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Ionic Liquids Entrapped in Reverse Micelles as Nanoreactors for Bimolecular Nucleophilic Substitution Reaction. Effect of the Confinement on the Chloride Ion Availability

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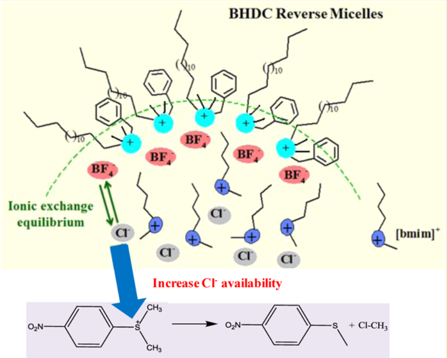
Supporting Information

ABSTRACT: In this work was explored how the confinement of two ionic liquids (ILs), 1-butyl-3-methylimidazolium chloride (bmimCl) and 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$), inside toluene/benzyl-*n*-hexadecyldimethylammonium chloride (BHDC) reverse micelles (RMs) affects the Cl$^-$ nucleophilicity on the bimolecular nucleophilic substitution (S$_N$2) reaction between this anion and dimethyl-4-nitrophenylsulfonium trifluoromethanesulfonate. The results obtained show that, upon confinement, the ionic interactions between the ILs with the cationic surfactant polar head group and the surfactant counterion modify substantially the performance of both ILs as solvents. In toluene/BHDC/bmimCl RMs, the Cl$^-$ interacts strongly with bmim$^+$ (and/or BHD$^+$) in such a way that its nucleophilicity is reduced in comparison with neat IL. In toluene/BHDC/bmimBF$_4$ RMs, an ionic exchange equilibrium produces segregation of bmim$^+$ and BF$_4^-$ ions, changing the composition of the RMs interface and affecting dramatically the Cl$^-$ availability. These results show the versatility of this kind of organized system to alter the ionic organization and influence on reaction rate when used as nanoreactors.



■ INTRODUCTION

Ionic liquids (ILs) have received significant attention as powerful alternatives to conventional molecular organic solvents.[1−3] Negligible vapor pressure, combined with excellent chemical and thermal stability, ease of recyclability, and widely tunable properties such as polarity, hydrophobicity, and solvent miscibility through appropriate modification of the cation and anion, makes ILs neoteric solvents for a number of chemical processes.[1,2] Most ILs used are based on *N*,*N*′-dialkylimidazolium cations, especially 1-butyl-3-methylimidazolium (bmim$^+$, Scheme 1) and different anions such as tetrafluoroborate (BF$_4^-$, Scheme 1), hexafluorophosphate (PF$_6^-$), and bis(trifluoromethylsulfonyl)imide (Tf$_2$N$^-$).

Reversed micelles (RMs) are spatially ordered macromolecular assemblies of surfactants formed in a nonpolar solvent, in which the polar head groups of the surfactants point inward and the hydrocarbon chains point toward the nonpolar medium.[4−6] RMs are an interesting subject due to their broad applications in chemical reactions, separation science, materials science, and the pharmaceutical industry, among others.[4,7] These nanoscale aggregates are suitable media for processes that involve hydrophobic and hydrophilic reactants in a variety of chemical and biological reactions.[4,7−10] There are a wide range of surfactants that form RMs in both the presence and absence of cosurfactants, including anionic, cationic, and nonionic molecules.[4−28] One of them, the cationic surfactant, benzyl-*n*-hexadecyldimethylammonium chloride (BHDC, Scheme 1), can form RMs in aromatic solvents without addition of a cosurfactant.[4,11,21,24] Although the traditional solvent used as polar component in BHDC RMs is water,[11,21,24] different ILs[25−29] can be entrapped in the polar core. Recent studies have showed that the structure of the entrapped IL depends strongly on the used surfactant reaching a situation where layers of cation and anion were proposed with an exchange of the surfactant and ionic liquid anions.[25−28]

Actually, these RM systems formed utilizing ILs as polar components are very attractive.[25−40] These IL RMs have gained attention because of their potential applications owing to the unique features of both ILs and RMs. The RMs provide hydrophobic or hydrophilic nanodomains, thereby expanding the potential uses of ILs in chemical reactions, allowing the use

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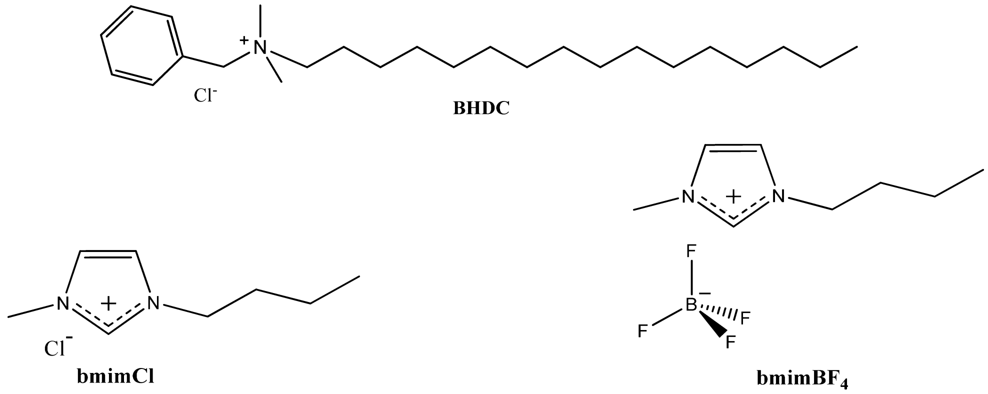
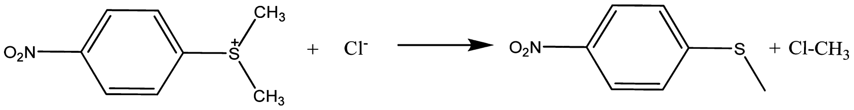
Scheme 1. Molecular Structures of BHDC, bmimCl, and bmimBF_4



Scheme 2. S_N2 Reaction of Cl^- with Dimethyl-4-nitrophenylsulfonium (S^+)



of smaller quantities of IL compared to that required for bulk-phase IL reactions.[1,2]

It is well-known that the physicochemical properties of polar solvents (including ILs) entrapped inside RMs change dramatically from those of the bulk solvents as a result of specific interactions and confined geometries.[4,12] Whether altering physicochemical properties of ILs inside RMs affects solute species as reactants and the course of reactions remains to be explored. Nucleophilic substitution reactions provide a familiar avenue for examination of solvent effects on chemical reactions.[1,41−44] Our aim is to show that changes in the properties of the entrapped ILs (bmimCl and bmimBF_4) are reflected on the reactivity of nucleophilic substitution processes. As a chemical probe, we use the nucleophilic substitution of Cl^- on dimethyl-4-nitrophenylsulfonium (S^+ in Scheme 2).[43,44] Our results point that Cl^- nucleophilicity in toluene/BHDC/bmimCl RMs is lower than in neat IL, as a consequence of ion-pairs formation between Cl^- and the cationic head group of the surfactant. In the case of toluene/BHDC/bmimBF_4, the reactivity is mainly governed by an ion-exchange process between Cl^- and BF_4^-, in such a way that the composition of the entrapped IL hardly depends on the surfactant concentration.

