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PAPER

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†

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The behavior of the ionic liquid (IL) 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]) entrapped in two reverse micelles (RMs) formed in an aromatic solvent as dispersant pseudophase: [bmim][Tf₂N]/benzyl-*n*-hexadecyldimethylammonium chloride (BHDC)/chlorobenzene and [bmim][Tf₂N]/sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT)/chlorobenzene, was investigated using dynamic light scattering (DLS), FT-IR and ¹H NMR spectroscopies. DLS results reveal the formation of RMs containing [bmim][Tf₂N] as a polar component since the droplet size values increase as the W_s ($W_s = \frac{[\text{bmim}][\text{Tf}_2\text{N}]}{[\text{surfactant}]}$) increases. Furthermore, it shows that the RMs consist of discrete spherical and non-interacting droplets of [bmim][Tf₂N] stabilized by the surfactants. Important differences in the structure of [bmim][Tf₂N] entrapped inside BHDC RMs, in comparison with the neat IL, are observed from the FT-IR and ¹H NMR measurements. The electrostatic interactions between anions and cations from [bmim][Tf₂N] and BHDC determine the solvent structure encapsulated inside the nano-droplets. It seems that the IL structure is disrupted due to the electrostatic interaction between the [Tf₂N][−] and the cationic BHDC polar head (BHD⁺) giving a high ion pair degree between BHD⁺ and [Tf₂N][−] at a low IL content. On the other hand, for the AOT RMs there is no evidence of strong IL–surfactant interaction. The electrostatic interaction between the SO₃[−] group and the Na⁺ counterion in AOT seems to be stronger than the possible [bmim]⁺–SO₃[−] interaction at the interface. Thus, the structure of [bmim][Tf₂N] encapsulated is not particularly disrupted by the anionic surfactant at all W_s studied, in contrast to the BHDC RM results. Nevertheless, there is evidence of confinement in the AOT RMs because the [bmim]⁺–[Tf₂N][−] interaction is stronger than in bulk solution. Thus, the IL is more associated upon confinement. Our results reveal that the [bmim][Tf₂N] structure can be modified in a different manner inside RMs by varying the kind of surfactant used to create the RMs and the IL content (W_s). These facts can be very important if these media are used as nanoreactors because unique microenvironments can be easily created by simply changing the RM components and W_s .

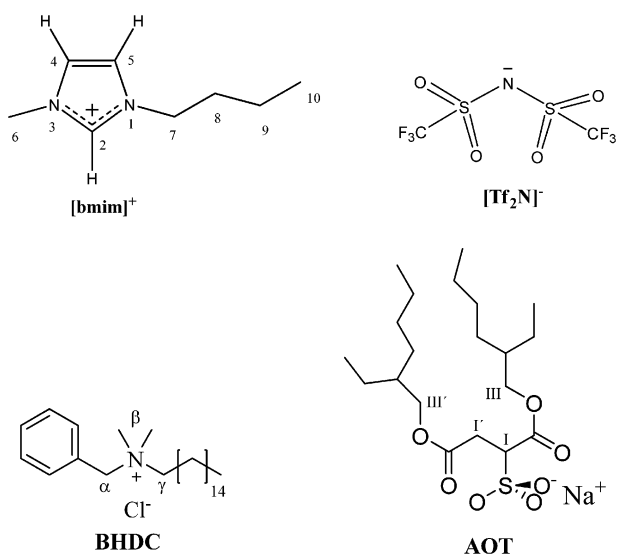
Introduction

Reversed micelles (RMs) are spatially ordered macromolecular assembly of surfactants formed in a non-polar solvent, in which the polar head groups of the surfactants point inward and the hydrocarbon chains point toward the non-polar medium.^{1–3} RMs have been an interesting subject for the past

decades due to their broad applications in chemical reactions, separation science, material science, and in the pharmaceutical industry, among others.⁴ These nanoscale aggregates are suitable media for processes that involve hydrophobic and hydrophilic reactants in a variety of chemical and biological reactions.^{1,2} Moreover, the macroscopic homogeneity and transparency of these systems permit the use of continuous spectrometric techniques.² There are a wide range of surfactants that form RMs, including anionic, cationic and nonionic molecules.^{1–32} Probably, the anionic surfactant most frequently used to create RMs is sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT, Scheme 1).^{6–8,11,12,28,30,32} Water,^{6,28,30} or other polar solvents^{8,12,31} added to the AOT systems are entrapped in the polar core, forming a polar pool surrounded by a layer of surfactant molecules dispersed in the non-polar pseudophase.

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† Electronic supplementary information (ESI) available: Fig. S1: FT-IR spectra of [bmim][Tf₂N] inside AOT/chlorobenzene RMs at different W_s values, in the region of 760–740 cm^{−1}; and Fig. S2: FT-IR spectra of [bmim][Tf₂N] inside AOT/chlorobenzene RMs at different W_s values in the region of 3100–3200 cm^{−1}. See DOI: 10.1039/c2cp23481e



Scheme 1 Molecular structure of [bmim]⁺, [Tf₂N]⁻, AOT and BHDC. Specific protons observed in NMR spectra are identified.

The cationic surfactant, benzyl-*n*-hexadecyldimethylammonium chloride (BHDC, Scheme 1), also forms RMs in aromatic solvents without addition of a cosurfactant.^{7,10,28,30,32}

It is well known that the physicochemical properties of the polar solvent entrapped inside RMs change dramatically from the bulk solvents as a result of specific interactions and confined geometries.^{2,6-8,11,12,22,28,31,32} Moreover, it has been demonstrated that the effect of the kind of surfactant used to create RMs is crucial for the understanding of the polar solvent structure. For example, previous studies performed in our group have shown very peculiar and interesting water properties inside RMs that exist only due to the confinement effect and the interaction with the surfactant at the interface. Thus, the water properties are different for water molecules sequestered inside anionic and cationic RM systems. The water molecules entrapped inside the AOT/benzene RMs show their electron donor ability enhanced in comparison with bulk water. On the other hand, the water molecules entrapped inside the BHDC/benzene RMs appear to be non-electron donating because of their interaction with the cationic surfactant polar head group.^{28,30,32}

Ionic Liquids (ILs) have received significant attention as powerful alternatives to conventional molecular organic solvents.³³⁻³⁵ 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.³⁶ Most of the ILs used are based on *N,N'*-dialkylimidazolium cations, especially 1-butyl-3-methylimidazolium ([bmim]⁺ in Scheme 1) and different anions such as tetrafluoroborate ([BF₄]⁻), hexafluorophosphate ([PF₆]⁻) and bis(trifluoromethylsulfonyl)imide ([Tf₂N]⁻ in Scheme 1).

