicity of the water. Also, the studies indicated that IPM penetrates more the micellar interface than ML, both in Na-AOT and in bmim-AOT RMs.

The obtained results provide kinetic evidence of the effect of replacing the Na^+ cation by $bmim^+$ on the composition and interfacial properties of AOT RMs, and the influence of replacing the external solvent *n*-Hp by the biocompatible IPM and ML.

The present work shows that when studying reactions in reverse micellar systems it is important to take into account the location of the counterion in the RM and the effect of this on the stabilization of the reaction intermediate. In some cases, as in the hydrolysis of benzoyl chloride OMe in bmim-AOT RMs, this factor is very important, not only produces changes in the reaction rates but also in the mechanism.

The obtained results in this work are consistent with those previously found using the ^1H NMR technique and also allowed to detect the different penetration of the biocompatible external solvents in bmim-AOT RMs, which it was not possible by ^1H NMR. Therefore, the use of chemical reactions as a probe is a valuable alternative in investigating the interfacial composition and interfacial properties of RMs, since it is very sensitive to the properties of the medium and is complementary to other techniques, such as NMR.

4. EXPERIMENTAL SECTION

4.1. Materials

The IL bmim-AOT was synthesized in our lab through the procedure previously described[63] and Na-AOT was purchased from Sigma (> 99% purity). Both surfactants were dried under vacuum prior to use. ML (≥ 98% purity), IPM (≥ 98% purity) and *n*-Hp (HPLC quality) from Sigma were used without prior purification. Ultrapure water was obtained from Milli-Q (Millipore) equipment. The benzoyl halides OMe and CF_3 from Sigma were of the highest commercially available purity and were used as supplied.

4.2. Methods

Preparation of RMs solutions. Stock solutions of bmim-AOT and Na-AOT in *n*-Hp, IPM and ML were prepared by mass and volumetric dilution. Individual solutions of RMs were prepared from the stock solutions, incorporating H_2O with calibrated microsyringes. Thus, each reverse micelle solution contains a different amount of water, defined as W_0 = [water]/[surfactant]. Solutions of different surfactant concentrations were also prepared from the stock solutions, incorporating pure solvent and H_2O. The solutions were shaken in a sonication bath to obtain optically transparent solutions with a single phase.

Kinetic Procedure. The hydrolysis reaction was followed by monitoring the UV-vis absorbance of the benzoil halide OMe or CF_3, using a Cary 50 UV-Visible Spectrophotometer with thermostated cell holders. The wavelengths used for the kinetic studies fell between 280-295 nm depending on the micellar system. All experiments were carried out at 25 °C. Stock solutions of the benzoil halides in *n*-Hp, IPM and ML were prepared. Appropriate amount of surfactant/nonpolar solvent stock solution and water was transferred into UV-Vis quartz cuvette to obtain the desired micellar system. After thermostating for 10 min, the reaction was initiated by the addition of the benzoil halide from stock solution. The experiments were performed under pseudo first-order conditions were the substrate was always smaller than water concentration ([OMe] and [CF_3] = $1x10^{-4}$ M). The experiments were performed once since previous experiments showed good reproducibility (results could be reproduced with an error margin of 5%).[56,57] See more details of the kinetic experiments in the supplementary information.

ASSOCIATED CONTENT

Supporting Information. Typical UV-vis spectra for the reaction of OMe in the studied RMs (page S3). Determination of K_{OMe} (pages S4-S5). Log k_i as a function of W_0 for OMe hydrolysis in Na-AOT/ML and bmim-AOT/ML RMs (page S6). Log k_i as a function of W_0 for OMe

hydrolysis in Na-AOT/IPM and bmim-AOT/IPM RMs (page S7). Typical UV-vis spectra for the reaction of CF_3 in the studied RMs (page S8). Determination of K_{CF3} (pages S9-S10). Absorbance versus time data for OMe and CF_3 hydrolysis in the studied RMs (pages S11-S869).

ACKNOWLEDGMENTS

Financial support from the Consejo Nacional de Investigaciones Científicas y Técnicas (PIP CONICET 112-2015-0100283), Universidad Nacional de Río Cuarto (PPI-UNRC 2016-2019), Agencia Nacional de Promoción Científica y Técnica (PICT 2012-0526, PICT 2015-0585, PICT 2018-0507), and Ministerio de Ciencia y Tecnología, Gobierno de la Provincia de Córdoba (PID 2013, PID 2018) is gratefully acknowledged. R.D.F. holds a research position at CONICET. N.D. thanks CONICET for a research fellowship. LGR thanks the Ministerio de Economia y Competitividad of Spain (project CTQ2017-84354-P), Xunta de Galicia (GR 2007/085; IN607C 2016/03 and Centro singular de investigación de Galicia accreditation 2016–2019, ED431G/09) and the European Regional Development Fund (ERDF) is gratefully acknowledged.