■ EXPERIMENTAL SECTION

Benzyl-*n*-hexadecyldimethylammonium chloride (BHDC), from Sigma (> 99% purity), was dried at reduced pressure prior use. Toluene from Sigma (HPLC quality), was used without prior purification. The ILs 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF_4) and 1-butyl-3-methylimidazolium chloride (bmimCl) were obtained from IoliTec (>99% purity). Prior to use, bmimBF_4 was discolored with activated charcoal, filtrated through basic aluminum oxide, and dried at reduced pressure at 60 °C for 4 h.[45] To avoid atmospheric water, bmimCl was manipulated under an inert atmosphere. The substrate dimethyl-4-nitrophenylsulfonium (S^+) trifluoromethanesulfonate was synthesized following the literature procedure.[43]

Preparation of BHDC RMs Solutions. Stock solutions of BHDC in toluene were prepared by mass and volumetric dilution. Aliquots of these stock solutions were used to make individual reverse micelle solutions with different amounts of IL (bmimBF_4 or bmimCl), defined as W_s = [IL]/[BHDC]. The solutions of toluene/BHDC/bmimCl at different bmimCl content were prepared by weight. The incorporation of bmimBF_4 into each micellar solution was performed using calibrated microsyringes. The resulting solutions were clear with a single phase, and they were used in the kinetic experiments. The W_s was varied between 0 and 1.2 for toluene/BHDC/bmimBF_4 RMs and between 0 and 0.9 for toluene/BHDC/bmimCl. It was not possible to obtain higher values of W_s due to turbidity problems. The lowest value for W_s ($W_s = 0$) corresponds to a system without the IL addition. It is important to note that, at room temperature, bmimBF_4 and bmimCl are not soluble in toluene[46] or in toluene/BHDC solutions at surfactant concentrations lower than the critical micelle concentration (cmc; around 0.01 M).[21]

Kinetic Procedure. Nucleophilic substitution reactions were followed by monitoring the UV−vis absorbance of the demethylated sulfide product (Scheme 2) using a Cary 500 scan UV−Vis-NIR spectrophotometer with thermostated cell holders. In all experiments, the wavelength used for kinetic studies was 345 nm. All the experiments were carried out under pseudo-first-order conditions where the sulfonium salt concentration ($[S^+] = 5 \times 10^{-5}$ M) was always smaller than $[Cl^-]$. All experiments were carried out at 35.0 ± 0.1 °C. Detailed procedures for the different systems under study are reported in the Supporting Information. The molar volume values of bmimCl and bmimBF_4 were estimated using the density and molar mass values obtained from the literature.[2] Kinetics were studied by following the integrated method where the integrated first order rate equation was fitted to the kinetic data, using a nonlinear regression analysis program to give the pseudo-first-order rate constants, k_{obs}. Kinetic data are reproducible with a 3% deviation.

■ RESULTS AND DISCUSSION

The aim of this work was to analyze the nucleophilic reactivity of entrapped Cl^- as well as the possibility of its exchange with other anions that may be present in the media. Consequently, the results obtained are presented in different sections corresponding to the studies performed in the three RMs used: (i) BHDC in toluene in the absence of polar component; (ii) toluene/BHDC/bmimCl, and (iii) toluene/BHDC/bmimBF_4. In sections (i) and (ii), Cl^- is the only anion present in the medium and is supplied by the surfactant (i) or by both the surfactant and the ionic liquid entrapped (ii). In section (iii), Cl^- is supplied by the surfactant but it competes with BF_4^- (very poor nucleophilic anion)[1,3] in the solvation of the surfactant and $bmim^+$ cations. Additionally, the studies

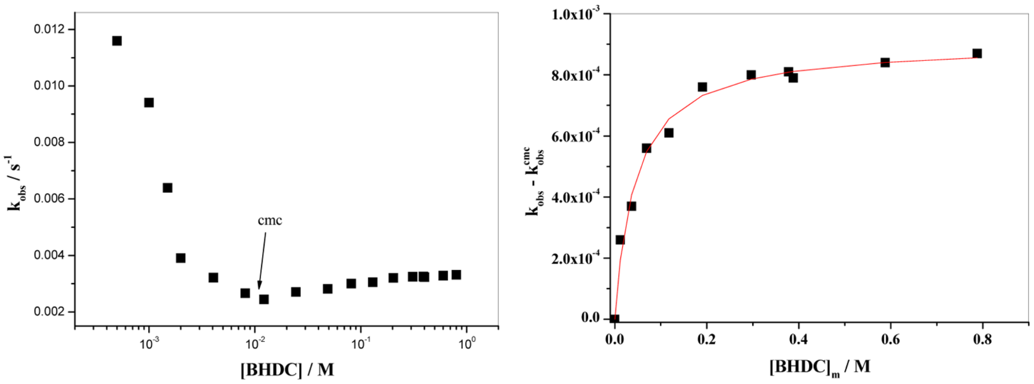


Figure 1. (Left) k_{obs} values as a function of [BHDC] for the reaction of chloride ions with S^+ in toluene/BHDC before and after the cmc. $W_s = 0$, $[S^+] = 5 \times 10^{-5}$ M. $T = 35.0$ °C. (Right) Plot of $k_{obs} - k_{obs}^{cmc}$ values as a function of $[BHDC]_m$ according to eq 11.

performed in homogeneous media (bmimBF$_4$ and toluene) are presented in the Supporting Information (section 2).

i. Reactivity Studies in Toluene/BHDC RMs at $W_s = 0$. Typical absorbance spectra of the reaction mixture in toluene/BHDC RMs at different times are presented in Figure S4 in the Supporting Information. The observed rate constants, k_{obs}, obtained in toluene/BHDC RMs varying the [BHDC] are shown in Figure 1. Two regions should be considered according to the critical micelle concentration of BHDC (around 0.01 M[21]). For [BHDC] < cmc, the surfactant exists in its monomomeric form, forming ion pairs with chloride counterions. As it has been reported for molecular solvents, formation of ion pairs increases with salt concentration in such a way that the fraction of free chloride nucleophiles available to react with sulfonium ions decreases on increasing [BHDC], and consequently, the observed rate constant also decreases.