One of the newest RM systems created utilize different ILs as a polar component (IL RMs).³⁷⁻⁴⁹ The most used IL in this kind of system is [bmim][BF₄],^{37,40a,b,d,e,41c,46b,47,49} however, few reports about the encapsulation of [bmim][PF₆]^{44c} or [bmim][Tf₂N]³⁷ in RMs are found in the literature. These IL RMs have gained attention because of their potential applications

owing to the unique features of both ILs and RMs. The ILs offer a wide choice of structures varying the cation and anion combination, including chiral structures. The RMs provide hydrophobic or hydrophilic nano-domains, thereby expanding the potential uses of ILs in chemical reactions and allowing the use of smaller quantity of IL compared to that required for bulk-phase IL reactions.³⁶ The most common surfactant used to create IL RMs is the nonionic Triton X-100 (TX-100).^{37,38a-c,42,44,47} The results obtained by different authors suggest that when ILs are entrapped in TX-100 RMs, the ILs do not interact strongly with the nonionic surfactant at the RMs interface and, in consequence their structure and properties remain quite similar in comparison with the behavior of neat ILs. On the other hand, studies about ILs entrapped in RMs formed by ionic surfactants such as the cationic BHDC^{37,46,49} are very scarce. In this sense, recently³⁷ the microenvironment of the polar core generated in [bmim][BF₄]/BHDC/benzene and [bmim][Tf₂N]/BHDC/benzene systems was investigated and compared with [bmim][BF₄]/TX-100/benzene and [bmim][Tf₂N]/TX-100/benzene, using absorption spectroscopy and dynamic light scattering (DLS). In that work we demonstrated the existence of true ILs/surfactant/benzene RMs and that the structure of the ILs entrapped depends strongly on the surfactant used. Additionally, this work was the first investigation about the use of the BHDC surfactant to encapsulate two different ILs.³⁷ Taking into account these results, very recently⁴⁹ we characterized by ¹H, ¹¹B, and ¹⁹F NMR spectroscopy the differences between the RMs formed by BHDC and TX-100 as surfactants, using [bmim][BF₄] as the polar phase and benzene-*d*₆ as non-polar media. NMR data showed distinct differences in the behavior of [bmim][BF₄] depending on the surfactant head group used. Minor changes in the chemical shifts were observed for [bmim]⁺ and [BF₄]⁻ in the presence of TX-100 suggesting that the surfactant and the IL do not interact strongly at the RM interface. On the other hand, the large changes observed in the spectroscopic parameters for the BHDC RMs are consistent with the formation of the layer of [bmim]⁺ and [BF₄]⁻ and migration of the counterion Cl⁻ within the BHDC RMs.

On the other hand, only two investigations using the AOT surfactant and ILs are found in the literature.^{48,50} The first study, performed by Cheng *et al.*,⁴⁸ showed the formation of direct micelles using AOT as surfactant and two different ILs: [bmim][PF₆] and propylammonium formate (PAF) as internal and external pseudophase, respectively. In this case, [bmim][PF₆] is dispersed in the non-polar cores of AOT micelles in the PAF-rich phase, but does not interact with the anionic surfactant polar head group. Consequently, its bulk structure is not modified. In the second study, Moniruzzaman *et al.*⁵⁰ reported the formation of AOT RMs using 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([omim][Tf₂N]) as external continuous phase, 1-hexanol as a cosurfactant and water as a polar solvent entrapped in the polar core. In this system, [omim][Tf₂N] does not interact with the anionic surfactant because it is the external phase and surfactant head groups are located toward the interior of the RMs, in consequence the IL properties remain unaltered. Thus, in contrast to the few reports about IL entrapped in BHDC RMs, there is no information about the use of AOT to prepare RMs using ILs as a polar component. According to that and considering the

dramatic changes observed in the structure of polar solvents entrapped in RMs,^{11,12,28,30,32} an interesting topic to study is to know how the structure of the ILs is modified inside different ionic RMs and how these properties can be modified to improve their potential application, for example, in the field of nanomaterials or enzymatic reactions. Consequently, the aim of this work is to prepare RMs with [bmim][Tf₂N] as polar solvent and to study simultaneously the effect that different interfaces (using AOT and BHDC as surfactants) and the variation of the [bmim][Tf₂N] content W_s ($W_s = \frac{[\text{bmim}][\text{Tf}_2\text{N}]}{[\text{surfactant}]}$) has on the structure of the IL entrapped by the different RMs. To the best of our knowledge there is no information about the encapsulation of [bmim][Tf₂N] inside AOT RMs, using an aromatic solvent as dispersant pseudophase. To test the formation of [bmim][Tf₂N] RMs and to get more information about the molecular interactions present in these systems, we have chosen DLS, FT-IR and ¹H NMR spectroscopies. In this sense, the DLS technique is commonly used to reveal the formation of novel reversed micellar systems^{12,37,42,51} and, FT-IR and ¹H NMR are techniques that provide useful information about the molecular interactions which is used to obtain knowledge about the microstructure of RMs.^{11,49,52–57}

Results

The results obtained in this work are presented in two sections. In the first part, we show the data using the DLS technique and, in the second part we report the results obtained using ¹H NMR and FT-IR spectroscopies.

DLS experiments

The systems conformed by [bmim][Tf₂N]/AOT/chlorobenzene and [bmim][Tf₂N]/BHDC/chlorobenzene were studied through the DLS technique, to evaluate the formation of the reversed micellar media. Chlorobenzene was chosen as a non-polar solvent because it is capable of forming clear and stable ternary mixtures with [bmim][Tf₂N] and AOT or BHDC surfactants.

In these new reversed micellar systems, the first question to answer is if the IL is effectively entrapped by the surfactant creating true RMs in chlorobenzene. Thus, DLS is used to assess this matter because if [bmim][Tf₂N] is really encapsulated to form RMs, the droplets size must increase as the W_s value increases with a linear tendency (swelling law of RMs) as it is well established for water and other polar solvents/surfactant RMs.^{2,12,37} This feature can also demonstrate that [bmim][Tf₂N]/surfactant/chlorobenzene consists of discrete spherical and non-interacting droplets of [bmim][Tf₂N] stabilized by the surfactant layer. On the other hand, if [bmim][Tf₂N] is not entrapped by the surfactant, the droplet sizes should be insensitive or decrease with the polar solvent addition.⁵¹

Since in this work, all the DLS experiments were carried out at fixed surfactant concentration (0.1 M), we consider appropriate to introduce the apparent diameter (d_{app}) values in order to make interpretations of our data using a similar approach performed by other authors.⁵⁴ In Fig. 1, we report the d_{app} values obtained for the reversed micellar systems studied at different W_s values. As it can be seen in Fig. 1 there is an increase in the droplets size when the [bmim][Tf₂N] content increases in both systems, showing that the IL is entrapped by

