PAPER

A protic ionic liquid, when entrapped in cationic reverse micelles, can be used as a suitable solvent for a bimolecular nucleophilic substitution reaction†

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In this work, we have explored how the confinement of the protic ionic liquid (IL) ethylammonium nitrate (EAN) inside toluene/benzyl-*n*-hexadecyldimethylammonium chloride (BHDC) reverse micelles (RMs) affects the Cl⁻ nucleophilicity on the bimolecular nucleophilic substitution (S$_N$2) reaction between this anion and dimethyl-4-nitrophenylsulfonium trifluoromethanesulfonate. To the best of our knowledge this is the first report where toluene/BHDC RMs use EAN as a polar component and it is used as a nanoreactor for carrying out kinetic experiments. Dynamic light scattering results reveal the formation of RMs containing the protic IL. The kinetic results show that upon confinement, EAN becomes a suitable solvent for the S$_N$2 reaction while in homogeneous media it is a bad option. Entrapped in BHDC RMs, due to the strong hydrogen bond interactions, EAN behaves as an aprotic-like IL which cannot deactivate the nucleophilic power of Cl⁻ and yet increases the substrate solubility. These facts show the versatility of this kind of organized system to alter the polar solvent entrapped and its influence on the reaction rate when it is used as a nanoreactor.

Introduction

Reverse 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.[1–3] RMs are an interesting subject due to their broad applications in chemical reactions, separation science, materials science, and the pharmaceutical industry, among others.[1,4] These nanoscale aggregates are suitable media for processes that involve hydrophobic and hydrophilic reactants in a variety of chemical and biological reactions.[1,4–7] There are a wide range of surfactants that form RMs, including anionic, cationic and nonionic molecules.[1–16] One of them, the cationic surfactant benzyl-*n*-hexadecyldimethylammonium chloride (BHDC, Scheme 1), can form RMs in aromatic solvents without the addition of a cosurfactant.[1,8,17–23]
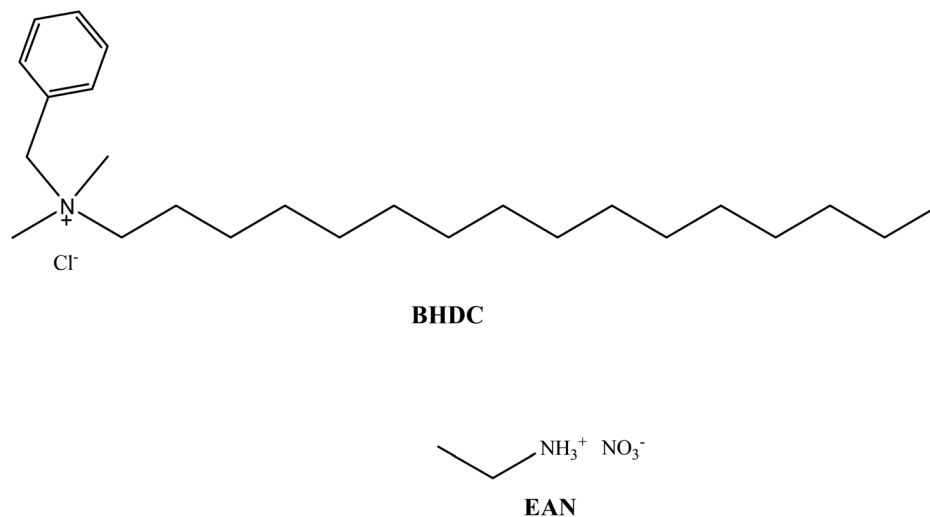
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†Electronic supplementary information (ESI) available: Fig. S1: Absorption spectra of the reaction of Cl⁻ with S⁺ in neat EAN at 30 °C; Fig. S2: Absorbance at 340 nm as a function of time in the reaction shown in Fig. 2; Table S1: k_{obs} values obtained in toluene/BHDC/EAN RMs varying the [BHDC] at different W_s and derivation of the rate equation. See DOI: 10.1039/c5ob02664d

Ionic liquids (ILs) have received significant attention as powerful alternatives to conventional molecular organic solvents.[24–26] According to their proton availability, ILs can be classified as protic or aprotic.[27] In particular, protic ILs have been used in several applications.[24,28] Ethylammonium nitrate (EAN, Scheme 1) is a widely studied protic IL and it is known that it has many similarities to water such as high polarity and the ability to form hydrogen bonds.[29,30]

The use of protic ILs (predominantly EAN) in organized systems is usually as a replacement for water as the polar phase in direct micelles or vesicles. In this regard, very recently Greaves *et al.*[31] reported in detail the background of this field. However, with regard to the formation of RMs containing protic ILs, much less information is available. These RMs can provide potential applications owing to the unique features of both ILs and RMs. However, the majority of studies on protic ILs employed non-ionic surfactants such as alkyl oligoethylene oxide (C$_n$E$_m$)[32,33] or Brijs[34] and they normally used, as the non-polar phase, *n*-alkanes or benzene[34] and EAN as the polar phase.[35–37] Only a few studies by Zech *et al.*[35–37] have focused on the use of a cationic surfactant, particularly 1-hexadecyl-3-methyl imidazolium chloride (C$_{16}$mimCl), with decanol as a cosurfactant, EAN as the polar phase, and dodecane as the non-polar continuous phase.[35,36]

With regard to BHDC RMs, although the traditional solvent used as a polar component in this cationic RM is water,[8,17]

BHDC

NH_3^+ NO_3^-

EAN

Scheme 1 Molecular structures of BHDC and EAN.