For [BHDC] larger than the cmc, the incorporation of both S^+ and Cl^- to the RMs increases their local concentrations and consequently increases the rate of the reaction. It must be recalled that above the cmc the monomeric [BHDC] remains constant and the rate constant for the reaction in the organic solvent should be constant, as it will be discussed later. For a quantitative analysis, a kinetic model can be proposed to show how after the BHDC RMs formation, S^+ can be incorporated into the RMs (as is expressed by eq 1) favored by its low solubility in toluene and overcoming the electrostatic repulsion between S^+ and BHD^+.

$$S_o^+ + BHDC_m \rightleftharpoons S_m^+ \qquad (1)$$

where S_o^+ and S_m^+ symbolize the substrate in the organic pseudophase and in the RMs, respectively. $BHDC_m$ represents the cationic RMs.

As it is conventional for micellar aggregates, the concentration of micellized[47] surfactant defined as $[BHDC]_m$(where $[BHDC]_m = [BHDC]_{tot} - \text{cmc}$) can be calculated, and if the mass balance for S^+ ($[S^+]_{tot} = [S^+]_o + [S^+]_m$) is considered, the partition constant of the substrate (K_m) is defined as eq 2:

$$K_m = \frac{[S^+]_m}{[S^+]_o[BHDC]_m} \qquad (2)$$

The overall reaction rate can be expressed as the sum of the rate in the organic pseudophase and in the RMs, as eq 3:

$$\text{rate} = k'_o[S^+]_o + k'_m[S^+]_m \qquad (3)$$

where $[S^+]_o$ and $[S^+]_m$ are the concentration of S^+ in the organic pseudophase (toluene and BHDC at cmc) and in the RMs, respectively, with both referring to the total volume. k'_o and k'_m are the pseudo-first-order rate constant values in the organic pseudophase and in BHDC RMs, respectively. Moreover, the pseudo-first-order rate constant k'_m can be expressed as the multiplication of the bimolecular rate constant (k_2^m) and the local concentration of the reagent in excess,[48] Cl^-, as eq 4 shows:

$$k'_m = k_2^m[Cl^-]_m^m \qquad (4)$$

where $[Cl^-]_m^m$ is the Cl^- concentration in the RMs referring to the volume of the RMs (V_m). This concentration can be expressed also as the multiplication of the fraction of neutralized charge, β, and [BHDC][49] (eq 5).

$$k'_m = k_2^m\beta[BHDC]_m^m \qquad (5)$$

Additionally, the surfactant concentrations referred to the micellar phase volume ($[BHDC]_m^m$) can be expressed in concentrations referred to the total volume, ($[BHDC]_m$), taking into consideration the volume fraction occupied by the micellar phase, V_{tot}/V_m, as eq 6 shows.

$$k'_m = k_2^m\beta\frac{V_{tot}}{V_m}[BHDC]_m \qquad (6)$$

The concentrations can be transformed into concentrations referred to the total volume of the system by taking into account just the phase volumes[8] (eq 7).

$$\frac{V_{tot}}{V_m} = \frac{1}{\bar{V}_{BHDC}[BHDC]_m} \qquad (7)$$

where $\bar{V}_{BHDC}$ is the molar volume of BHDC. Thus, eq 6 can be rewritten as

$$k'_m = k_2^m\beta\frac{1}{\bar{V}_{BHDC}} \qquad (8)$$

When the BHDC RMs are formed, the rate constant in the organic pseudophase (toluene + BHDC surfactant monomers), k'_o in eq 3, can be assumed as the k_{obs} value in the cmc (k_{obs}^{cmc}) and equal to 2.45×10^{-3} s^{-1}. Taking into account eqs 1–8, the concentration of the substrate in the RMs can be expressed as eq 9:

$$[S^+]_m = \frac{K_m[BHDC]_m}{1 + K_m[BHDC]_m}[S^+]_{tot} \qquad (9)$$

Thus, k_{obs} can be expressed as eq 10:

$$k_{obs} = k_{obs}^{cmc} + \frac{k_2^m \beta}{\overline{V}_{BHDC}} \frac{K_m[BHDC]_m}{1 + K_m[BHDC]_m} \tag{10}$$

In order to present the results more clearly, eq 10 is modified as eq 11 shows:

$$k_{obs} - k_{obs}^{cmc} = \frac{\frac{k_2^m \beta K_m}{\overline{V}_{BHDC}}[BHDC]_m}{1 + K_m[BHDC]_m} \tag{11}$$

Thus, the experimental data obtained for toluene/BHDC RMs at [BHDC] > cmc were analyzed by eq 11 and are presented in Figure 1, right. From the fitting of the results, values of K_m = 22.4 M^{-1} and $k_2^m \beta$ = 3.95 × 10^{-4} M^{-1} s^{-1} were obtained using the value of $\overline{V}_{BHDC}$ = 0.42 M^{-1}. To estimate k_2^m, it is necessary to know the value of β. Previous studies showed that, independently of the RMs composition,[49] β remains constant around 0.96. By using this value, we have estimated the bimolecular rate constant at the RM as $k_2^m \approx 4.1 \times 10^{-4}$ M^{-1} s^{-1}.

Reactivity of Cl^- ions in RMs is considerably smaller than the one obtained in neat $bmimBF_4$, $k_2 = 2.6 \times 10^{-3}$ M^{-1} s^{-1}, where no ion-pairs were observed (see the Supporting Information). Based on polarity effects[43,44] for the chloride ions reactivity with S^+ and because the polarity of BHDC RMs at W_s = 0 is lower[25] than that for neat $bmimBF_4$, we expect higher reactivity in the micelle than in the neat ionic liquid. However, experimental results show that the reactivity is higher in neat $bmimBF_4$ than in the RMs, suggesting that extra stabilization of Cl^- ions as ion-pairs at the RMs decreases their reactivity.

ii. Reactivity Studies in Toluene/BHDC/bmimCl RMs. Prior to studying the reaction in this system and because it is not known if bmimCl is truly encapsulated by BHDC to form RMs, dynamic light scattering (DLS) experiments (see experimental details in the Supporting Information) were performed at a fixed surfactant concentration (0.05 M). Hence, the RMs solutions are not at infinite dilution, and thus, it is appropriate to introduce an apparent hydrodynamic diameter (d_{app}) in order to describe the results. Figure S5 shows the d_{app} values for toluene/BHDC/bmimCl at different W_s content. As can be seen, there is an increase in the droplet size values when the IL content increases, showing that bmimCl is effectively entrapped by the surfactant layer, yielding RMs. Moreover, the fact that the droplet size values increase with the W_s shows that the IL is interacting with BHDC at the interface of RMs.[4,12]

Figure 2 plots the k_{obs} values obtained in toluene/BHDC/bmimCl RMs as a function of the reverse micelle composition. For comparative proposes, the composition of the reverse micelle is reported as [Cl^-]. The [Cl^-] was obtained considering that both the bmimCl and the surfactant are sources of Cl^-. In this way, the [Cl^-] was obtained as [Cl^-] = (1 + W_s) × [BHDC], where W_s = [bmimCl]/[BHDC]. Note that the experiments were performed at different [BHDC] and W_s (see data in Table S1 in the Supporting Information). For comparative proposes, the rate constants obtained in neat $bmimBF_4$ (using also bmimCl as a source of Cl^-; see section 2.1 in the Supporting Information) are also plotted showing that the rate constant in independent of [Cl^-] in the RMs but has a linear dependence in the neat $bmimBF_4$. Two facts emerge from Figure 2: (i) k_{obs} values in the toluene/BHDC/bmimCl RMs are independent of the [Cl^-] and the W_s. (ii) The magnitude of k_{obs} values in the RMs is very similar to those obtained in the absence of polar solvent (Figure 1, left), but it is larger than that in neat $bmimBF_4$ at any [Cl^-].