REFERENCES

(1) Langevin, D. Micelles and Microemulsions. *Annu. Rev. Phys. Chem.* **1992**, *43* (1), 341–369. https://doi.org/10.1146/annurev.pc.43.100192.002013.

(2) Correa, N. M.; Silber, J. J.; Riter, R. E.; Levinger, N. E. Nonaqueous Polar Solvents in Reverse Micelle Systems. *Chem. Rev.* **2012**, *112* (8), 4569–4602. https://doi.org/10.1021/cr200254q.

(3) Pileni, M. P. Reverse Micelles as Microreactors. *J. Phys. Chem.* **1993**, *97* (27), 6961–6973. https://doi.org/10.1021/j100129a008.

(4) Eastoe, J.; Hollamby, M. J.; Hudson, L. Recent Advances in Nanoparticle Synthesis with Reversed Micelles. *Adv. Colloid Interface Sci.* **2006**, *128–130*, 5–15. https://doi.org/10.1016/j.cis.2006.11.009.

(5) Levinger, N. E.; Swafford, L. A. Ultrafast Dynamics in Reverse Micelles. *Annu. Rev. Phys. Chem.* **2009**, *60* (1), 385–406. https://doi.org/10.1146/annurev.physchem.040808.090438.

(6) Baruah, B.; Roden, J. M.; Sedgwick, M.; Correa, N. M.; Crans, D. C.; Levinger, N. E. When Is Water Not Water? Exploring Water Confined in Large Reverse Micelles Using a Highly Charged Inorganic Molecular Probe. *J. Am. Chem. Soc.* **2006**, *128* (39), 12758–12765. https://doi.org/10.1021/ja0624319.

(7) Lépori, C. M. O.; Correa, N. M.; Silber, J. J.; Vaca Chávez, F.; Falcone, R. D. Interfacial Properties Modulated by the Water Confinement in Reverse Micelles Created by the Ionic Liquid-like Surfactant Bmim-AOT. *Soft Matter* **2019**, *15* (5), 947–955. https://doi.org/10.1039/C8SM02217H.

(8) Lépori, C. M. O.; Correa, N. M.; Silber, J. J.; Falcone, R. D. How the Cation 1-Butyl-3-Methylimidazolium Impacts the Interaction between the Entrapped Water and the Reverse Micelle Interface Created with an Ionic Liquid-like Surfactant. *Soft Matter* **2016**, *12* (3), 830–844. https://doi.org/10.1039/C5SM02421H.

(9) Zhang, X.; Chen, Y.; Liu, J.; Zhao, C.; Zhang, H. Investigation on the Structure of Water/AOT/IPM/Alcohols Reverse Micelles by Conductivity, Dynamic Light Scattering, and Small Angle X-Ray Scattering. *J. Phys. Chem. B* **2012**, *116* (12), 3723–3734. https://doi.org/10.1021/jp210902r.

(10) Dib, N.; Falcone, R. D.; Acuña, A.; García-Río, L. Characterization of Reverse Micelles Formulated with the Ionic-Liquid-like Surfactant Bmim-AOT and

Comparison with the Traditional Na-AOT: Dynamic Light Scattering, 1 H NMR Spectroscopy, and Hydrolysis Reaction of Carbonate as a Probe. *Langmuir* **2019**, *35* (39), 12744–12753. https://doi.org/10.1021/acs.langmuir.9b01083.

(11) Dib, N.; Falcone, R. D.; Acuña, A.; García-Río, L. The Ionic Liquid-Surfactant Bmim-AOT and Nontoxic Lipophilic Solvents as Components of Reverse Micelles Alternative to the Traditional Systems. A Study by 1H NMR Spectroscopy. *J. Mol. Liq.* **2020**, *304*, 112762. https://doi.org/10.1016/j.molliq.2020.112762.

(12) Correa, N. M.; Durantini, E. N.; Silber, J. J. Non-Aqueous Reverse Micelles Media for the SNAr Reaction between 1-Fluoro-2,4-Dinitrobenzene and Piperidine. *J. Phys. Org. Chem.* **2006**, *19* (12), 805–812. https://doi.org/10.1002/poc.1042.