different aprotic ILs[18–23] have been entrapped in the polar core but no information on the possibility of using EAN is available. This system is interesting to explore since it is well known that the physicochemical properties of polar solvents (water and aprotic ILs) entrapped inside RMs change dramatically from those of the bulk solvents as a result of specific interactions and confined geometries.[1,9,18–21,23] This can cause, for example, alterations in the reactants and in the course of the reactions. In particular, nucleophilic substitution reactions provide a familiar route for the examination of solvent effects on chemical reactions.[23,24,38–41] It is possible to use the nucleophilic substitution reaction of Cl^- with dimethyl-4-nitrophenyl-sulfonium (S^+ in Scheme 2) as a chemical probe.[23,40,41] Previously, we have studied the same S_N2 reaction in toluene/ BHDC RMs but with 1-butyl-3-methylimidazolium tetrafluoro-borate ($bmimBF_4$) as an encapsulated aprotic IL.[23] We observed that upon confinement, the ionic interactions between the cationic surfactant polar head groups and the surfactant counterion modify substantially the performance of the aprotic IL as a solvent. Taking into account this background, the aim of the present work was to show that a protic solvent, EAN, can be used as a worthy reaction medium when it is entrapped in BHDC RMs while it is a bad option in homogeneous media. Here, it is important to note that the aim of our work is not to try to discover new materials or transformations but to use a chemical reaction as a model reaction to evaluate the solvent effect in a complex system such as RMs.

Results and discussion

In order to explore the effect of confinement on EAN in the S_N2 reaction studied, the nucleophilic reactivity of Cl^- in homogeneous and confined media was evaluated. Thus, the results obtained are presented in two different sections corresponding to the studies performed in (i) neat EAN and (ii) toluene/BHDC/EAN RMs at different IL contents defined as $W_s = [EAN]/[BHDC]$.

The S_N2 reaction was followed by monitoring of the absorbance changes at $\lambda = 340$ nm corresponding to the formation of the demethylated sulfide product (Scheme 2). 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 the $[Cl^-]$.

Studies in neat EAN

Absorbance spectra of the mixture of Cl^- and S^+ in neat EAN at different times are presented in Fig. S1.† Ammonium chloride (NH_4Cl) as a source of Cl^- ions was used and the variation of the Cl^- concentration between 1×10^{-2} M and 0.2 M was performed. As can be observed in Fig. S1,† no absorbance changes using the protic IL as a solvent were detected, even after a long time of reaction. Similar results were found by Hallett et al.[41] for the same reaction performed in water and methanol. The authors explained the absence of reaction as due to the strong hydrogen bond interaction between the
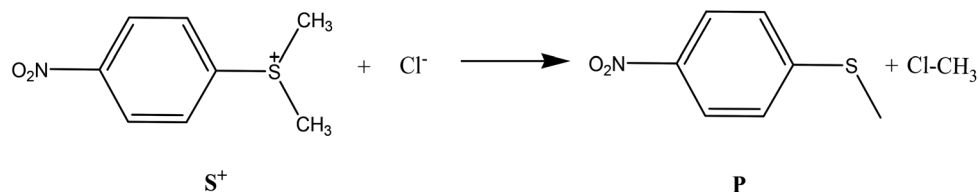
Scheme 2 The S_N2 reaction of Cl^- with dimethyl-4-nitrophenylsulfonium (S^+) to produce methyl-4-nitrophenyl sulfide (P) and $Cl–CH_3$.

solvents and the nucleophile, thus reducing its reactivity. In fact, EAN presents a high Kamlet-Taft's α parameter value (0.85 (ref. 25)), which is consistent with the ability of the solvent to interact through hydrogen bonds. In consequence, the Cl$^-$ anions in EAN are not available to act as a nucleophile because they are associated with the ethylammonium cation.[41]

Studies in toluene/BHDC/EAN RMs

Prior to studying the S_N2 reaction in the toluene/BHDC/EAN system and because it is not known whether EAN is truly encapsulated by BHDC to form RMs, dynamic light scattering (DLS) experiments were performed. When new RMs are explored, a crucial question has to be answered: is the polar solvent effectively entrapped by the surfactant creating true RMs or is dissolved only in the organic solvent/surfactant mixture without any molecular organization (bicontinuous structureless microemulsion)?[42] DLS normally is used to assess this matter because if the polar solvent (water for example) is really encapsulated and interacting with the RM interface, the droplet sizes must increase, as the water content (W_0 = [water]/[surfactant]) increases with a linear tendency (swelling law of RMs) as is well established for other RMs.[9,17,43] A deviation from the linearity of the droplet sizes indicates that the RM droplet–droplet interactions are favored, thus changing the shape of the RMs prior to the phase separation.[23,44–47] On the other hand, if the polar solvent is not encapsulated by the surfactant the droplet sizes could remain constant or even decrease with the polar solvent addition.[42] In the present work, as the RM solutions are not at infinite dilution (DLS experiments were performed at a fixed surfactant concentration equal to 0.2 M) it is appropriate to introduce an apparent hydrodynamic diameter (d_{app}) in order to describe the results.[48] Fig. 1 shows the d_{app} values for the toluene/BHDC/EAN system at different W_s values. As can be seen, there is an increase in the droplet size values when the

IL content increases, showing that EAN is effectively entrapped by the surfactant layer, yielding RMs. The sizes obtained for toluene/BHDC/EAN RMs are comparable to the values reported previously for aprotic ILs entrapped in BHDC RMs.[18,20,21,23,43] However, the amount of protic IL that the toluene/BHDC RMs dissolves is quite small, W_s = 0.3. Similar results have been reported by Dai *et al.*[49] in the ternary system cyclohexane/TX-100/EAN (W_s = 0.4) and by Zech *et al.*[36] in dodecane/decanol/C$_{16}$mimCl/EAN (W_s = 0.18).