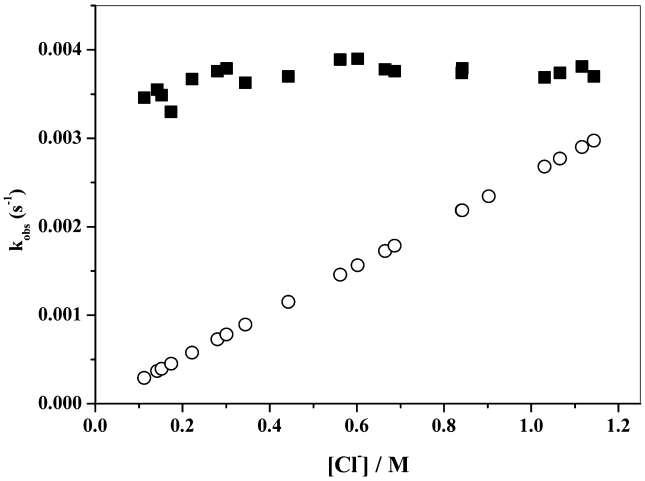
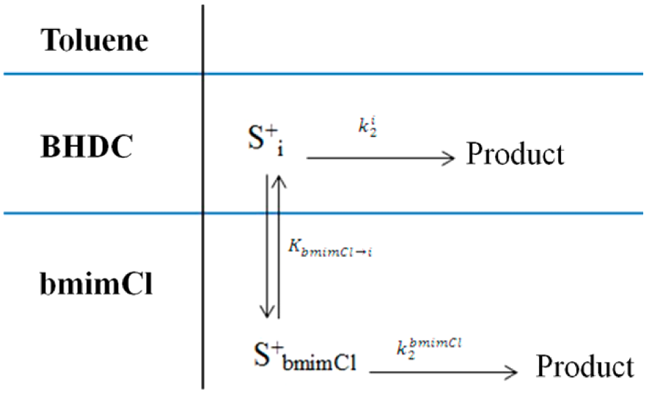


Figure 2. Pseudo-first-order rate constants (k_{obs}) as a function of [Cl^-] in (■) toluene/BHDC/bmimCl (at different [BHDC] and W_s, where [Cl^-] = (1 + W_s) × [BHDC]), and in (○) neat $bmimBF_4$ (where [Cl^-] = [bmimCl]). T = 35.0 °C. [S^+] = 5 × 10^{-5} M.

The first fact (i) can be interpreted considering the following kinetic model. In these RMs, it is possible to consider that S^+ is practically distributed between the bmimCl pool and the interface as Scheme 3 shows.

Scheme 3. Schematic Representation of the Reaction Site in Toluene/BHDC/bmimCl



Thus, a new partition constant $K_{bmimCl \to i}$ can be defined (eq 12).

$$K_{bmimCl \to i} = \frac{[S^+]_i}{[S^+]_{bmimCl}} W_s \tag{12}$$

where the concentrations are referred to the total volume and W_s. At this point, is important to consider the differentiation between two- and three-component RMs systems. For two-component RMs (toluene/BHDC at W_s = 0), the surfactant concentration can be varied keeping almost constant the continuous medium concentration. This is the reason why the S^+ distribution constant is obtained by eq 2. In the case of three-component RMs (toluene/BHDC/bmimCl), it is not possible to increase the surfactant concentration while keeping constant the concentrations of the other components.[50] For this reason, the distribution constant is given as a molar ratio

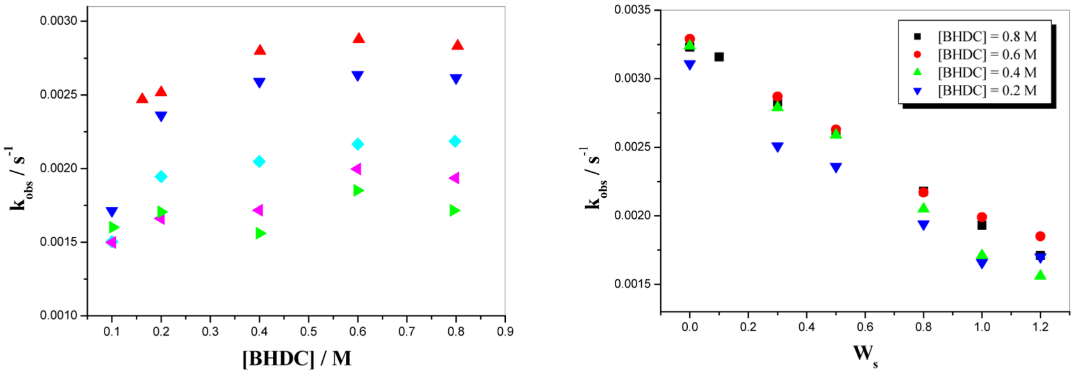


Figure 3. (Left) k_{obs} values as a function of [BHDC] in toluene/BHDC/bmimBF_4 at different W_s. W_s: (red up triangle) 0.3, (blue down triangle) 0.5, (aqua tilted square) 0.8, (purple left triangle) 1.0, and (green right triangle) 1.2. $[S^+] = 5 \times 10^{-5}$ M. $T = 35.0$ °C. (Right) k_{obs} values as a function of W_s in toluene/BHDC/bmimBF_4 at different [BHDC]. $[S^+] = 5 \times 10^{-5}$ M. $T = 35.0$ °C.

(eq 12). Equivalence between both distribution constants, taking into consideration the concentration of the continuous medium in two-component RMs, can be obtained as K_m[toluene] = $K_{bmimCl\to i}$.