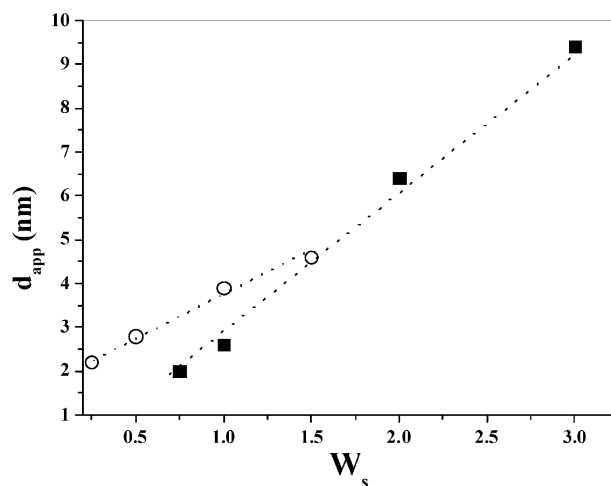


Fig. 1 Apparent diameter (d_{app}) values of the [bmim][Tf₂N] RMs obtained at 25 °C varying W_s . (■) BHDC/chlorobenzene and (○) AOT/chlorobenzene RMs. [Surfactant] = 0.1 M. The straight lines were plotted to guide the eye.

the surfactants layer yielding RMs. Also, the linear tendency on the droplets size values is observed in the whole W_s range for the AOT and BHDC RMs. Interestingly, the largest changes varying the W_s are observed for the BHDC RM droplets in comparison with the AOT RM droplets; however, the anionic droplets size values are larger than the cationic ones at the same W_s . Unfortunately, it is not possible to obtain higher W_s values than 1.5 for AOT RMs because phase separation occurs above this threshold.

¹H NMR experiments

In order to explore all the RMs studied, different protons were investigated. First, we present the results obtained by sensing the aromatic H in position 2 of the imidazolium cation (Scheme 1) defined as H2 [bmim]⁺ and, next the protons nearest to the polar head groups in BHDC and AOT surfactants (Scheme 1).

H2 [bmim]⁺. Fig. 2 displays the ¹H NMR spectra for [bmim][Tf₂N] in BHDC RMs at different [bmim][Tf₂N] contents in the region of H2 [bmim]⁺. We focus on the peak associated with this proton because this peak is particularly sensitive to its environment.⁵⁸ In Fig. 3 are shown the data corresponding to the H2 [bmim]⁺ chemical shift in all the RMs prepared. As it can be seen, the H2 [bmim]⁺ signal shifts upfield when W_s is increased in both RMs, however, the magnitude of the shift is different for BHDC than AOT systems. In BHDC RMs (Fig. 3), the signal appears substantially further downfield compared to the value observed for AOT RMs (Fig. 3). For example, at $W_s = 0.25$, the H2 [bmim]⁺ signal appears almost 2 ppm downfield in BHDC RMs compared to AOT RMs. Furthermore, even in the largest BHDC RMs measured, the H2 [bmim]⁺ signal peaks more than 0.7 ppm downfield from the value in neat [bmim][Tf₂N] (8.5 ppm). In the AOT RMs, although the signal shifts upfield when [bmim][Tf₂N] is added (Fig. 3), the changes are smaller in comparison with the corresponding changes for BHDC RMs. Nevertheless, at low W_s the H2 [bmim]⁺ clearly experiences a microenvironment

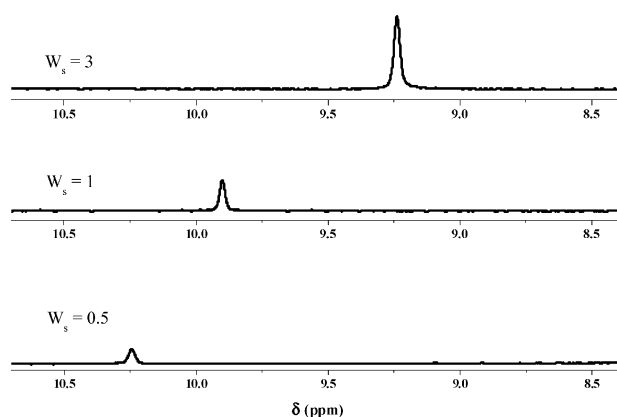


Fig. 2 ^1H NMR spectra collected in [bmim][Tf₂N]/BHDC/chlorobenzene RMs at different [bmim][Tf₂N] contents (W_s), in the region of H2 [bmim]⁺. [BHDC] = 0.1 M.

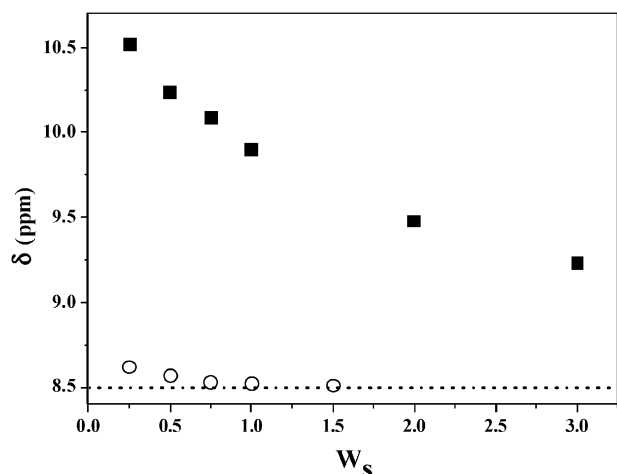


Fig. 3 ^1H NMR chemical shifts of H2 [bmim]⁺ in: (■) [bmim][Tf₂N]/BHDC/chlorobenzene and (○) [bmim][Tf₂N]/AOT/chlorobenzene RMs at different W_s . [Surfactant] = 0.1 M. The corresponding value for neat [bmim][Tf₂N] (···) is included for comparison.

relatively different than the one at a higher [bmim][Tf₂N] content. Moreover, even at the maximum W_s reached in the AOT RMs, the δ value for H2 [bmim]⁺ is not equal to the value found for the neat [bmim][Tf₂N] (see the straight line in Fig. 3).

All these evidence suggest an environment quite different for [bmim]⁺ in BHDC *versus* AOT RMs, at the same IL content.