(13) Correa, N. M.; Biasutti, M. A.; Silber, J. J. Micropolarity of Reverse Micelles of Aerosol-OT in n-Hexane. *J. Colloid Interface Sci.* **1995**, *172* (1), 71–76. https://doi.org/10.1006/jcis.1995.1226.

(14) Heatley, F. A 1H Nuclear Magnetic Resonance Chemical-Shift Study of Inverted Microemulsions of Aerosol OT in Benzene and Cyclohexane. Partitioning of Water between Hydrocarbon and Aqueous Phases. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1988**, *84* (1), 343. https://doi.org/10.1039/f19888400343.

(15) Girardi, V. R.; Silber, J. J.; Mariano Correa, N.; Darío Falcone, R. The Use of Two Non-Toxic Lipophilic Oils to Generate Environmentally Friendly Anionic Reverse Micelles without Cosurfactant. Comparison with the Behavior Found for Traditional Organic Non-Polar Solvents. *Colloids Surfaces A Physicochem. Eng. Asp.* **2014**, *457*, 354–362. https://doi.org/10.1016/j.colsurfa.2014.05.077.

(16) Moniruzzaman, M.; Tamura, M.; Tahara, Y.; Kamiya, N.; Goto, M. Ionic Liquid-in-Oil Microemulsion as a Potential Carrier of Sparingly Soluble Drug: Characterization and

Cytotoxicity Evaluation. *Int. J. Pharm.* **2010**, *400* (1–2), 243–250. https://doi.org/10.1016/j.ijpharm.2010.08.034.

(17) Moniruzzaman, M.; Kamiya, N.; Goto, M. Ionic Liquid Based Microemulsion with Pharmaceutically Accepted Components: Formulation and Potential Applications. *J. Colloid Interface Sci.* **2010**, *352* (1), 136–142. https://doi.org/10.1016/j.jcis.2010.08.035.

(18) Moniruzzaman, M.; Kamiya, N.; Nakashima, K.; Goto, M. Formation of Reverse Micelles in a Room-Temperature Ionic Liquid. *ChemPhysChem* **2008**, *9* (5), 689–692. https://doi.org/10.1002/cphc.200700802.

(19) Paul, B. K.; Moulik, S. P. *Ionic Liquid-Based Surfactant Science: Formulation, Characterization, and Applications*; John Wiley & Sons, 2015.

(20) Welton, T. Ionic Liquids: A Brief History. *Biophys. Rev.* **2018**, *10* (3), 691–706. https://doi.org/10.1007/s12551-018-0419-2.

(21) Austen Angell, C.; Ansari, Y.; Zhao, Z. Ionic Liquids: Past, Present and Future. *Faraday Discuss.* **2012**, *154*, 9–27. https://doi.org/10.1039/C1FD00112D.

(22) Egorova, K. S.; Gordeev, E. G.; Ananikov, V. P. Biological Activity of Ionic Liquids and Their Application in Pharmaceutics and Medicine. *Chem. Rev.* **2017**, *117* (10), 7132–7189. https://doi.org/10.1021/acs.chemrev.6b00562.

(23) Rogers, R. D.; Voth, G. A. Ionic Liquids. *Acc. Chem. Res.* **2007**, *40* (11), 1077–1078. https://doi.org/10.1021/ar700221n.

(24) Hayes, R.; Warr, G. G.; Atkin, R. Structure and Nanostructure in Ionic Liquids. *Chem. Rev.* **2015**, *115* (13), 6357–6426. https://doi.org/10.1021/cr500411q.

(25) Dean, P. M.; Pringle, J. M.; MacFarlane, D. R. Structural Analysis of Low Melting

574 Organic Salts: Perspectives on Ionic Liquids. *Phys. Chem. Chem. Phys.* **2010**, *12* (32),
575 9144. https://doi.org/10.1039/c003519j.

576 (26) Holbrey, J. D.; Seddon, K. R. The Phase Behaviour of 1-Alkyl-3-Methylimidazolium
577 Tetrafluoroborates; Ionic Liquids and Ionic Liquid Crystals. *J. Chem. Soc. Dalt. Trans.*
578 **1999**, No. 13, 2133–2140. https://doi.org/10.1039/a902818h.

579 (27) Carmichael, A. J.; Seddon, K. R. Polarity Study of Some 1-Alkyl-3-
580 Methylimidazolium Ambient-Temperature Ionic Liquids with the Solvatochromic Dye,
581 Nile Red. *J. Phys. Org. Chem.* **2000**, *13* (10), 591–595. https://doi.org/10.1002/1099-
582 1395(200010)13:10<591::AID-POC305>3.0.CO;2-2.