In order to derive a kinetic model, it should be considered that chloride ions sources are both the surfactant and the ionic liquid and the reactions can proceed simultaneously in the dispersed nanodroplet and at the interface of the RMs. Under these premises, the following rate equation can be obtained (see the Supporting Information for derivation, section 4).

$$k_{obs} = \left\{ \frac{k_2^{bmimCl}}{\bar{V}_{bmimCl}}(1-\beta+W_s) + \frac{k_2^{i}K_{bmimCl\to i}}{\bar{V}_{BHDC}}\beta \right\} \frac{1}{K_{bmimCl\to i}+W_s} \qquad (13)$$

where k_2^{bmimCl} and k_2^{i} are the bimolecular rate constants at the ionic liquid droplet and the interface of the RMs, respectively, and $\bar{V}_{bmimCl}$ and $\bar{V}_{BHDC}$ are the molar volumes of the ionic liquid and the surfactant. Taking into account that the S^+ has positive charge and negligible solubility in toluene, is possible to assume that is practically located in the IL pool ($K_{bmimCl\to i} \ll W_s$). Moreover $\beta \approx 0.96$ so that $(1-\beta+W_s) \approx W_s$ and eq 13 can be simplified:

$$\begin{aligned} k_{obs} &= \frac{k_2^{bmimCl}}{\bar{V}_{bmimCl}} + \frac{k_2^{i}K_{bmimCl\to i}}{\bar{V}_{BHDC}}\frac{\beta}{W_s} \\ &\approx \frac{k_2^{bmimCl}}{\bar{V}_{bmimCl}} + \frac{k_2^{i}}{\bar{V}_{BHDC}}\frac{K_{bmimCl\to i}}{W_s} \end{aligned} \qquad (14)$$

As $K_{bmimCl\to i} \ll W_s$, then $(K_{bmimCl\to i}/W_s) \ll 1$ and consequently the second term in eq 14 can be ignored. Thus, $k_{obs} \approx k_2^{bmimCl}/\bar{V}_{bmimCl}$ and considering $\bar{V}_{bmimCl} = 0.157$ M^{-1}, the k_{obs}value (mean value from data shown in Table S1) is around 3.7×10^{-3} s^{-1}, where a value of $k_2^{bmimCl} \approx 5.8 \times 10^{-4}$ M^{-1} s^{-1} is obtained. From this model, it is easy to explain the kinetic behavior showed in Figure 2 where k_{obs} values are independent of the RMs composition. The local Cl^- concentration inside the RMs is almost constant due to both the very low degree of surfactant dissociation and the high Cl^- concentration as a constituent of the ionic liquid. It implies that, under these experimental conditions, where S^+ is almost totally located in the nanodroplet, the observed rate constant should be independent of the surfactant concentration as well as on the W_s values.

The bimolecular rate constant in toluene/BHDC/bmimCl is 4 times smaller than the corresponding value in neat bmimBF_4 ($k_2 = 2.6 \times 10^{-3}$ M^{-1} s^{-1}), and suggests that upon confinement the ability of Cl^- to act as nucleophile is reduced. As neat solvent bmimCl ($\pi^* = 1.13$, where π^* is the solvent polarity/polarizability scale) is slightly more polar[51] than bmimBF_4 ($\pi^* = 0.96$), therefore a slower reaction in bmimCl than in bmimBF_4 would be expected. However, the discrepancies in the bimolecular rate constant values seem to be too large to be due to only to the polarity of the medium. In this sense, a probable explanation of these facts would be that when bmimCl is entrapped in BHDC RMs, the Cl^- interacts strongly with $bmim^+$ (and/or BHD^+), producing a medium with low $[Cl^-]$ free to react. On the other hand, it is important to mention that the k_2 value obtained in toluene/BHDC/bmimCl RMs cannot be compared with the corresponding value in bmimCl neat and cannot be measured because the IL is solid at room temperature (melting point 65 °C).[2,46]

iii. Reactivity Studies in Toluene/BHDC/bmimBF_4 RMs.

Previous multinuclear NMR studies[26] demonstrated the exchange between BF_4^- and Cl^- ions in BHDC RMs. Thus, the study of the nucleophilic substitution reaction as a chemical probe to provide quantitative information concerning the mentioned exchange in toluene/BHDC/bmimBF_4 RMs was used. In the presence of bmimBF_4 entrapped in toluene/BHDC RMs, the kinetic behavior of Cl^- ions is quite different from that observed in toluene/BHDC/bmimCl. In Figure 3 and Table S2 are summarized the data collected in toluene/BHDC/bmimBF_4 varying the [BHDC] at different W_s.

Figure 3, right shows that, when increasing the W_s, the k_{obs} values decrease due to the dilution of Cl^- ions in the RMs; however, this effect is less than the expected. For example, for [BHDC] = 0.8 M, when increasing the W_s from 0.1 to 1.2, the k_{obs} value decreases approximately in half. However, since such variation of W_s implies that [bmimBF_4] increases from 0.08 to 0.96 M, consequently a 12 times dilution in the local $[Cl^-]$ around a 12 times reduction in the k_{obs} value would be expected. The less reduction observed can be explained considering the ionic exchange[52] equilibrium present in the RMs. The equilibrium, where Cl^- (from the BHDC) at the interface is displaced by BF_4^- from the pool, can be expressed as eq 15.

$$(Cl^-)_i + (BF_4^-)_{IL} \rightleftarrows (Cl^-)_{IL} + (BF_4^-)_i \qquad (15)$$

When W_s increases, the bmimBF_4 concentration also increases, producing an increment in the ratio $[BF_4^-]/[Cl^-]$ at the interface and more Cl^- moves to the pool. Thus, increasing the amount of bmimBF_4 entrapped, the $[\text{Cl}^-]$ at the pool decreases less than expected.

In toluene/BHDC/bmimCl RMs, the reaction takes place in the pool because of the electrostatic repulsions between S^+ and the cationic interface, and as a consequence can be assumed that $K_{\text{bmimCl}\to i} \ll 1$. A similar behavior can be expected in toluene/BHDC/bmimBF_4 RMs, where S^+ reacts with Cl^- (from BHDC dissociation) in the bmimBF_4 pool. The rate of the reaction is defined as rate = $k'_{\text{bmimBF}_4}[S^+]_{\text{bmimBF}_4}$. Taking into consideration the procedure performed before for the RMs containing bmimCl, it is possible to obtain the following rate equation (see the Supporting Information for a complete rate equation deduction):

$$k_{\text{obs}}[\text{BHDC}]W_s = \frac{k_2^{\text{bmimBF}_4}}{\bar{V}_{\text{bmimBF}_4}}[\text{Cl}^-]_{\text{bmimBF}_4} \tag{16}$$

where $[\text{Cl}^-]_{\text{bmimBF}_4}$ is the concentration of chloride ions in the nanodroplet referred to the total volume of the system. This concentration can be obtained by solving the following quadratic equation derived by consideration of the previously mentioned ionic exchange equilibrium:

$$(1 - K_{\text{BF}_4^-}^{\text{Cl}^-})([\text{Cl}^-]_{\text{bmimBF}_4})^2 + \{[(\beta - 1) + (1 - \beta + W_s)K_{\text{BF}_4^-}^{\text{Cl}^-}] \times [\text{BHDC}]\}[\text{Cl}^-]_{\text{bmimBF}_4} - K_{\text{BF}_4^-}^{\text{Cl}^-}(1 - \beta + W_s)[\text{BHDC}]^2 = 0 \tag{17}$$

To solve eq 17, it is necessary to know the value of $K_{\text{BF}_4^-}^{\text{Cl}-}$. To obtain this value, an iterative method was performed, where for each W_s and [BHDC] a value of $K_{\text{BF}_4^-}^{\text{Cl}-}$ was assumed and then the $[\text{Cl}^-]_{\text{bmimBF}_4}$ was calculated. The best fit was obtained with $K_{\text{BF}_4^-}^{\text{Cl}-} = 0.025$. With this value, the validity of eq 16 was checked, and from the slope of the plot $k_{\text{obs}}[\text{BHDC}]W_s$ vs $[\text{Cl}^-]_{\text{bmimBF}_4}$ (Figure 4) the second rate order constant can be determined.