Surfactant's protons. The surfactant's protons also can be used as a probe to study the microenvironment created in these RMs. For example, in Fig. 4 are displayed the ^1H NMR spectra collected for [bmim][Tf₂N] in BHDC RMs at different IL content, in the region of BHDC benzyl methylene protons (Scheme 1). Fig. 5 and 6 show the ^1H NMR chemical shift of the protons nearest to the polar head groups for BHDC and AOT (see Scheme 1) RMs studied at different W_s . The peak positions of protons near to the quaternary N in the BHDC surfactant (Fig. 5) such as benzyl methylene (α), N-methyl (β) and methylene protons (γ) were assigned as found in the literature.¹⁰ Similarly, the AOT proton signal values (Fig. 6)

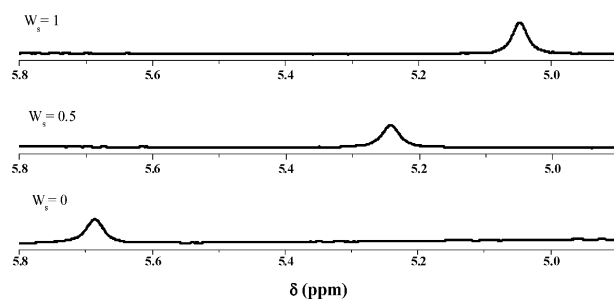


Fig. 4 ^1H NMR spectra collected in [bmim][Tf₂N]/BHDC/chlorobenzene RMs at different IL contents in the region of BHDC α protons. [BHDC] = 0.1 M.

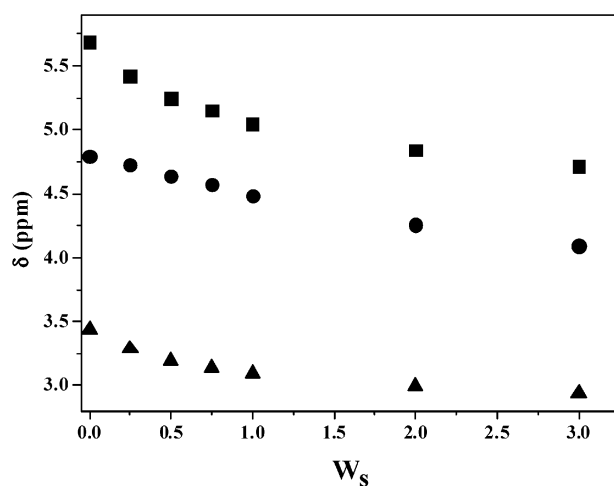


Fig. 5 ^1H NMR signals of BHDC surfactant protons in [bmim][Tf₂N]/BHDC/chlorobenzene at different W_s . α : (■), β : (▲), γ : (●). Labels refer to Scheme 1. [BHDC] = 0.1 M.

in the head group region (H_I, H_{I'}, H_{III} and H_{III'} in Scheme 1) were consistent with the values found in the literature.^{55,56}

All the signals associated with BHDC protons display upfield shifts as W_s increases (Fig. 5). For example, the α protons shift from 5.68 ppm at $W_s = 0$ to 4.71 ppm at $W_s = 3$.

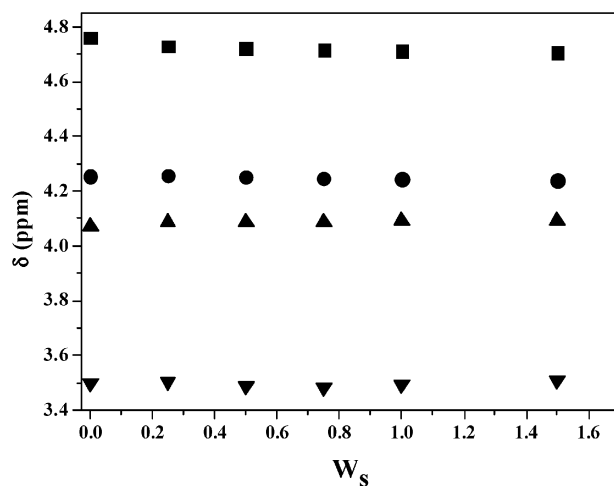


Fig. 6 ^1H NMR signals of AOT surfactant protons in [bmim][Tf₂N]/AOT/chlorobenzene at different W_s . I: (■), I': (▼), III: (●), III': (▲). Labels refer to Scheme 1. [AOT] = 0.1 M.

The β protons shift from 4.78 ppm in the absence of [bmim][Tf₂N] to 4.08 ppm at the maximum amount of bmimTf₂N entrapped and finally the γ protons shift from 3.43 ppm at $W_s = 0$ to 2.93 ppm at $W_s = 3$.

On the other hand, all proton signals associated with the AOT surfactant (Fig. 6) shift in less magnitude than those observed for the cationic one. For example, the H_I proton shifts from 4.75 ppm at $W_s = 0$ to 4.70 ppm at $W_s = 1.5$. The protons H_{III}, H_{III'} and H_V are practically constant at 4.25, 4.07 and 3.50 ppm, respectively, at all the W_s evaluated.

These results demonstrate that the IL affects more the protons of the BHDC surfactant than the AOT ones and suggest that the environment around the polar head group of the BHDC changes whereas AOT is less altered.

FT-IR experiments

To obtain more insight on the behavior of [bmim][Tf₂N] entrapped in the different RMs and the effect of the variation of W_s , we study different vibration modes of the [bmim][Tf₂N] entrapped by the surfactants. We choose to monitor the S–N–S stretching mode of the anion [Tf₂N][−] and the C–H stretching modes of the cation [bmim]⁺ and, the results were compared to the neat IL stretching vibration modes.

Symmetric S–N–S stretching band (ν_{S-N-S}^s). The vibrational spectra of different salts, including ILs, with the [Tf₂N][−] anion as a component are well-known and have been extensively investigated.^{59–68} This multiatomic anion has several infrared bands that can be analyzed,^{60,61} especially in the region 730–800 cm^{−1}, where three [Tf₂N][−] bands appear. One of these bands is assigned to a S–N–S symmetric stretching mode (ν_{S-N-S}^s)^{60,67} and is particularly sensitive to the ionic strength,^{62–64} even though [Tf₂N][−] has been considered as a non-coordinating anion.^{69,70} This band experiences a hypsochromic shift of about 5 cm^{−1} when the [Tf₂N][−] concentration increases, which is associated to ion pair formation.^{60,64,67} Similar effect is observed when the mentioned frequency values of [Tf₂N][−] and the neutral Tf₂N–H molecule are compared. In the latter case, it is observed that the S–N–S stretching mode value is shifted to higher frequencies due to the decrease of the negative charge density over the nitrogen atom of [Tf₂N][−].⁷¹

In Fig. 7 typical FT-IR spectra of [bmim][Tf₂N] inside BHDC/chlorobenzene RMs at different W_s values, in the region of 770–735 cm^{−1} corresponding to the ν_{S-N-S}^s of [Tf₂N][−], are reported. Spectra obtained for [bmim][Tf₂N]/AOT/chlorobenzene RMs are presented in Fig. S1 (ESI† section). Shifts of the ν_{S-N-S}^s values upon increase of W_s in the RMs studied are shown in Fig. 8. As it can be observed, all the S–N–S stretching frequency values for RMs are higher than those corresponding to neat [bmim][Tf₂N] (740 cm^{−1}). Additionally, Fig. 8 also shows that the ν_{S-N-S}^s values for [bmim][Tf₂N] in AOT RMs are practically constant, around 748 cm^{−1}, in the whole W_s range studied. However, for BHDC RMs although the spectroscopic changes are small, especially at low W_s values, differences are observed in comparison with the anionic RMs and the bulk value. For example at $W_s = 0.25$, the ν_{S-N-S}^s value is around 751 cm^{−1}, showing strengthening of the S–N bond in comparison to neat [bmim][Tf₂N].