583 (28) Urahata, S. M.; Ribeiro, M. C. C. Structure of Ionic Liquids of 1-Alkyl-3-
584 Methylimidazolium Cations: A Systematic Computer Simulation Study. *J. Chem. Phys.*
585 **2004**, *120* (4), 1855–1863. https://doi.org/10.1063/1.1635356.

586 (29) Jian-long, W.; ZHAO, D.; ZHOU, E.; DONG, Z. Desulfurization of Gasoline by
587 Extraction with N-Alkyl-Pyridinium-Based Ionic Liquids. *J. Fuel Chem. Technol.*
588 **2007**, *35* (3), 293–296. https://doi.org/10.1016/S1872-5813(07)60022-X.

589 (30) Cornellas, A.; Perez, L.; Comelles, F.; Ribosa, I.; Manresa, A.; Garcia, M. T. Self-
590 Aggregation and Antimicrobial Activity of Imidazolium and Pyridinium Based Ionic
591 Liquids in Aqueous Solution. *J. Colloid Interface Sci.* **2011**, *355* (1), 164–171.
592 https://doi.org/10.1016/j.jcis.2010.11.063.

593 (31) Lin, X.-S.; Zou, Y.; Zhao, K.-H.; Yang, T.-X.; Halling, P.; Yang, Z.
594 Tetraalkylammonium Ionic Liquids as Dual Solvents–Catalysts for Direct Synthesis of
595 Sugar Fatty Acid Esters. *J. Surfactants Deterg.* **2016**, *19* (3), 511–517.
596 https://doi.org/10.1007/s11743-016-1798-7.

(32) Anouti, M.; Caillon-Caravanier, M.; Le Floch, C.; Lemordant, D. Alkylammonium-Based Protic Ionic Liquids Part I: Preparation and Physicochemical Characterization. *J. Phys. Chem. B* **2008**, *112* (31), 9406–9411. https://doi.org/10.1021/jp803483f.

(33) Jiang, Y.-Y.; Wang, G.-N.; Zhou, Z.; Wu, Y.-T.; Geng, J.; Zhang, Z.-B. Tetraalkylammonium Amino Acids as Functionalized Ionic Liquids of Low Viscosity. *Chem. Commun.* **2008**, No. 4, 505–507. https://doi.org/10.1039/B713648J.

(34) Hunt, P. A.; Kirchner, B.; Welton, T. Characterising the Electronic Structure of Ionic Liquids: An Examination of the 1-Butyl-3-Methylimidazolium Chloride Ion Pair. *Chem. - A Eur. J.* **2006**, *12* (26), 6762–6775. https://doi.org/10.1002/chem.200600103.

(35) Vanyúr, R.; Biczók, L.; Miskolczy, Z. Micelle Formation of 1-Alkyl-3-Methylimidazolium Bromide Ionic Liquids in Aqueous Solution. *Colloids Surfaces A Physicochem. Eng. Asp.* **2007**, *299* (1–3), 256–261. https://doi.org/10.1016/j.colsurfa.2006.11.049.

(36) Niedermeyer, H.; Hallett, J. P.; Villar-Garcia, I. J.; Hunt, P. A.; Welton, T. Mixtures of Ionic Liquids. *Chem. Soc. Rev.* **2012**, *41* (23), 7780. https://doi.org/10.1039/c2cs35177c.

(37) Montalbán, M. G.; Bolívar, C. L.; Díaz Baños, F. G.; Víllora, G. Effect of Temperature, Anion, and Alkyl Chain Length on the Density and Refractive Index of 1-Alkyl-3-Methylimidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2015**, *60* (7), 1986–1996. https://doi.org/10.1021/je501091q.

(38) Triolo, A.; Russina, O.; Fazio, B.; Triolo, R.; Di Cola, E. Morphology of 1-Alkyl-3-Methylimidazolium Hexafluorophosphate Room Temperature Ionic Liquids. *Chem. Phys. Lett.* **2008**, *457* (4–6), 362–365. https://doi.org/10.1016/j.cplett.2008.04.027.

(39) Pal, A.; Maan, R. Micellization Behavior of Anionic Surface Active Ionic Liquid 1-Butyl-3-Methylimidazolium Dodecylbenzenesulfonate in Aqueous Solutions of Nonionic Polymer Polyethylene Glycol: Insights into Competing Mechanisms. *J. Mol. Liq.* **2019**, *274*, 183–192. https://doi.org/10.1016/j.molliq.2018.10.127.