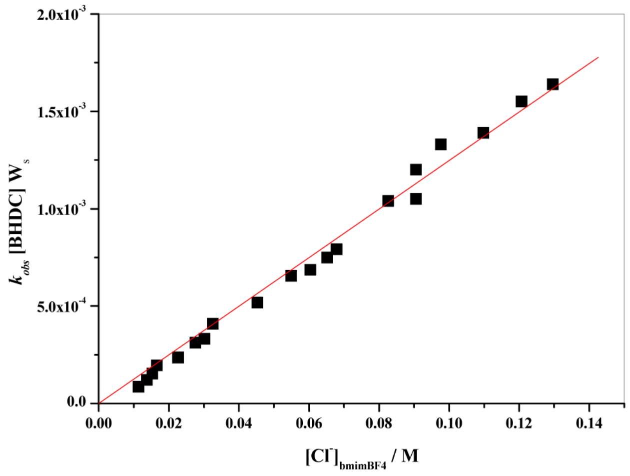


Figure 4. Plot of k_{obs} $[\text{BHDC}]W_s$ values as a function of $[\text{Cl}^-]_{\text{bmimBF}_4}$ according eq 16.

Thus, a value of $(k_2^{\text{bmimBF}_4}/\bar{V}_{\text{bmimBF}_4}) = 0.0125$ was obtained, and taking into consideration that the molar volume of bmimBF_4 is 0.187 M^{-1}, $k_2^{\text{bmimBF}_4} = 2.3 \times 10^{-3}$ M^{-1} s^{-1} was estimated. This value is similar to that obtained for the same reaction in neat bmimBF_4, confirming the validity of the procedure.

Thus, the value of $K_{\text{BF}_4^-}^{\text{Cl}-} = 0.025$ indicates that the Cl^- prefers to be located at the interface interacting with the cationic surfactant polar head group. Even that the value of the distribution constant is small, the high concentrations of bmimBF_4 and BHDC employed makes it so that the exchange takes place in large magnitude. For example, at $W_s = 0.5$, the $[\text{Cl}^-]$ is twice that of $[\text{BF}_4^-]$, and this means that 13% of the Cl^- will be incorporated into the pool displacing, the ion BF_4^- to the interface. By means of eq 17, considering $\beta = 0.96$, $K_{\text{BF}_4^-}^{\text{Cl}-} = 0.025$, and the mass balance for the ionic species (see the Supporting Information), the concentrations of Cl^- and BF_4^- present at the interface and in the pool for each W_s studied were calculated and the results are shown in Figure 5.

It is important to note that the percentage of BF_4^- present at the interface decreases by increasing the W_s. For example, at $W_s = 0.1$ approximately 40% of BF_4^- ions are present at the interface as counterion of the surfactant, while the amount of ions decreases to 10% at $W_s = 1.2$. This behavior of BF_4^- at the BHDC interface was observed before for a similar system.[26] From FT-IR and NMR[25,26] experiments in BHDC RMs entrapping bmimBF_4, an electrostatic interaction between the positive charge of BHDC head group (BHD^+) and the anion BF_4^- was proposed. Thus, this interaction affects considerably the bmimBF_4 structure (at the interface) when it is encapsulated in the cationic RMs. As the positive charge is located exclusively in the quaternary nitrogen atom of BHD^+ while the positive charge is delocalized in the bmim^+ ion (see Scheme 1),[53] we expect a stronger interaction between BF_4^- and the BHD^+ head group than with its own bmim^+ cations forming probably an ion pair. These facts are evidence that bmimBF_4 encapsulated in BHDC RMs does not have the same effect on the Cl^- availability as in the homogeneous media. Consequently, when bmimBF_4 is entrapped in BHDC RMs, strong IL−interface interaction and significant changes in the structural organization of the RMs interface are observed.

■ CONCLUSIONS

In summary, how the confinement of two different ionic liquids (bmimBF_4 and bmimCl) inside toluene/BHDC RMs, varying the W_s, affects the nucleophilicity of Cl^- on the bimolecular nucleophilic substitution reaction of dimethyl-4-nitrophenylsulfonium has been demonstrated. For the first time, toluene/BHDC/ionic liquid RMs were used as nanoreactors for carrying out kinetic experiments. The results show that, upon confinement, the ionic interactions with the cationic surfactant polar head group and the surfactant counterion modifies substantially the performance of both ionic liquids as solvent. In toluene/BHDC/bmimCl RMs, the observed rate constant values are independent of the $[\text{Cl}^-]$ and W_s. This result is compatible with the dimethyl-4-nitrophenylsulfonium ion being located inside the nanodroplet in such a way that changes in the RM composition does not alter the local concentration of Cl^- that is available to react. The bimolecular rate constant obtained inside the pool is smaller than that in neat bmimBF_4, allowing one to conclude that ion pairing is more important in the RMs than in bulk ionic liquid due to Cl^- interactions with bmim^+ (and/or BHD^+). In toluene/BHDC/bmimBF_4, the rate of reaction is strongly dependent on the W_s content and the results can be explained considering the presence of ionic exchange equilibrium in the RMs. This equilibrium produces a segregation of bmim^+ and BF_4^- ions, changing the composition of the RMs interface and affecting dramatically the Cl^-

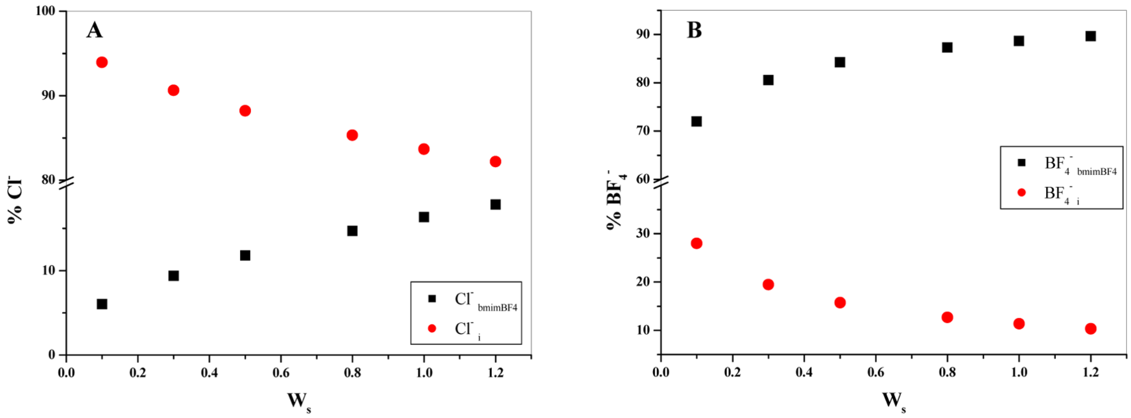


Figure 5. Estimated percentages corresponding to the total concentration of Cl^- (A) and BF_4^- (B), at the interface and pool as a function of W_s in toluene/BHDC/bmimBF_4 RMs.

availability. These facts show the versatility of this kind of organized system to alter the ionic organization and its influence when they are used as nanoreactors because unique microenvironments simply changing the W_s can be easily created.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Procedure for DLS and kinetic experiments; tables of kinetic data and deduction of rate equations for toluene/BHDC/bmimCl and toluene/BHDC/bmimBF_4 RMs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Hallett, J. P.; Welton, T. Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2. *Chem. Rev.* **2011**, *111*, 3508−3576.

