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## ARTICLE TYPE

**Spontaneous emulsification in ionic liquid/water systems and its use for solids templating**Magdalena Kowacz,<sup>\*a</sup> José M. S. S. Esperança,<sup>a</sup> and Luís Paulo N. Rebelo<sup>\* a</sup>*Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX*

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We report on the spontaneous formation of nano-sized ionic liquid/water (IL/W) emulsions in a simple system solely composed of an IL and aqueous solution of an inorganic salt. The IL ions play a dual role, that of both surfactant and dispersed phase. No extra surfactant is needed to promote emulsification. The droplets generation at the IL/W interface is captured by nanoparticulate and porous films that imprint the morphology of this unstable interface. The emulsion droplets are employed to create core/shell microcrystals with potential functionality.

**Introduction**

It has been recognized that, under specific conditions, spontaneous emulsification can occur in systems composed of two immiscible liquids with the help of at least one third component (usually a surfactant or sometimes a cosolvent).<sup>1</sup> Two main concepts, relevant to our experiments, are proposed to explain the spontaneous formation of emulsions, namely i) negative interface tension and ii) diffusion and stranding mechanism.<sup>1</sup> In the first approach, the adsorption of a surfactant at the liquid/liquid interface induces transient negative interface tension and the mechanical instability of the interface. In the second scenario, one liquid condenses upon the diffusive separation of the second liquid component, e.g. if water is added to a mixture of alcohol and oil, the alcohol diffuses out of the oil phase and drags with it some of the oil molecules that become stranded in the aqueous phase and nucleate into droplets. Diffusion and stranding mechanisms generally produce kinetically stabilized emulsions with average drop sizes in the range of 1 μm – 20 μm (although diameters as small as 200 nm have also been obtained).<sup>1, 2</sup> Negative interface tension phenomena can result in the formation of microemulsions that are thermodynamically stable, optically isotropic systems with drop sizes below 100 nm.<sup>1, 3</sup> The small size of the droplets led to the hypothesis that these systems may be entropy-stabilized.<sup>4</sup>

The nanoscale liquid/liquid dispersions promise a wide range of applications. They can solubilise a variety of polar and nonpolar substances in their nanodomains<sup>5</sup>; therefore, they are useful as microreactors<sup>6</sup> or drug delivery systems<sup>7</sup>, are employed in the purification and extraction of biomolecules<sup>8</sup>, as well as in the synthesis of inorganic nanostructures.<sup>9</sup> Their main disadvantage is that these processes normally require high concentrations of surfactant. Herein we report on the spontaneous formation of nano-sized emulsions in a simple system composed of only an ionic liquid and an aqueous solution of inorganic salt.

**Results and discussion**

Our experiments demonstrated that in biphasic systems composed of water-immiscible ionic liquid (IL) and aqueous solution of inorganic salt, 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>12</sub>mim][NTf<sub>2</sub>] and 10 mM Na<sub>2</sub>CO<sub>3</sub> or 10 mM Cs<sub>2</sub>CO<sub>3</sub>, or 2-hydroxyethyltrimethylammonium bis(trifluoromethylsulfonyl)imide [Ch][NTf<sub>2</sub>]<sup>10</sup> and 10 mM Na<sub>2</sub>CO<sub>3</sub>, nano-sized IL in water (IL/W) emulsions are spontaneously generated (as determined by DLS). When the concentration of Na<sub>2</sub>CO<sub>3</sub> is increased to 1 M or when different combinations of inorganic cation and anion are used (K<sub>2</sub>CO<sub>3</sub>, NaCl, KCl or CaCl<sub>2</sub>), spontaneous emulsification does not occur any more (DLS measurements do not detect any objects with a given hydrodynamic radius), although mixing (salting in) of IL and aqueous phase takes place (as indicated by FTIR-ATR). Therefore the spontaneous formation of nanoscale dispersions is both salt and concentration specific.