(40) Bhat, P. A.; Chat, O. A.; Dar, A. A. Studies on Binary Mixtures of Pluronic P123 and Twin Tailed 1-Butyl-3-Methyl-Imidazolium Aerosol OT - Aggregation Behavior and Impact on Naproxen and Rifampicin Partitioning. *J. Mol. Liq.* **2017**, *241*, 114–122. https://doi.org/10.1016/j.molliq.2017.05.140.

(41) Singh, G.; Singh, G.; Kang, T. S. Micellization Behavior of Surface Active Ionic Liquids Having Aromatic Counterions in Aqueous Media. *J. Phys. Chem. B* **2016**, *120* (6), 1092–1105. https://doi.org/10.1021/acs.jpcb.5b09688.

(42) Pal, A.; Yadav, A. Mixed Micellization of a Trisubstituted Surface Active Ionic Liquid 1-Dodecyl-2,3-Dimethylimidazolium Chloride [C12bmim][Cl] with an Amphiphilic Drug Amitriptyline Hydrochloride AMT: A Detailed Insights from Conductance and Surface Tension Measurements. *J. Mol. Liq.* **2019**, *279*, 43–50. https://doi.org/10.1016/j.molliq.2019.01.107.

(43) Sun, S.; Lu, D.; Huang, Q.; Liu, Q.; Yao, Y.; Shi, Y. Reversible Surface Activity and Self-Assembly Behavior and Transformation of Amphiphilic Ionic Liquids in Water Induced by a Pillar[5]Arene-Based Host-Guest Interaction. *J. Colloid Interface Sci.* **2019**, *533*, 42–46. https://doi.org/10.1016/j.jcis.2018.08.051.

(44) Rao, V. G.; Mandal, S.; Ghosh, S.; Banerjee, C.; Sarkar, N. Ionic Liquid-in-Oil Microemulsions Composed of Double Chain Surface Active Ionic Liquid as a Surfactant: Temperature Dependent Solvent and Rotational Relaxation Dynamics of Coumarin-153 in [Py][TF 2 N]/[C 4 Mim][AOT]/Benzene Microemulsions. *J. Phys.*

644 *Chem. B* **2012**, *116* (28), 8210–8221. https://doi.org/10.1021/jp304668f.

645 (45) Ali, M. K.; Moshikur, R. M.; Wakabayashi, R.; Tahara, Y.; Moniruzzaman, M.;
646 Kamiya, N.; Goto, M. Synthesis and Characterization of Choline–Fatty-Acid-Based
647 Ionic Liquids: A New Biocompatible Surfactant. *J. Colloid Interface Sci.* **2019**, *551*,
648 72–80. https://doi.org/10.1016/j.jcis.2019.04.095.

649 (46) Thoppil, A. A.; Chennuri, B. K.; Gardas, R. L. Insights into the Structural Changes of
650 Bovine Serum Albumin in Ethanolammonium Laurate Based Surface Active Ionic
651 Liquids. *J. Mol. Liq.* **2019**, *290*, 111229. https://doi.org/10.1016/j.molliq.2019.111229.

652 (47) Mustahil, N. A.; Baharuddin, S. H.; Abdullah, A. A.; Reddy, A. V. B.; Abdul Mutalib,
653 M. I.; Moniruzzaman, M. Synthesis, Characterization, Ecotoxicity and
654 Biodegradability Evaluations of Novel Biocompatible Surface Active Lauroyl
655 Sarcosinate Ionic Liquids. *Chemosphere* **2019**, *229*, 349–357.
656 https://doi.org/10.1016/j.chemosphere.2019.05.026.

657 (48) Dai, X.; Qiang, X.; Li, J.; Yao, T.; Wang, Z.; Song, H. Design and Functionalization of
658 Magnetic Ionic Liquids Surfactants (MILSs) Containing Alkyltrimethylammonium
659 Fragment. *J. Mol. Liq.* **2019**, *277*, 170–174.
660 https://doi.org/10.1016/j.molliq.2018.12.096.

661 (49) Blach, D.; Pessêgo, M.; Silber, J. J.; Correa, N. M.; García-Río, L.; Falcone, R. D.
662 Ionic Liquids Entrapped in Reverse Micelles as Nanoreactors for Bimolecular
663 Nucleophilic Substitution Reaction. Effect of the Confinement on the Chloride Ion
664 Availability. *Langmuir* **2014**, *30* (41), 12130–12137.
665 https://doi.org/10.1021/la501496a.