Additionally from Fig. 1, it is interesting to mention that the droplet size values increase slightly (only 0.5 nm) with W_s, suggesting that the IL is interacting weakly with BHDC at the interface of RMs.[18,20,21]

As was mentioned above, we have studied previously[23] the same S_N2 reaction in BHDC RMs; particularly in that work we performed kinetic experiments also in neat toluene and toluene/BHDC RMs at W_s = 0. In both cases, the reaction takes place but different behaviors were observed.[23] In neat toluene, always working below the critical micellar concentration, the formation of ion pairs between Cl$^-$ and its counterion increases with the salt concentration, in such a way that the fraction of free Cl$^-$ available as a nucleophile to react with sulfonium ions decreases and consequently the observed rate constant also decreases.[23] In toluene/BHDC RMs at W_s = 0, the incorporation of S$^+$ into the RMs is favored (in comparison with toluene) and the presence of Cl$^-$ at the interface of the RMs allows the observation of the reaction.[23]

Taking into account these backgrounds and the ability of RMs to alter the structure of the polar solvent entrapped, in the present contribution we want to explore whether the presence of RMs can affect or not the performance of a bad solvent for nucleophilic substitution reactions such as EAN. In this regard, in toluene/BHDC/EAN RMs the S_N2 reaction was studied by varying the [BHDC] but keeping constant the [S$^+$] and W_s values. Typical kinetic results in toluene/BHDC/EAN RMs are shown in Fig. 2. Also an example of the absorbance change at λ = 340 nm as a function of time at [BHDC] = 0.1 M and W_s = 0.05 is shown in Fig. S2.† As can be seen in these figures and contrary to the results obtained in neat EAN (Fig. S1†), the reaction in toluene/BHDC/EAN is observed.

The reaction of the sulfonium S$^+$ with the chloride ion presented in Scheme 2 is a bimolecular reaction, whose kinetics follows the rate law described by eqn (1):

$$\text{rate} = \frac{d[P]}{dt} = k_2[\text{Cl}^-][\text{S}^+] \qquad (1)$$

If [Cl$^-$] $\gg$ [S$^+$], a pseudo first order behavior for the kinetics of the reaction, is assumed in order to quantify the reaction rate. Thus, the expression for the observable rate constant (k_{obs}) can be defined as eqn (2):

$$k_{obs} = k_2[\text{Cl}^-] \qquad (2)$$

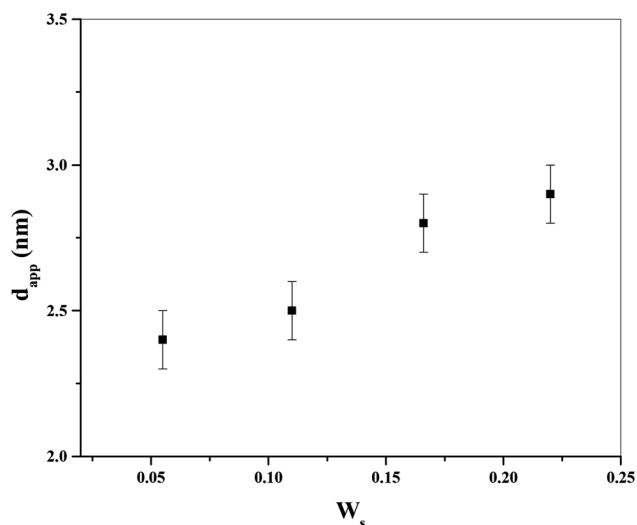where k_2 is the second order rate constant and [Cl$^-$] is the total nucleophile concentration.

Fig. 1 Apparent diameter (d_{app}) values for toluene/BHDC/EAN RMs obtained at 30 °C by varying W_s. [BHDC] = 0.2 M.
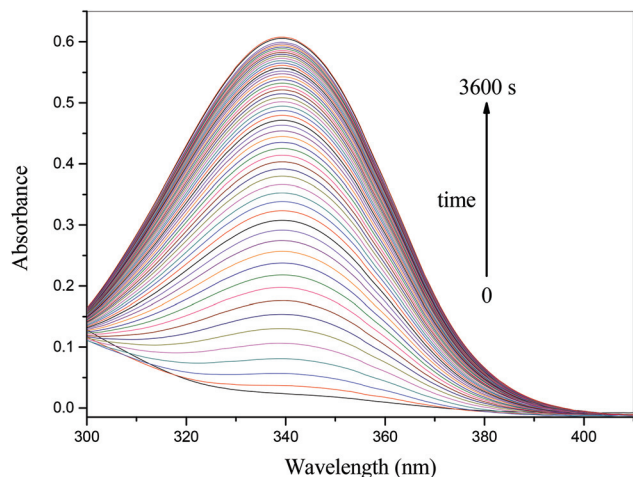
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Fig. 2 Absorption spectra of the reaction of Cl⁻ with S⁺ in toluene/BHDC/EAN RMs at W_s = 0.05. [BHDC] = 0.1 M. [S⁺] = 5 × 10⁻⁵ M. T = 30 °C. The spectra were recorded at 60 second intervals.

Fig. 4 k_{obs} values as a function of W_s in toluene/BHDC/EAN at different [BHDC]$_{tot}$. [BHDC]$_{tot}$ (M): (▲) 0.10, (■) 0.15 and (●) 0.2. [S⁺] = 5 × 10⁻⁵ M. T = 30 °C.

As in the RMs, the BHDC surfactant was used as the source of Cl⁻ ions (see the structure in Scheme 1), k_{obs} values obtained in toluene/BHDC/EAN RMs at different total concentrations of BHDC ([BHDC]$_{tot}$) and W_s are shown in Fig. 3.