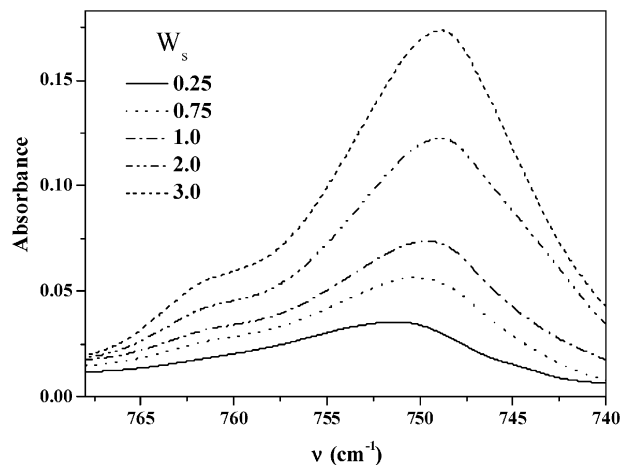


Fig. 7 FT-IR spectra of [bmim][Tf₂N] inside BHDC/chlorobenzene RMs at different W_s values, in the region of 770–740 cm^{−1} (ν_{S-N-S}^s). [BHDC] = 0.1 M. The chlorobenzene bands have been subtracted. IR path length cell = 0.015 mm.

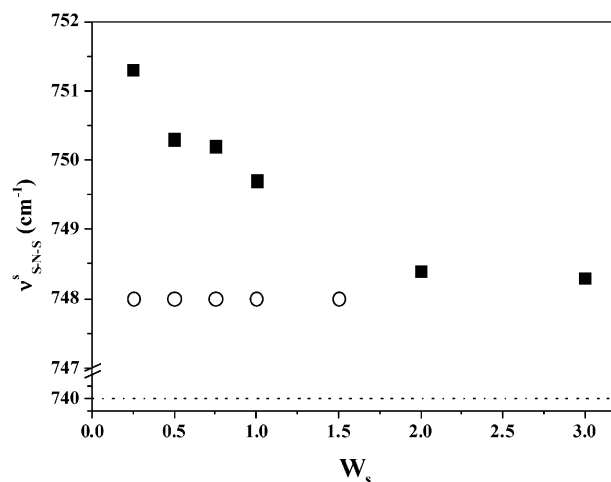


Fig. 8 Shift of the S–N–S symmetric stretching frequency (ν_{S-N-S}^s) upon increasing W_s in different [bmim][Tf₂N]/surfactant/chlorobenzene RMs: (■) BHDC and (○) AOT. [Surfactant] = 0.1 M. The corresponding value for neat [bmim][Tf₂N] (···) is included for comparison.

C–H stretching band (ν_{C-H}). For the ILs composed of 1-alkyl-3-methyl imidazolium, the infrared peaks found between 3100 and 3200 cm^{−1} are assigned to the aromatic C–H stretching modes of C(2)–H and C(4,5)–H on the imidazolium cation (Scheme 1).^{72,73} The band that peaks at lower frequency is assigned to the C(2)–H stretching modes, while the band at the higher frequencies is attributed to the C(4,5)–H stretching modes.⁷² The C(2)–H group has a larger positive charge density than the C(4,5)–H groups, which leads to smaller force constants and thus lower frequencies.⁷⁴ In neat [bmim][Tf₂N], the maxima for these stretching modes appear at 3121 and 3157 cm^{−1}, respectively.⁷² The meaning of the aromatic C–H vibration modes in neat ILs is quite confusing. These vibration modes have been particularly studied in the past and were assigned to the imidazolium C–H···anion H-bonding modes.^{75,76} Although the importance of the H-bond between the imidazolium C(2)–H and anions was stressed repeatedly,^{77–80} the role of the H-bond in the IL structure is not clear. Some authors claim that the role

played by H-bond interactions controls the structure and properties observed in pure ILs.^{70,79–81} For example, Golding *et al.*⁸¹ have shown a weak electrostatic interaction in the absence of the H in C(2) of the cation 1,2,3-trisubstituted imidazolium and the ion $[\text{Tf}_2\text{N}]^-$. According to that, Köddermann *et al.*⁷⁰ claim H-bond formation of 1-alkyl-3-methyl imidazolium and $[\text{Tf}_2\text{N}]^-$ from FT-IR results. However, other authors⁷² suggest that there is no need to invoke H-bond interaction between imidazolium and $[\text{Tf}_2\text{N}]^-$ to interpret the $\nu_{\text{C-H}}$ FT-IR spectra of $[\text{bmim}][\text{Tf}_2\text{N}]$. In this sense, we think that to clarify the idea is important to define criteria about which C–H···anion interaction can be considered as H-bond interaction.^{82–84} Thus, Wulf *et al.*⁸⁴ mention studies on imidazolium-based ILs with strong coordinating anions such as thiocyanate or dicyanamide, where H-bonding plays a crucial role in their interpretations. However, Lassègues *et al.*⁸² suggest that in the case of weakly coordinating anions such as $[\text{Tf}_2\text{N}]^-$, there are many studies leading to the opposite conclusion.^{80h,83} For example, Tsuzuki *et al.*^{80h} claim that the nature of the C(2)–H···anion interaction is completely different from that of a conventional H-bond and remains negligibly small compared to the electrostatic interactions. In this sense, in a previous work³⁷ using the molecular probe 1-methyl-8-oxyquinolinium betaine (QB) which is extremely sensitive to the H-bond donor capacity of the medium,^{6–8} we have not detected H-bond donor ability from the $[\text{bmim}]^+$ neither as neat $[\text{bmim}][\text{BF}_4]$ and $[\text{bmim}][\text{Tf}_2\text{N}]$ nor encapsulated in BHDC/benzene and TX-100/benzene RMs. Nevertheless, the situation seems to be still quite conflictive.