666 (50) Cabaleiro-Lago, C.; Garcia-Río, L.; Hervés, P.; Pérez-Juste, J. Effects of Zwitterionic
667 Vesicles on the Reactivity of Benzoyl Chlorides. *J. Phys. Chem. B* **2006**, *110* (16),

668 8524–8530. https://doi.org/10.1021/jp060683q.

669 (51) Bunton, C. A.; Gillitt, N. D.; Mhala, M. M.; Moffatt, J. R.; Yatsimirsky, A. K. Micellar
670 Charge Effects upon Hydrolyses of Substituted Benzoyl Chlorides. Their Relation to
671 Mechanism †. *Langmuir* **2000**, *16* (23), 8595–8603. https://doi.org/10.1021/la000109k.

672 (52) Bunton, C. A. Micellar Charge Effects as Mechanistic Criteria in Spontaneous
673 Hydrolyses of Acid Chlorides. *J. Phys. Org. Chem.* **2005**, *18* (2), 115–120.
674 https://doi.org/10.1002/poc.747.

675 (53) Campos-Rey, P.; Cabaleiro-Lago, C.; Hervés, P. Promoting Mechanistic Changes:
676 Solvolysis of Benzoyl Halides in Nonionic Microemulsions. *J. Phys. Chem. B* **2009**,
677 *113* (35), 11921–11927. https://doi.org/10.1021/jp9039463.

678 (54) Campos-Rey, P.; Cabaleiro-Lago, C.; Hervés, P. Solvolysis of Substituted Benzoyl
679 Chlorides in Nonionic and Mixed Micellar Solutions. *J. Phys. Chem. B* **2010**, *114* (44),
680 14004–14011. https://doi.org/10.1021/jp107538v.

681 (55) García-Río, L.; Leis, J. R. Microemulsion-Promoted Changes of Reaction Mechanisms:
682 Solvolysis of Substituted Benzoyl Chlorides. *Chem. Commun.* **2000**, No. 6, 455–456.
683 https://doi.org/10.1039/a909531d.

684 (56) Fernández, E.; García-Río, L.; Parajó, M.; Rodriguez-Dafonte, P. Influence of Changes
685 in Water Properties on Reactivity in Strongly Acidic Microemulsions. *J. Phys. Chem. B*
686 **2007**, *111* (19), 5193–5203. https://doi.org/10.1021/jp0706073.

687 (57) García-Río, L.; Hervella, P.; Rodríguez-Dafonte, P. Solvolysis of Benzoyl Halides in
688 Water/NH 4 DEHP/Isooctane Microemulsions. *Langmuir* **2006**, *22* (18), 7499–7506.
689 https://doi.org/10.1021/la0606953.

690 (58) Romsted, L. S. Surfactants in Solution; Mitta, K. L., Lindman, B., Eds.; Plenum Press:

New York, 1984; Vol. 2, p 1015.

(59) Bunton, C. A.; Savelli, G. Organic Reactivity in Aqueous Micelles and Similar Assemblies; 1986; pp 213–309. https://doi.org/10.1016/S0065-3160(08)60169-0.

(60) Bunton, C. A. Reaction Kinetics in Aqueous Surfactant Solutions. *Catal. Rev.* **1979**, *20* (1), 1–56. https://doi.org/10.1080/03602457908065104.

(61) Quina, F. H.; Chaimovich, H. Ion Exchange in Micellar Solutions. 1. Conceptual Framework for Ion Exchange in Micellar Solutions. *J. Phys. Chem.* **1979**, *83* (14), 1844–1850. https://doi.org/10.1021/j100477a010.

(62) Garcia-Rio, L.; Leis, J. R.; Iglesias, E. Influence of Water Structure on Solvolysis in Water-in-Oil Microemulsions. *J. Phys. Chem.* **1995**, *99* (32), 12318–12326. https://doi.org/10.1021/j100032a041.

(63) Brown, P.; Butts, C. P.; Eastoe, J.; Fermin, D.; Grillo, I.; Lee, H.-C.; Parker, D.; Plana, D.; Richardson, R. M. Anionic Surfactant Ionic Liquids with 1-Butyl-3-Methyl-Imidazolium Cations: Characterization and Application. *Langmuir* **2012**, *28* (5), 2502–2509. https://doi.org/10.1021/la204557t.