Two facts emerge from Fig. 3: (i) the k_{obs} values increase with the amount of BHDC but not in a linear tendency at all the W_s evaluated as could be expected for a simple S_N2 reaction; (ii) the k_{obs} values in the RMs are dependent on the EAN content. In Fig. 4, the k_{obs} values in the toluene/BHDC/EAN RMs are plotted as a function of the EAN content, at [BHDC]$_{tot}$ constant.

As can be observed, at low W_s (0.02–0.11), k_{obs} has similar values in the toluene/BHDC/EAN RMs and they are independent of the EAN content. Only when the W_s value is large enough (W_s = 0.17) is there an impact on the rate constant which decreases dramatically. It should be noted that even at
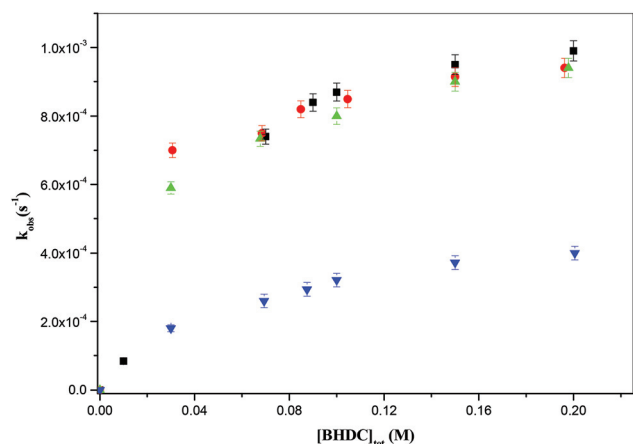
this W_s value the reaction is still observed. It is evident that the Cl⁻ availability is responsible for the changes in the rates of the reaction.
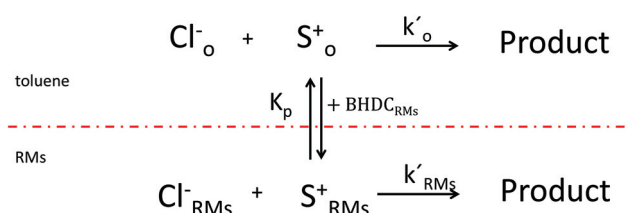
In order to explain the results obtained for the BHDC RMs at different [BHDC] and W_s, it is important to consider which kinetic model is appropriate to analyse the data.

In view of the S⁺ chemical structure, it is possible that the substrate solubilizes (in different magnitudes) in two regions of the toluene/BHDC/EAN system: the organic and the RM pseudophases. Thus, the overall reaction can be described as Scheme 3 illustrates.

As, in the present work, we used [BHDC] > critical micellar concentration (cmc) value (0.01 M),[50] S⁺ is incorporated into the RMs (as is expressed by eqn (3)) favored by its low solubility in the aromatic solvent.

$$S_o^+ + BHDC_{RMs} \rightleftharpoons S^+_{RMs} \qquad (3)$$
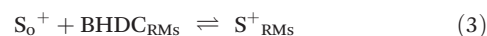
where S^+_o and S^+_{RMs} symbolize the substrate in toluene and in the RM pseudophases, respectively. BHDC$_{RMs}$ represents the cationic RMs. As is conventional for micellar aggregates, the concentration of the micellized[51] surfactant defined as [BHDC]$_{RMs}$ (where [BHDC]$_{RMs}$ can be approximated to [BHDC]$_{tot}$ − cmc) can be calculated, and if the mass balance

Fig. 3 k_{obs} values as a function of total concentration of BHDC ([BHDC]$_{tot}$) in toluene/BHDC/EAN at different W_s. W_s: (■) 0.02, (●) 0.05, (▲) 0.11 and (▼) 0.17. [S⁺] = 5 × 10⁻⁵ M. T = 30 °C.

Scheme 3 Schematic representation of the reaction sites in toluene/BHDC/EAN RMs. S^+_o, Cl^-_o, Cl^-_{RMs} and S^+_{RMs} are the reactants in the organic and the RM pseudophases, respectively.

for S⁺ ([S⁺]_tot = [S⁺]_o + [S⁺]_RMs) is considered, the partition constant of the substrate (K_p) is defined as eqn (4):

$$K_p = \frac{[S^+]_{RMs}}{[S^+]_o[BHDC]_{RMs}} \tag{4}$$

Taking into consideration the procedure used previously for the RMs containing other ILs,[23] it is possible to obtain the following rate equation (see the ESI† for a complete rate equation deduction):

$$k_{obs} = k_{obs}^{cmc} + \frac{k_2^{RMs}\beta}{\bar{V}_{BHDC}} \frac{K_p[BHDC]_{RMs}}{1 + K_p[BHDC]_{RMs}} \tag{5}$$

where k_{obs}^{cmc} and k_2^{RMs} are the second order rate constant values in the cmc and [BHDC] > cmc, respectively. [BHDC]_RMs is the surfactant concentration with respect to the total volume, $\bar{V}_{BHDC}$ is the molar volume of BHDC and β is the fraction of the surfactant neutralized charge.[23]

As Fig. 4 showed no dependence on the k_{obs} values at low W_s, the experimental data obtained for toluene/BHDC/EAN RMs at W_s between 0.02 and 0.11 were analyzed using eqn (5), and for example, in Fig. 5 the fitting at W_s = 0.02 is presented.

From the fitting of the results at W_s values between 0.02 and 0.11 and using $\bar{V}_{BHDC}$ = 0.42 M⁻¹, average values of K_p = 25.1 ± 0.7 M⁻¹ and $k_2^{RMs}\beta$ = 4.4 ± 0.2 × 10⁻⁴ M⁻¹ s⁻¹ were obtained. To estimate k_2^{RMs} it is necessary to know the value of β. Previous studies showed that, independently of the RM composition,[23] β remains constant around 0.96; thus using this value we have estimated $k_2^{RMs} \approx$ 4.6 ± 0.2 × 10⁻⁴ M⁻¹ s⁻¹. Additionally, the K_p value confirms that in the toluene/BHDC/EAN RMs, S⁺ is practically located at the RM interface. Moreover, the partition constant value is larger than that in the absence of a polar solvent[23] (K_p = 22.4 ± 0.6 M⁻¹ at W_s = 0). Thus, for example, at [BHDC] = 0.2 M, 83% of the substrate is incorporated into the toluene/BHDC/EAN RMs.