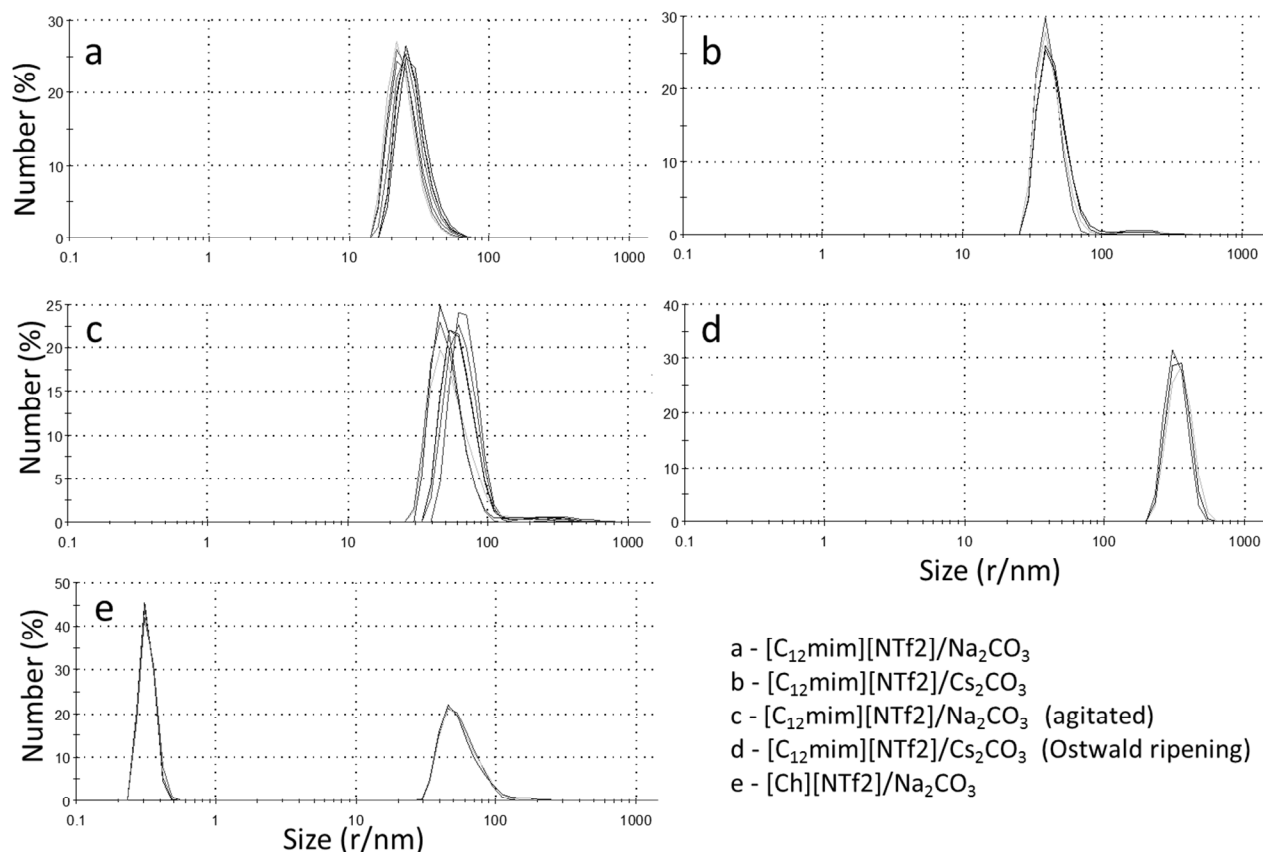
**Size and stability of the IL/W emulsions**

The presence of nanoscale droplets is confirmed by DLS measurements. The average radius of the droplets ranges from 25 nm in [C<sub>12</sub>mim][NTf<sub>2</sub>]/Na<sub>2</sub>CO<sub>3</sub> to 43.5 nm in [C<sub>12</sub>mim][NTf<sub>2</sub>]/Cs<sub>2</sub>CO<sub>3</sub> to 57 nm in [Ch][NTf<sub>2</sub>]/Na<sub>2</sub>CO<sub>3</sub> (Fig. 1). When IL and aqueous phases are initially mixed by hand-agitation, in the [C<sub>12</sub>mim][NTf<sub>2</sub>]/Na<sub>2</sub>CO<sub>3</sub> system, the droplet radius increases to 65 nm (Fig. 1 c). The nano-sized emulsions can be created only by a spontaneous mechanism at appropriate conditions or by the application of a very high external force<sup>11</sup>. As manual agitation provides very mild mixing conditions, also in the latter case, the driving mechanism responsible for the emergence of nanoscale IL/W dispersions has to be spontaneously generated in the system. The IL/W emulsions droplets are relatively uniform in size with an average polydispersity index, PDI = 0.3 for [C<sub>12</sub>mim][NTf<sub>2</sub>] and PDI = 0.5 for [Ch][NTf<sub>2</sub>] as a dispersed phase. When [C<sub>12</sub>mim][NTf<sub>2</sub>]/Cs<sub>2</sub>CO<sub>3</sub> (IL/W) phase is separated