Fig. 9 shows the FT-IR spectra of $[\text{bmim}][\text{Tf}_2\text{N}]$ incorporated in BHDC/chlorobenzene RMs at different W_s values, in the region of 3200–3100 cm^{-1} . The spectra obtained for $[\text{bmim}][\text{Tf}_2\text{N}]/\text{AOT}/\text{chlorobenzene}$ RMs are collected in Fig. S2 (ESI† section). As it is observed from Fig. 9 and Fig. S2 (ESI†), both aromatic C–H stretching modes in the BHDC and AOT RMs can be studied. Shifts of the C(2)–H and C(4,5)–H stretching frequency upon increasing W_s in different RMs are plotted in Fig. 10A and B. The results show that both C–H stretching frequency values are shifted to low frequency

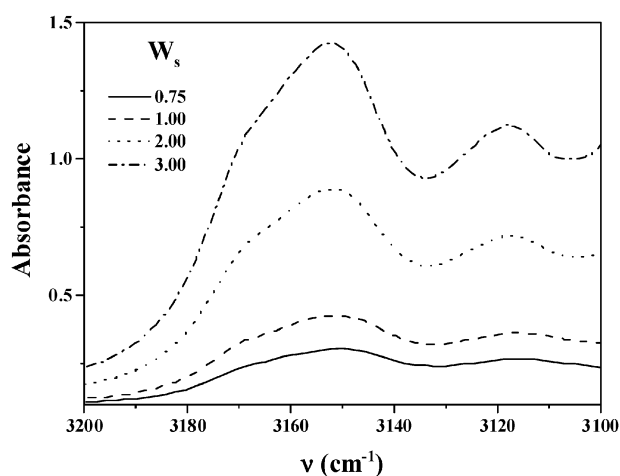


Fig. 9 FT-IR spectra of $[\text{bmim}][\text{Tf}_2\text{N}]$ inside BHDC/chlorobenzene RMs at different W_s values, in the region of 3100–3200 cm^{-1} . $[\text{BHDC}] = 0.1$ M. The chlorobenzene bands have been subtracted. IR path length cell = 0.5 mm.

in BHDC and AOT RMs in comparison with the corresponding values for neat $[\text{bmim}][\text{Tf}_2\text{N}]$. BHDC RM is the system that shows more important changes when $[\text{bmim}][\text{Tf}_2\text{N}]$ is incorporated to the RMs, especially at low W_s (Fig. 10A and B). For example, at $W_s = 0.25$ the $\nu_{\text{C(2)-H}}$ and $\nu_{\text{C(4,5)-H}}$ appear at 3112 cm^{-1} and 3147 cm^{-1} , respectively, while in neat $[\text{bmim}][\text{Tf}_2\text{N}]$ the values appear at 3121 and 3157 cm^{-1} . These spectral changes are observed until $W_s = 1$, after that the frequency values are practically constant. As it can be observed from this figure, both C–H vibration modes are affected when $[\text{bmim}][\text{Tf}_2\text{N}]$ is entrapped inside BHDC RMs. However, for AOT RMs the $\nu_{\text{C-H}}$ values for both vibration modes are practically constant (3117 and 3151 cm^{-1}) at all the W_s ranges studied.

Discussion

The data presented in this work have several important aspects to discuss. From the DLS data it is possible to conclude that $[\text{bmim}][\text{Tf}_2\text{N}]$ is encapsulated by the surfactants layer yielding true RMs since there is an increase in the droplet sizes as the $[\text{bmim}][\text{Tf}_2\text{N}]$ content increases, in all the systems studied.

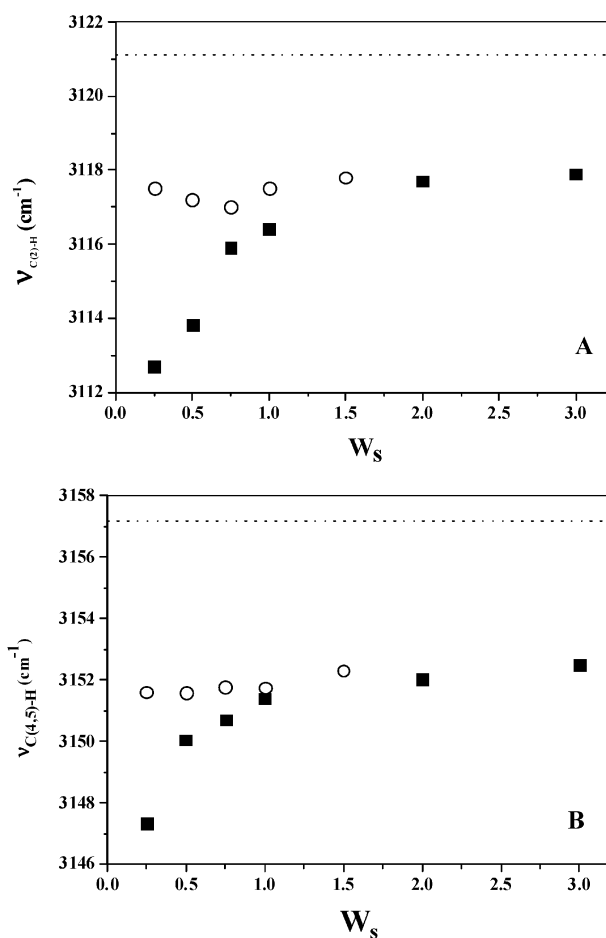


Fig. 10 Shift of the aromatic C–H stretching frequencies of $[\text{bmim}]^+$ (A: $\nu_{\text{C(2)-H}}$ and B: $\nu_{\text{C(4,5)-H}}$) upon increasing W_s in different $[\text{bmim}][\text{Tf}_2\text{N}]/\text{surfactant}/\text{chlorobenzene}$ RMs: (■) BHDC and (○) AOT. $[\text{Surfactant}] = 0.1$ M. The corresponding value for neat $[\text{bmim}][\text{Tf}_2\text{N}]$ (···) is included for comparison.

Besides, the linear tendency observed in the whole W_s range investigated for AOT and BHDC RMs indicates that, under these conditions the [bmim][Tf₂N]/surfactant/chlorobenzene RMs are discrete and non-interacting spherical droplets.^{2,37}

Since the polar head group in both surfactants is completely different,^{85,86} it is not possible to compare the d_{app} values obtained for AOT and BHDC thus, we will compare our data separately.