If the same analysis is performed for the RMs at the maximum of EAN entrapped (W_s = 0.17) where the k_{obs} values
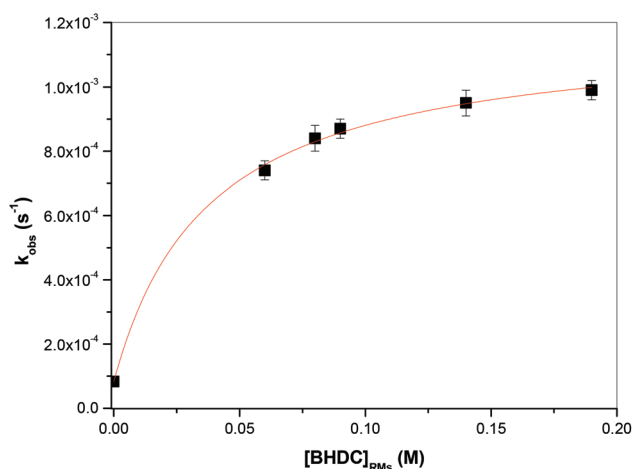
dramatically decrease in comparison with the values obtained at W_s values between 0.02 and 0.11 (Fig. 4), values of k_2^{RMs} = 1.7 ± 0.2 × 10⁻⁴ M⁻¹ s⁻¹ and K_p = 18 ± 2 M⁻¹ are obtained. This drop in the rate constant value (about 4 times) can be explained considering that in the RMs at the maximum of W_s reached, the polar solvent interacts much less with the interface than at low W_s, and thus a reduction in the nucleophilic power of Cl⁻ is expected. However, it is important to note that even at W_s = 0.17 the behavior of EAN confined in BHDC RMs is not equal to the neat EAN, where the reaction does not take place.

In comparison with the previous results using the aprotic IL bmimBF₄,[23] the reactivity of Cl⁻ ions in toluene/BHDC/EAN RMs is smaller ($k_2^{bmimBF_4}$ = 2.3 ± 0.1 × 10⁻³ M⁻¹ s⁻¹).[23] In Table 1, the second order rate constant values obtained in both RMs and homogeneous media are presented. Interestingly, in the EAN case the most notable fact is that the RMs produce strong alterations in the protic solvent when entrapped in BHDC RMs which entirely affects the Cl⁻ nucleophilicity in comparison with its behavior in homogeneous media. These alterations are more important than the changes observed in the systems using bmimBF₄ (Table 1).

Hence, we show evidence that EAN can be considered as a good solvent for the S_N2 reaction while in homogeneous media it is a bad option. In order to explain these results, we propose that the key is the magnitude of the hydrogen bond of EAN when the solvent is in confinement. In this regard, the ability of ILs to form hydrogen bonds with a solute or between the ions in a neat solvent has been described in terms of two competing equilibria.[24,25] In the EAN case (a protic solvent), the cation first interacts through hydrogen bonds with its counterion according to eqn (6):

$$Ethyl–NH_3^+ + NO_3^- \rightleftharpoons ethyl–NH_3^+ \cdots NO_3^- \tag{6}$$

Additionally, the cation ethyl–NH₃⁺ can also complex with the Cl⁻ present in the reaction media (eqn (7)):

$$Ethyl–NH_3^+ + Cl^- \rightleftharpoons ethyl–NH_3^+ \cdots Cl^- \tag{7}$$

Since in the reaction media both equilibria (eqn (6) and (7)) can be involved,[24,25] from the results in neat EAN (where no reaction is observed) it is possible to deduce that the amount of free Cl⁻ (eqn (7)) is clearly very low. In contrast, in BHDC RMs we observe a reaction and this is due to the availability of

Fig. 5 Plot of k_{obs} values as a function of [BHDC]_RMs in toluene/BHDC/EAN at W_s = 0.02 analyzed according to eqn (5).

Table 1 Second order rate constant (k_2) values obtained in neat ILs and those entrapped in BHDC RMs

System	k_2 (M⁻¹ s⁻¹)
Neat solvent	
EAN	N.D.
bmimBF₄	2.6 ± 0.1 × 10⁻³ [a]
RMs	
Toluene/BHDC/EAN	4.6 ± 0.2 × 10⁻⁴
Toluene/BHDC/bmimBF₄	2.3 ± 0.1 × 10⁻³ [a]

N.D.: no reaction detected. [a] Data from ref. 23.

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Cl^- to react because EAN is entrapped in the organized media. This fact suggests that the amount of ethylammonium associated with the Cl^- ions (ethyl–$NH_3^+ \cdots Cl^-$) is smaller than ethyl–$NH_3^+ \cdots NO_3^-$ (eqn (6)). We believe that this phenomenon is enhanced as a consequence of the IL–interface interactions present in the BHDC RMs. In this context, the interactions between the cationic surfactant and the ions present in the interfacial zone also have to be considered. It seems that the cationic surfactant moiety (BHD^+) cannot be solvated by NO_3^-; thus, at the interface the interaction between $BHD^+ \cdots Cl^-$ is stronger than $BHD^+ \cdots NO_3^-$, and ethylammonium only interacts with NO_3^-. This behavior has been observed before in BHDC RMs containing other ILs such as 1-butyl-3-methyl-imidazolium trifluoroacetate (bmimTfA).[21] In that work, the results suggested that even though the IL–surfactant interaction was weak (as in the present case), the ion pairing effect between $bmim^+$–TfA^- was substantially enhanced upon confinement, altering the structure and properties of the entrapped bmimTfA. Thus, the consequence of the confinement in BHDC RMs is that EAN is more auto-associated (stronger hydrogen bond interaction between ethyl–NH_3^+ and NO_3^-) than in bulk solution. These strongly associated EAN molecules interact weakly with the BHDC interface, generating only small changes in the droplet sizes of the RMs, as DLS show (Fig. 1).