(2) Welton,T.; Wasserscheid, P. *Ionic Liquids in Synthesis*; VCH-Wiley: Weinheim, 2002.

(3) Welton, T. Ionic liquids in catalysis. *Coord. Chem. Rev.* **2004**, *248*, 2459−2477.

(4) Correa, N. M.; Silber, J. J.; Riter, R. E.; Levinger, N. E. Nonaqueous polar solvents in reverse micelle systems. *Chem. Rev.* **2012**, *112*, 4569−4602.

(5) De, T. K.; Maitra, A. Solution behaviour of Aerosol OT in non-polar solvents. *Adv. Colloid Interface Sci.* **1995**, *59*, 95−193.

(6) Moulik, S. P.; Paul, B. K. Structure, dynamics and transport properties of microemulsions. *Adv. Colloid Interface Sci.* **1998**, *78*, 99−195.

(7) Eastoe, J.; Gold, S.; Rogers, S.; Wyatt, P.; Steytler, D. C.; Gurgel, A.; Heenan, R. K.; Fan, X.; Beckman, E. J.; Enick, R. M. Designed CO_2-philes stabilize water-in-carbon dioxide microemulsions. *Angew. Chem., Int. Ed.* **2006**, *45*, 3675−3677.

(8) Andujar-Matalobos, M.; Garcia-Rio, L.; Lopez-Garcia, S.; Rodriguez-Dafonte, P. Polarity of the interface in ionic liquid in oil microemulsions. *J. Colloid Interface Sci.* **2011**, *363*, 261−267.

(9) García-Río, L.; Leis, J. R. Microemulsion-promoted changes of reaction mechanisms: Solvolysis of substituted benzoyl chlorides. *Chem. Commun.* **2000**, 455−456.

(10) Rispens, T.; Engberts, J. B. F. N. Micellar catalysis of Diels-Alder reactions: Substrate positioning in the micelle. *J. Org. Chem.* **2002**, *67*, 7369−7377.

(11) McNeil, R.; Thomas, J. K. Benzylhexadecyldimethylammonium chloride in microemulsions and micelles. *J. Colloid Interface Sci.* **1981**, *83*, 57−65.

(12) Falcone, R. D.; Silber, J. J.; Correa, N. M. What are the factors that control non-aqueous/AOT/n-heptane reverse micelle sizes? A dynamic light scattering study. *Phys. Chem. Chem. Phys.* **2009**, *11*, 11096−11100.

(13) Faeder, J.; Albert, M. V.; Ladanyi, B. M. Molecular dynamics simulations of the interior of aqueous reverse micelles: A Comparison between Sodium and Potassium Counterions. *Langmuir* **2003**, *19*, 2514−2520.

(14) Abel, S.; Sterpone, F.; Bandyopadhyay, S.; Marchi, M. Molecular modeling and simulations of AOT−water reverse micelles in isooctane: structural and dynamic properties. *J. Phys. Chem. B* **2004**, *108*, 19458−19466.

(15) Harpham, M. R.; Ladanyi, B. M.; Levinger, N. E. The effect of the counterion on water mobility in reverse micelles studied by molecular dynamics simulations. *J. Phys. Chem. B* **2005**, *109*, 16891−16900.

(16) Cringus, D.; Lindner, J.; Milder, M. T. W.; Pshenichnikov, M. S.; Vohringer, P.; Wiersma, D. A. Femtosecond water dynamics in reverse-micellar nanodroplets. *Chem. Phys. Lett.* **2005**, *408*, 162−168.

(17) Piletic, I. R.; Moilanen, D. E.; Levinger, N. E.; Fayer, M. D. What nonlinear-IR Experiments Can Tell You about Water that the IR spectrum cannot. *J. Am. Chem. Soc.* **2006**, *128*, 10366−10367.

(18) Dokter, A. M.; Woutersen, S.; Bakker, H. J. Inhomogeneous dynamics in confined water nanodroplets. *Proc. Nat. Acad. Sci. U. S. A.* **2006**, *103*, 15355−15358.

(19) Cringus, D.; Bakulin, A.; Lindner, J.; Vohringer, P.; Pshenichnikov, M. S.; Wiersma, D. A. Ultrafast energy transfer in water-AOT reverse micelles. *J. Phys. Chem. B* **2007**, *111*, 14193−14207.

(20) Kondo, M.; Heisler, I. A.; Meech, S. R. Ultrafast reaction dynamics in nanoscale water droplets confined by ionic surfactants. *Faraday Discuss.* **2010**, *145*, 185−203.

(21) Jada, A.; Lang, J.; Zana, R. Ternary water in oil microemulsions made of cationic surfactants, water and aromatic solvents. 1. Water solubility studies. *J. Phys. Chem.* **1990**, *94*, 381−387.

(22) Baptista, M. S.; Tran, C. D. Electrical conductivity, near-infrared absorption, and thermal lens spectroscopic studies of percolation of microemulsions. *J. Phys. Chem. B* **1997**, *101*, 4209−4217.

(23) Grand, D. Electron Transfer in Reverse Micellar Solutions: Influence of the Interfacial Bound Water. *J. Phys. Chem. B* **1998**, *102*, 4322−4326.

(24) Agazzi, F. M.; Falcone, R. D.; Silber, J. J.; Correa, N. M. Solvent blends can control cationic reversed micellar interdroplet interactions. The effect of n-heptane:benzene mixture on BHDC reversed micellar interfacial properties: droplet sizes and micropolarity. *J. Phys. Chem. B* **2011**, *115*, 12076−12084.

(25) Falcone, R. D.; Correa, N. M.; Silber, J. J. On the formation of new reverse micelles: A comparative study of benzene/surfactants/ionic liquids systems using UV−visible absorption spectroscopy and dynamic light scattering. *Langmuir* **2009**, *25*, 10426−10429.