The sizes obtained for the cationic RMs in the present work are comparable to the values reported previously for two BHDC RMs: [bmim][BF₄]/BHDC/benzene and [bmim][Tf₂N]/BHDC/benzene.³⁷ In that work, we found that the RMs containing [bmim][BF₄] as polar domain were much larger than the ones containing [bmim][Tf₂N].³⁷ To explain these results it is important to consider that the RMs droplet sizes depend, among many other variables, on the effective packing parameter of the surfactants, v/al_c , in which v and l_c are the volume and the length of the hydrocarbon chain, respectively, and a is the surfactant head group area.⁸⁶ The RM sizes are larger when the surfactant packing parameter values are smaller.⁸⁷ For example, when water is encapsulated in AOT/isooctane RMs,⁸⁶ the hydrogen bond interaction with the AOT polar head group increases the surfactants' a values with the consequent decrease in the surfactant packing parameter and the increase in the RM droplet size. Also, we have recently¹² demonstrated using DLS that in non-aqueous AOT/*n*-heptane RMs, the polar solvents–AOT interactions are the key for the RMs droplet sizes control. Thus, the large droplets size values obtained for [bmim][BF₄] entrapped in BHDC RMs were explained considering that the anion [BF₄][−] interacts stronger with the surfactant polar head group than [Tf₂N][−] and, consequently penetrates the RMs interface, increases the effective interfacial area, decreasing the surfactant packing parameter and increasing the RMs size.

Our d_{app} values for BHDC RMs presented here are larger than the corresponding values for water/BHDC/chlorobenzene,⁸⁵ showing that the BHDC–polar solvent (BHDC–water and BHDC–[bmim][Tf₂N]) interactions are different. We think that the BHDC–[bmim][Tf₂N] interactions (particularly BHD⁺–[Tf₂N][−]) could be stronger than BHDC–water interactions, decreasing the surfactant packing parameter of the cationic surfactant and in consequence increasing the RMs droplets size in comparison with the aqueous RM values. Thus, we suggest that the [Tf₂N][−] anion interacts stronger than water with the cationic polar head group. It is well known^{28,29} that in aqueous BHDC RMs, the cationic polar head group is solvated by ion–dipole interactions with the non-bonding electron pair of oxygen. In consequence, it is not surprising that the ionic interaction between the [Tf₂N][−] and the cationic moiety of BHDC increases the effective interfacial area of BHDC, decreasing the surfactant packing parameter and increasing the RMs size in comparison with the aqueous BHDC RMs. These results also suggest an ion separation of the ionic components of [bmim][Tf₂N] inside the BHDC RMs, as it was proposed before in similar IL BHDC RMs.^{37,49}

On the other hand, although the d_{app} values found for [bmim][Tf₂N] AOT RMs are comparable to those obtained for water⁵ and other non-aqueous polar solvents encapsulated in AOT RMs¹² at the same W_s , the small droplet size changes observed when [bmim][Tf₂N] is added to the AOT RMs, which are the

organized media that encapsulate the least amount of [bmim][Tf₂N], suggest that there is a weak IL–AOT interaction. We think that probably [bmim]⁺ prefers to interact with [Tf₂N][−], making stronger the ion-pair association and showing a weak interaction toward the anionic AOT polar head. Consequently, no large changes in the packing parameter and in the droplet sizes are expected. Similar results were found when dimethylformide or dimethylacetamide is encapsulated inside AOT RMs.¹²

The variations in the values of the ¹H NMR chemical shift of H2 [bmim]⁺ (Fig. 3) and the vibration mode values (ν_{S-N-S}^{δ} and ν_{C-H} in Fig. 8 and 10, respectively) observed between [bmim][Tf₂N] in BHDC RMs and neat [bmim][Tf₂N] are evidence of an important perturbation on the IL entrapped in BHDC RMs. Evidently there are effects (or interactions) that are not present in the neat [bmim][Tf₂N] structure or even in the AOT RMs. As it was suggested before,^{37,49} an electrostatic interaction between the positive charge of the BHDC head group and the [Tf₂N][−] anion can be the main reason to explain the results obtained in the present work. Thus, this interaction can affect considerably the [bmim][Tf₂N] structure when it is encapsulated in the cationic RMs. As the positive charge is located exclusively in the quaternary nitrogen atom of the BHDC head group while the positive charge is delocalized in the [bmim]⁺ ion (see Scheme 1),⁸⁸ we expect a stronger interaction between [Tf₂N][−] and the BHD⁺ head group than with its own [bmim]⁺ cations forming the ion pairing. Thus, we assume that the ion pair degree in [bmim][Tf₂N] must be altered when it is encapsulated inside the BHDC RMs, especially at a low IL content. As it was mentioned before the S–N–S stretching mode can be used as an ion pair sensor^{60,64} thus, the high frequency value obtained at low W_s in the BHDC RMs shown in Fig. 8 agrees with a strong electrostatic interaction between [Tf₂N][−] and BHDC. Apparently, the interaction diminishes the negative density over the [Tf₂N][−] anion and shifts the frequency to higher values.⁷¹ When W_s is increased, the proportion of IL associated with BHDC diminishes and for this reason the S–N–S frequency value shifts to lower values. The cation [bmim]⁺ also shows the significant structure alteration upon encapsulation, as shown by the ¹H NMR data and the C–H vibration modes (Fig. 3 and 10). A possible cause for such changes around [bmim]⁺ in the ¹H NMR and FTIR spectra would be if the BHDC surfactant counterion (Cl[−]) exchanged with the [Tf₂N][−]. That is, in BHDC RMs the anions [Tf₂N][−] partition to the interfacial region replacing the regular Cl[−] counterion and placing the [Tf₂N][−] in near proximity to the positive surfactant head group, BHD⁺. Thus, all the results observed for the BHDC RMs demonstrate significant changes in structural organization of the RMs. Even in bulk solution, some ILs have shown the propensity to form regular structures rather than remaining completely isotropic like standard organic solvents.⁸⁹ In this sense, layering (or segregation) of ILs has been observed in homogeneous systems.⁹⁰ As a result, it is not surprising that the RMs environment would lead to a new IL organization.⁸⁹ Thus, effects on both the cation and the anion of the [bmim][Tf₂N] when combined with the cationic surfactant are observed. The FT-IR and ¹H NMR data interpretations are consistent with [Tf₂N][−] replacing chloride ions at the interface allowing [bmim]⁺ to interact with the chloride ion in the layer

removed from the interface. Moreover, the ^1H signal of [bmim][Cl] in chloroform reveals a substantial downfield shift of H2 [bmim] $^+$ to ~ 10.5 ppm, which is very similar to chemical shifts observed in our ^1H NMR results at low W_s (Fig. 3). Additionally, Berg *et al.*⁹¹ have shown that C(2)–H stretching mode of 1-hexyl-3-methylimidazolium chloride ([hmim][Cl]) appears at lower frequency in comparison with the value obtained for neat [hmim][PF₆]. Thus, we suggest that the [bmim] $^+$ interacting with the Cl $^-$ counterion diminishes the positive charge density over [bmim] $^+$ with the consequent lower $\nu_{\text{C-H}}$ frequency shifts (Fig. 10). Similar shifts are observed for the C–H stretching frequencies of the neutral imidazole molecule and the imidazolium cation, where the $\nu_{\text{C-H}}$ value for imidazole appears at a lower value than the positive imidazolium.⁷⁴ It is well known that reduction on the positive charge density over the imidazolium cation shifts the C–H frequencies to lower values.⁷⁴ Additionally, Fig. 10A and B show that all the IL aromatic C–H stretching modes are altered in BHDC RMs. These facts show that the presence of the ion pairing formation (BHD $^+$ –[Tf₂N] $^-$) at the interface could be more important than the H-bond interaction between C(2)–H [bmim] $^+$ and the anions present. Furthermore, analyzing the ^1H NMR signal when BHDC is the surfactant used to encapsulate [bmim][Tf₂N], the protons near to the quaternary N (benzyl methylene, N-methyl and methylene) show downfield shifts (Fig. 5), denoting the influence of [Tf₂N] $^-$ on these protons.