Conclusions

In the present contribution we have shown how, upon confinement, EAN can be used as a suitable solvent for a S_N2 reaction, a situation quite different from the one observed in homogeneous media where EAN acts as any protic solvent complexing the nucleophile. Additionally, to the best of our knowledge this is the first report where toluene/BHDC RMs use EAN as a polar component and are used as nanoreactors for carrying out kinetic experiments. Thus, EAN entrapped in BHDC RMs strongly auto-associates, rendering an aprotic-like IL which is not able to deactivate the nucleophilic power of Cl^-. Finally, our results highlight the importance of RMs as nanoreactor media for classical reactions, where the reactants not only improve their solubilities but increase their reactivities in comparison with homogeneous media. These facts show how everything that happens in a homogeneous solution has to be reconsidered because of the fascinating effect of the confinement. We hope to stimulate the scientific community to use these attractive and unique nanoreactors to perform different kinds of chemical reactions and nanoparticle syntheses.

Experimental section

Benzyl-n-hexadecyldimethylammonium chloride (BHDC) from Sigma (>99% purity) was dried at reduced pressure prior to use. Toluene from Sigma (HPLC quality) was used without prior purification. The IL ethylammonium nitrate (EAN) was synthesized under anaerobic conditions following standard

procedures according to ref. 29 and 52. Thus, equimolar concentrations of nitric acid (from Sigma, 70% in water) and ethylamine (from Sigma, 70% in water) were used. Nitric acid was added slowly to ethylamine contained in a round-bottom flask over ice under stirring conditions. Excess water was removed by drying under vacuum. Prior to use EAN was discolored with activated charcoal and dried at reduced pressure at 60 °C for 4 hours.

The substrate dimethyl-4-nitrophenylsulfonium (S^+) trifluoromethanesulfonate was synthesized following the literature procedure.[40]

Preparation of BHDC RM 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, defined as W_s = [EAN]/[BHDC]. The incorporation of EAN into each micellar solution was performed using calibrated microsyringes. The resulting solutions were clear with a single phase and were used in the kinetic experiments. The W_s was varied between 0 and 0.3 for toluene/BHDC/EAN RMs. 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, EAN is not soluble in toluene and neither in toluene/BHDC solutions at surfactant concentrations lower than the critical micelle concentration (around 0.01 M).[50]

Kinetic procedure

Nucleophilic substitution reactions were followed by monitoring the UV-Vis absorbance of the demethylated sulfide product (Scheme 2) using a HP 8452A spectrophotometer with a thermostated cell holder. In all experiments the wavelength used for kinetic studies was 340 nm. All the experiments were carried out under pseudo first order conditions where the sulfonium salt concentration ([S^+] = 5 × 10^{-5} M) was always smaller than the [Cl^-]. All experiments were carried out at 30.0 ± 0.1 °C. Kinetics were studied by 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 observed rate constants, k_{obs}.[23,40,41] The pooled standard deviation of the kinetic data, using different prepared samples, was less than 5%. Because of solubility problems in the different media used in this study, we were forced to utilize the anion trifluoromethanesulfonate as the counterion of the cationic sulfonium. No rate differences were found previously between studies involving the different sulfonium salts in molecular solvents and ILs,[40,41] which is consistent with the view that the cationic center itself acts as the electrophilic site for the reaction.

Kinetic procedure in neat EAN

Stock solutions of NH_4Cl, as a source of Cl^-, dissolved in neat EAN were prepared by mass and volumetric dilution. Aliquots of these stock solutions containing Cl^- were added to a 1.0 cm path length UV/Vis quartz cuvette under anaerobic conditions, after which pure EAN was added to a total volume of 2 ml.

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After thermostating for 15 min, the reaction was initiated by injection of a stock solution containing the sulfonium electrophile dissolved in EAN. Spectra were recorded at regular time intervals using a spectrophotometer with a thermostated sample holder.

Kinetic procedure in BHDC RMs

When the reaction was investigated in toluene/BHDC/EAN RMs, the $[Cl^-]$ was modified varying only the [BHDC] ([BHDC] > cmc) at W_s = constant. Thus, an appropriate amount of toluene/BHDC/EAN stock solution to obtain the desired final $[Cl^-]$ in the micellar system was transferred to a 1.0 cm path length UV/Vis quartz cuvette to obtain a final volume of 2 ml. After thermostating for 15 min, the reaction was initiated by injection of a stock solution containing the sulfonium electrophile dissolved in toluene ($[S^+]$ = 5 × 10^{-3} M). Spectra were recorded at regular time intervals using a spectrophotometer with a thermostated sample holder.