(26) Falcone, R. D.; Baruah, B.; Gaidamauskas, E.; Rithner, C. D.; Correa, N. M.; Silber, J. J.; Crans, D. C.; Levinger, N. E. Layered structure of room temperature ionic liquids in microemulsions by multinuclear NMR spectroscopic studies. *Chem.—Eur. J.* **2011**, *17*, 6837−6846.

(27) Ferreyra, D. D.; Correa, N. M.; Silber, J. J.; Falcone, R. D. The effect of different interfaces and confinement on the structure of the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide entrapped in cationic and anionic reverse micelles. *Phys. Chem. Chem. Phys.* **2012**, *14*, 3460−3470.

(28) Blach, D.; Silber, J. J.; Correa, N. M.; Falcone, R. D. Electron donor ionic liquids entrapped in anionic and cationic reverse micelles. Effect of the interface on the ionic liquid −surfactant interactions. *Phys. Chem. Chem. Phys.* **2013**, *15*, 16746−16757.

(29) Pramanik, R.; Ghatak, C.; Rao, V. G.; Sarkar, S.; Sarkar, N. Room temperature ionic liquid in confined media: a temperature dependence solvation study in [bmim][BF4]/BHDC/benzene reverse micelles. *J. Phys. Chem. B* **2011**, *115*, 5971−5979.

(30) Acharya, D. P.; Hartley, P. G. Progress in microemulsion characterization. *Curr. Opin. Colloid Interface Sci.* **2012**, *17*, 274−280.

(31) Kunz, W.; Zemb, T.; Harrar, A. Using ionic liquids to formulate microemulsions: Current state of affairs. *Curr. Opin. Colloid Interface Sci.* **2012**, *17*, 205−211.

(32) Zech, O.; Kunz, W. Conditions for and characteristics of nonaqueous micellar solutions and microemulsions with ionic liquids. *Soft Matter* **2011**, *7*, 5507−5513.

(33) Qiu, Z. M.; Texter, J. Ionic liquids in microemulsions. *Curr. Opin. Colloid Interface Sci.* **2008**, *13*, 252−262.

(34) Gayet, F.; El Kalamouni, C.; Lavedan, P.; Marty, J. D.; Brulet, A.; Lauth-de Viguerie, N. Ionic liquid/oil microemulsions as chemical nanoreactors. *Langmuir* **2009**, *25*, 9741−9750.

(35) Moniruzzaman, M.; Kamiya, N.; Nakashima, K.; Goto, M. Formation of reverse micelles in a room-temperature ionic liquid. *ChemPhysChem* **2008**, *9*, 689−692.

(36) Moniruzzaman, M.; Kamiya, N.; Nakashima, K.; Goto, M. Water-in-ionic liquid microemulsions as a new medium for enzymatic reactions. *Green Chem.* **2008**, *10*, 497−500.

(37) Zhao, M.; Zheng, L.; Bai, X.; Li, N.; Yu, L. Fabrication of silica nanoparticles and hollow spheres using ionic liquid microemulsion droplets as templates. *Colloid Surface A* **2009**, *346*, 229−236.

(38) Rojas, O.; Tiersch, B.; Frasca, S.; Wollenberger, U.; Koetz, J. A new type of microemulsion consisting of two halogen-free ionic liquids and one oil component. *Colloid Surface A* **2010**, *369*, 82−87.

(39) Yu, S.; Yan, F.; Zhang, X.; You, J.; Wu, P.; Lu, J.; Xu, Q.; Xia, X.; Ma, G. Polymerization of Ionic Liquid-Based Microemulsions: A Versatile Method for the Synthesis of Polymer Electrolytes. *Macromolecules* **2008**, *41*, 3389−3392.

(40) Chen, Z.; Yan, F.; Qiu, L.; Lu, J.; Zhou, Y.; Chen, J.; Tang, Y.; Texter, J. Sustainable polymerizations in recoverable microemulsions. *Langmuir* **2010**, *26*, 3803−3806.

(41) Niedermeyer, H.; Hallett, J. P.; Villar-Garcia, I. J.; Hunt, P. a.; Welton, T. Mixtures of ionic liquids. *Chem. Soc. Rev.* **2012**, *41*, 7780−7802.

(42) Chiappe, C.; Pieraccini, D.; Saullo, P. Nucleophilic displacement reactions in ionic liquids: substrate and solvent effect in the reaction of NaN(3) and KCN with alkyl halides and tosylates. *J. Org. Chem.* **2003**, *68*, 6710−6715.

(43) Ranieri, G.; Hallett, J. P.; Welton, T. Nucleophilic reactions at cationic centers in ionic liquids and molecular solvents. *Ind. Eng. Chem. Res.* **2008**, *47*, 638−644.

(44) Hallett, J. P.; Liotta, C. L.; Ranieri, G.; Welton, T. Charge screening in the S_N2 reaction of charged electrophiles and charged nucleophiles: An ionic liquid effect. *J. Org. Chem.* **2009**, *74*, 1864−1868.

(45) Nockemann, P.; Binnemans, K.; Driesen, K. Purification of imidazolium ionic liquids for spectroscopic applications. *Chem. Phys. Lett.* **2005**, *415*, 131−136.

(46) Dupont, J.; Suarez, P. A. Z.; Consorti, C. S.; de Souza, R. F. Preparation of 1-butyl-3-methyl imidazolium-based room temperature ionic liquids. *Org. Synth.* **2002**, *79*, 236−236.

(47) Bunton, C. A.; Nome, F.; Quina, F. H.; Romsted, L. S. Ion binding and reactivity at charged aqueous interfaces. *Acc. Chem. Res.* **1991**, *24*, 357−364.

(48) García-Río, L.; Mejuto, J. C.; Pérez-Lorenzo, M. Microheterogeneous solvation for aminolysis reactions in AOT-based water-in-oil microemulsions. *Chem.—Eur. J.* **2005**, *11*, 4361−4373.

(49) Fernandez, E.; Garcia-Rio, L.; Rodriguez-Dafonte, P. Degree of counterion binding on water in oil microemulsions. *J. Colloid Interface Sci.* **2007**, *316*, 1023−1026.

(50) Garcia-Rio, L.; Leis, J. R.; Pena, M. E.; Iglesias, E. Transfer of the nitroso group in water/AOT/isooctane microemulsions: Intrinsic and apparent reactivity. *J. Phys. Chem.* **1993**, *97*, 3437−3442.

(51) Reichardt, C. Polarity of ionic liquids determined empirically by means of solvatochromic pyridinium N-phenolatebetaine dyes. *Green Chem.* **2005**, *7*, 339−351.

(52) Fernández, E.; García-Río, L.; Knörl, A.; Leis, J. R. Metal−ligand complexation in water-in-oil microemulsions. I. Thermodynamic approach. *Langmuir* **2003**, *19*, 6611−6619.

(53) McFarlane, D. R.; Sun, J.; Golding, J.; Meakin, P.; Forsyth, M. High conductivity molten salts based on the imide ion. *Electrochim. Acta* **2000**, *45*, 1271−1278.