On the other hand, the results found for [bmim][Tf₂N]/AOT/chlorobenzene RMs, especially the ^1H NMR chemical shifts and the vibration modes observed (Fig. 3, 6, 8 and 10), clearly show a different situation. In order to interpret these results, two different effects can be taken into account: (1) the proximity of vicinal SO₃ $^-$ groups at the AOT interface produces steric hindrance to interact with the more bulky imidazolium cation and, (2) the electrostatic interactions between the ions present in the system as it was mentioned above in the DLS analysis. We believe that the electrostatic interaction between the SO₃ $^-$ group and the Na $^+$ counterion present in the AOT surfactant molecule seems to be stronger than the possible [bmim] $^+$ –SO₃ $^-$ interaction at the interface. Thus, the structure of [bmim][Tf₂N] encapsulated is not particularly disrupted by the anionic surfactant at all W_s studied, in comparison to the BHDC RMs results. Moreover, if the AOT protons (near to the polar head group) are investigated small shifts are observed, showing practically constant values when [bmim][Tf₂N] is added to the system (Fig. 6). Thus, we think that the small changes observed in the AOT RMs are proof of a weak interaction between the surfactant and [bmim][Tf₂N], as it was shown by DLS and FT-IR spectroscopies. Besides, the FT-IR results shown in Fig. 10A and B suggest that no evidence of the H-bond donor ability of the imidazolium cation is detected. This came out because despite the fact that the AOT polar head group is very good in accepting hydrogen bond interaction,^{25,26} the C(2)–H of [bmim] $^+$ is not able to interact through H-bonding with the surfactant since both C(2)–H stretching modes appear practically unmodified when the IL is encapsulated in the anionic RMs.

Finally, it is important to note that in any case even at the maximum value of W_s reached the behavior (FT-IR or ^1H NMR results) of [bmim][Tf₂N] confined in both RMs never

reaches the characteristics observed for the neat [bmim][Tf₂N]. These results suggest that the ion pairing effect (with the surfactant or with the IL counterions) is substantially enhanced upon confinement, altering the structure and properties of the entrapped [bmim][Tf₂N]. In summary, our results reveal that the [bmim][Tf₂N] structure can be modified in a different manner inside RMs by varying the kind of surfactant used to create the RMs and the IL content (W_s). These facts can be very important if these media are used as nanoreactors because unique microenvironments can be easily created by simply changing the RM components and W_s .

Experimental section

Materials

Sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT), from Sigma (>99% purity), was used as received. Benzyl-*n*-hexadecyldimethylammonium chloride (BHDC), from Sigma (>99% purity), was recrystallized twice from ethyl acetate.^{7,9,37} Both surfactants were dried under vacuum prior to use. Chlorobenzene, from Sigma (HPLC quality), was used without prior purification.

The IL used, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]), was synthesized under anaerobic conditions using standard Schlenk techniques.⁹² Prior to use [bmim][Tf₂N] was discolored with activated charcoal, filtrated through aluminum oxide and dried under vacuum at 60 °C for 4 hours.⁹³

Methods

The stock solutions of surfactants in chlorobenzene were prepared by mass and volumetric dilution. Aliquots of these stock solutions were used to make individual reverse micelle solutions with different amounts of [bmim][Tf₂N], defined as $W_s = \frac{[\text{bmim}][\text{Tf}_2\text{N}]}{[\text{surfactant}]}$. The incorporation of [bmim][Tf₂N] into each micellar solution was performed using calibrated microsyringes. To obtain optically clear solutions they were shaken in a sonicating bath. The resulting solutions were clear solutions with a single phase. The W_s was varied between 0–3.0 for BHDC and 0–1.5 for AOT 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. In all cases, the surfactant concentration was kept constant and equal to 0.1 M. These samples were used in DLS analysis to determine reverse micelle size. Similar sample preparation was used for ^1H NMR and FT-IR experiments.

General

The apparent diameters of different [bmim][Tf₂N] RMs were determined by dynamic light scattering (DLS, Malvern 4700 with goniometer) with an argon-ion laser operating at 488 nm. Cleanliness of the cuvettes used for measurements was of crucial importance in obtaining reliable and reproducible data.⁹⁴ 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 chlorobenzene twice, then with the 0.1 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 chlorobenzene were collected to confirm cleanliness of the cuvettes. Prior to data acquisition, samples were equilibrated in the DLS instrument for 10 min at 25 °C. To obtain valid results from DLS measurements requires knowledge of the system's refractive index and viscosity in addition to well-defined conditions. The refractive indices and viscosities for the RM solutions were assumed to be the same as neat chlorobenzene.⁹⁵ Multiple samples at each size were made, 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 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 show that the polydispersity of the [bmim][Tf₂N] RMs size is less than 5%.

FT-IR spectra were recorded with a Nicolet IMPACT 400 FT-IR spectrometer. IR cells of the type Irtran-2 (0.5 and 0.015 mm of path length) from Wilmad Glass (Buena, NJ) were used. FT-IR spectra were obtained by co-adding 200 spectra at a resolution of 0.5 cm⁻¹, and the chlorobenzene spectrum was used as the background.

For the ¹H NMR experiments a Bruker 200 NMR spectrometer was used. The spectra were recorded at a digital resolution of 0.06 Hz per data point. The spectrometer probe temperature, 25 °C, was periodically monitored by measuring the chemical shift difference values between the two singlets of a methanol reference sample which is well-known that depends on the temperature.⁵⁴ The probe thermal stability was assured by the observation that successive measurements of the sample chemical shift (after 10 minutes in the probe for thermal equilibration) were within digital resolution limit. A capillary tube containing CDCl₃ was introduced in the NMR tube and was used as a frequency "lock". Chemical shifts were measured relative to internal TMS and the values were reproducible within 0.01 ppm. All NMR data were processed using MestReC 4.8.6 for window and plotted and fitted using OriginPro 7.

All the experiments were carried out at 25 ± 0.5 °C.

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