DLS experiments

The apparent diameters of toluene/BHDC/EAN RMs were determined by dynamic light scattering (DLS, Malvern 4700 with a goniometer) with an argon-ion laser operating at 488 nm. The cleanliness of the cuvettes used for measurements was of crucial importance for obtaining reliable and reproducible data.[53] Cuvettes were washed with ethanol and then with doubly distilled water and dried with acetone. Prior to use, the samples were filtered three times using an Acrodisc with a 0.2 μm PTFE membrane (Sigma) to avoid dust or particles present in the original solution. Before introducing each sample to the cuvette, it was rinsed with pure toluene twice and then with the 0.2 M surfactant stock solution, and finally with the sample to be analyzed. Prior to making measurements on a given day, the background signals from air and toluene were collected to confirm the cleanliness of the cuvettes. Prior to data acquisition, samples were equilibrated in the DLS instrument for 10 min at 30 °C. To obtain valid results from DLS measurements, knowledge of the system's refractive index and viscosity, in addition to well-defined conditions, is required. Since we worked with dilute solutions, the refractive indices and viscosities for the RM solutions were assumed to be the same as for neat toluene.[54,55] Multiple samples of each size were prepared, and thirty independent size measurements were made for each individual sample at the scattering angle of 90°. The instrument was calibrated before and during the course of the experiments using several different size standards. Thus, we are confident that the magnitudes obtained by DLS measurements can be taken as statistically meaningful for all the systems investigated. The algorithm used was CONTIN, and the DLS experiments showed that the polydispersity of the toluene/BHDC/EAN RM size is less than 5%.

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References

1 N. M. Correa, J. J. Silber, R. E. Riter and N. E. Levinger, *Chem. Rev.*, 2012, **112**, 4569–4602.

2 T. K. De and A. Maitra, *Adv. Colloid Interface Sci.*, 1995, **59**, 95–193.

3 S. P. Moulik and B. K. Paul, *Adv. Colloid Interface Sci.*, 1998, **78**, 99–195.

4 J. Eastoe, S. Gold, S. Rogers, P. Wyatt, D. C. Steytler, A. Gurgel, R. K. Heenan, X. Fan, E. J. Beckman and R. M. Enick, *Angew. Chem., Int. Ed.*, 2006, **45**, 3675–3677.

5 M. Andujar-Matalobos, L. Garcia-Rio, S. Lopez-Garcia and P. Rodriguez-Dafonte, *J. Colloid Interface Sci.*, 2011, **363**, 261–267.

6 L. García-Río and J. R. Leis, *Chem. Commun.*, 2000, 455–456.

7 T. Rispens and J. B. F. N. Engberts, *J. Org. Chem.*, 2002, **67**, 7369–7377.

8 R. McNeil and J. K. Thomas, *J. Colloid Interface Sci.*, 1981, **83**, 57–65.

9 R. D. Falcone, J. J. Silber and N. M. Correa, *Phys. Chem. Chem. Phys.*, 2009, **11**, 11096–11100.

10 S. Abel, F. Sterpone, S. Bandyopadhyay and M. Marchi, *J. Phys. Chem. B*, 2004, **108**, 19458–19466.

11 M. R. Harpham, B. M. Ladanyi and N. E. Levinger, *J. Phys. Chem. B*, 2005, **109**, 16891–16900.

12 D. Cringus, J. Lindner, M. T. W. Milder, M. S. Pshenichnikov, P. Vohringer and D. A. Wiersma, *Chem. Phys. Lett.*, 2005, **408**, 162–168.

13 A. M. Dokter, S. Woutersen and H. J. Bakker, *Proc. Nat. Acad. Sci. U. S. A.*, 2006, **103**, 15355–15358.

14 M. Kondo, I. A. Heisler and S. R. Meech, *Faraday Discuss.*, 2010, **145**, 185–203.

15 M. S. Baptista and C. D. Tran, *J. Phys. Chem. B*, 1997, **101**, 4209–4217.

16 D. Grand, *J. Phys. Chem. B*, 1998, **102**, 4322–4326.

17 F. M. Agazzi, R. D. Falcone, J. J. Silber and N. M. Correa, *J. Phys. Chem. B*, 2011, **115**, 12076–12084.

18 R. D. Falcone, N. M. Correa and J. J. Silber, *Langmuir*, 2009, **25**, 10426–10429.

19 R. D. Falcone, B. Baruah, E. Gaidamauskas, C. D. Rithner, N. M. Correa, J. J. Silber, D. C. Crans and N. E. Levinger, *Chem. – Eur. J.*, 2011, **17**, 6837–6846.

20 D. D. Ferreyra, N. M. Correa, J. J. Silber and R. D. Falcone, *Phys. Chem. Chem. Phys.*, 2012, **14**, 3460–3470.

21 D. Blach, J. J. Silber, N. M. Correa and R. D. Falcone, *Phys. Chem. Chem. Phys.*, 2013, **15**, 16746–16757.

22 R. Pramanik, C. Ghatak, V. G. Rao, S. Sarkar and N. Sarkar, *J. Phys. Chem. B*, 2011, **115**, 5971–5979.

23 D. Blach, M. Pessêgo, J. J. Silber, N. M. Correa, L. García-Río and R. D. Falcone, *Langmuir*, 2014, **30**, 12130–12137.

24 J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508–3576.

25 T. Welton and P. Wasserscheid, *Ionic Liquids in Synthesis*, VCH-Wiley, Weinheim, 2002.

26 T. Welton, *Coord. Chem. Rev.*, 2004, **248**, 2459–2477.

27 C. A. Angell, N. Byrne and J. P. Belieres, *Acc. Chem. Res.*, 2007, **40**, 1228–1236.

28 (*a*) J. Pernak, I. Goc and I. Mirska, *Green Chem.*, 2004, **66**, 323–329; (*b*) R. V. Hangarge, D. V. Jarikote and M. S. Shingare, *Green Chem.*, 2002, **4**, 266–268; (*c*) K. K. Laali and V. J. Gettwert, *J. Org. Chem.*, 2001, **66**, 35–40; (*d*) Y. Hu, J. Chen, Z. Le and Q. G. Zheng, *Synth. Commun.*, 2005, **35**, 739–744; (*e*) C. F. Poole, *J. Chromatogr. A*, 2004, **1037**, 49–82; (*f*) A. B. H. Md. Susan, A. Noda, S. Mitushima and M. Watanabe, *Chem. Commun.*, 2003, 938–939; (*g*) J. C. Galvez-Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapotke, K. Lohnwitz, P. Mayer, H. Noth, K. Polborn, C. J. Rohbonger, M. Suter and J. J. Weigand, *Inorg. Chem.*, 2005, **44**, 4237–4253; (*h*) M. U. Araos and G. G. Warr, *J. Phys. Chem. B*, 2005, **109**, 14275–14277; (*i*) R. Atkin and G. G. Warr, *J. Am. Chem. Soc.*, 2005, **127**, 11940–11941; (*j*) T. Jiang, H. X. Gao, B. X. Han, G. Y. Zhao, Y. H. Chang, W. Z. Wu, L. Gao and G. Y. Yang, *Tetrahedron Lett.*, 2004, **45**, 2699–2701; (*k*) M. Picquet, I. Tkatchenko, I. Tommasi, P. Wasserscheid and J. Zimmermann, *Adv. Synth. Catal.*, 2003, **345**, 959–962.

29 S. Ghosh, *J. Colloid Interface Sci.*, 2011, **360**, 672–680.

30 (*a*) D. F. Evans, S. H. Chen, G. W. Schriver and E. M. Arnett, *J. Am. Chem. Soc.*, 1981, **103**, 481–482; (*b*) R. Hayes, S. Imberti, G. G. Warr and R. Atkin, *Angew. Chem., Int. Ed.*, 2013, **52**, 4623–4627; (*c*) T. L. Greaves and C. J. Drummond, *Chem. Soc. Rev.*, 2008, **37**, 1709–1726.

31 T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2015, **115**, 11379–11448.

32 R. Atkin and G. G. Warr, *J. Phys. Chem. B*, 2007, **111**, 9309–9316.

33 J. C. Thater, V. Gerard and C. Stubenrauch, *Langmuir*, 2014, **30**, 8283–8289.

34 S. Ghosh, *J. Colloid Interface Sci.*, 2011, **360**, 672–680.

35 O. Zech, S. Thomaier, P. Bauduin, T. Ruck, D. Touraud and W. Kunz, *J. Phys. Chem. B*, 2009, **113**, 465–473.

36 O. Zech, S. Thomaier, A. Kolodziejski, D. Touraud, I. Grillo and W. Kunz, *J. Colloid Interface Sci.*, 2010, **347**, 227–232.

37 O. Zech, P. Bauduin, P. Palatzky, D. Touraud and W. Kunz, *Energy Environ. Sci.*, 2010, **3**, 846–851.

38 H. Niedermeyer, J. P. Hallett, I. J. Villar-Garcia, P. A. Hunt and T. Welton, *Chem. Soc. Rev.*, 2012, **41**, 7780–7802.

39 C. Chiappe, D. Pieraccini and P. Saullo, *J. Org. Chem.*, 2003, **68**, 6710–6715.

40 G. Ranieri, J. P. Hallett and T. Welton, *Ind. Eng. Chem. Res.*, 2008, **47**, 638–644.

41 J. P. Hallett, C. L. Liotta, G. Ranieri and T. Welton, *J. Org. Chem.*, 2009, **74**, 1864–1868.

42 A. M. Durantini, R. D. Falcone, J. J. Silber and N. M. Correa, *J. Phys. Chem. B*, 2013, **117**, 3818–3828.

43 R. D. Falcone, N. M. Correa, N. E. Levinger and J. J. Silber, Ionic liquids in soft confinement. Effect of the different reverse micelles interfaces on the entrapped ionic liquid structure, in *Ionic Liquid-Based Surfactant Science: Formulation, Characterization, and Applications*, ed. B. K. Paul and S. P. Moulik, 2015, ISBN-10: 1118834194, ISBN-13: 9781118834190.

44 F. M. Agazzi, N. M. Correa and J. Rodriguez, *Langmuir*, 2014, **30**, 9643–9653.

45 J. A. Gutierrez, M. A. Luna, N. M. Correa, J. J. Silber and R. D. Falcone, *New J. Chem.*, 2015, **39**, 8887–8895.

46 J. S. Florez, N. M. Correa, J. J. Silber, L. Sereno and P. G. Molina, *Soft Matter*, 2015, **11**, 2952–2962.

47 J. A. Gutierrez, R. D. Falcone, M. A. Lopez-Quintela, D. Buceta, J. J. Silber and N. M. Correa, *Eur. J. Inorg. Chem.*, 2014, **2014**, 2095–2102.

48 A. Salabat, J. Eastoe, K. J. Mutch and R. F. Tabor, *J. Colloid Interface Sci.*, 2008, **318**, 244–251.

49 C. Dai, S. Wang, M. Du, Y. Liu, D. Peng, Z. Yan and M. Zhao, *Colloid Polym. Sci.*, 2015, **293**, 1475–1481.

50 A. Jada, J. Lang and R. Zana, *J. Phys. Chem.*, 1990, **94**, 381–387.

51 C. A. Bunton, F. Nome, F. H. Quina and L. S. Romsted, *Acc. Chem. Res.*, 1991, **24**, 357–364.

52 T. L. Greaves, A. Weerawardena, C. Fong, I. Krodkiewska and C. J. Drummond, *J. Phys. Chem. B*, 2006, **110**, 22479–22487.

53 M. A. Sedgwick, A. M. Trujillo, N. Hendricks, N. E. Levinger and D. C. Crans, *Langmuir*, 2011, **27**, 948–954.

54 J. P. Blitz, J. L. Fulton and R. D. Smith, *J. Phys. Chem.*, 1988, **92**, 2707–2710.

55 H. Bohidar and M. Behboudina, *Colloids Surf., A*, 2001, **178**, 313–323.

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