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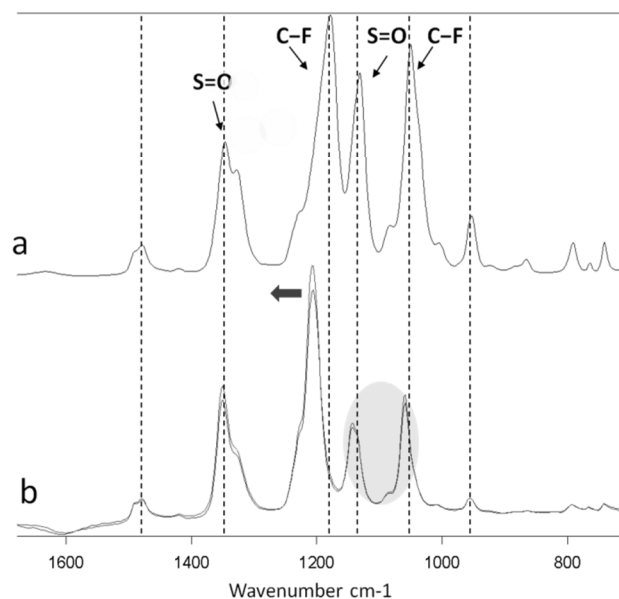
**Fig. 1** DLS measurements showing the radius ( $r$ ) of the droplets generated in aqueous phases of a) [C<sub>12</sub>mim][NTf<sub>2</sub>]/Na<sub>2</sub>CO<sub>3</sub>, b) [C<sub>12</sub>mim][NTf<sub>2</sub>]/Cs<sub>2</sub>CO<sub>3</sub>, c) [C<sub>12</sub>mim][NTf<sub>2</sub>]/Na<sub>2</sub>CO<sub>3</sub> where IL and aqueous phase were initially mixed by hand-agitation, d) aqueous phase of [C<sub>12</sub>mim][NTf<sub>2</sub>]/Cs<sub>2</sub>CO<sub>3</sub> separated from the underlying IL layer and left to equilibrate for two days and e) aqueous phase of [Ch][NTf<sub>2</sub>]/Na<sub>2</sub>CO<sub>3</sub>. In the latter system, after the extraction of the aqueous phase from contact with bulk ionic liquid (IL) phase, droplets ( $r = 57$  nm) vanished over time (only signal at  $r = 0.32$  nm, corresponding to the size of the individual IL ions, could be finally detected).

from the underlying IL phase for a few days, a characteristic Ostwald ripening process (growth of larger droplets at the expense of dissolution of smaller ones) takes place, what is expressed in the increase of the average droplet radius (165 nm) accompanied by their greater size uniformity (PDI = 0.04) (Fig. 1 d). Generally the spontaneously formed IL/W emulsions are stable for at least a month, when an aqueous phase is maintained in contact with the bulk IL phase (as a biphasic system). When the aqueous phase is sampled and examined separately, DLS measurements indicate the vanishing of the emulsion droplets in the [Ch][NTf<sub>2</sub>]/Na<sub>2</sub>CO<sub>3</sub> systems (Fig. 1 e). This suggests that for the IL with the more hydrophilic cation, [Ch]<sup>+</sup>, the IL/W emulsion is in equilibrium with the bulk IL phase, which corresponds to the concept of Winsor I type microemulsion<sup>12</sup> (oil/water emulsion in equilibrium with an excess oil phase). FTIR measurements give us some insight into the structure of nanoscale emulsions, thus suggesting reasons for the stability of the systems and for effectiveness of specific combinations of ions

25 in promoting the emulsification process.

#### Similarity of the dispersed and bulk IL phase – stability of the two phase system

The only difference between spectra of neat [Ch][NTf<sub>2</sub>] and [Ch][NTf<sub>2</sub>] dispersed and/or dissolved in the aqueous phase of the [Ch][NTf<sub>2</sub>]/Na<sub>2</sub>CO<sub>3</sub> biphasic system is a shift of the C-F peak<sup>13</sup> to higher wavenumbers (Fig. 2, arrow) and a change in proportions of pairs of C-F and S=O peaks<sup>13</sup> of the [NTf<sub>2</sub>]<sup>-</sup> anion (relative suppression of the respective signals on the right to 1182 cm<sup>-1</sup>, Fig. 2, shaded area). The former feature indicates a loss of the C-F---H-C intramolecular hydrogen bonding<sup>14</sup> between the hydrophobic compartments of the IL ions. The latter suggests more restricted vibrational freedom of the [NTf<sub>2</sub>]<sup>-</sup> anion (C-F and S=O signals at different wavenumbers correspond to distinct vibrational modes of those groups), therefore indicating enhanced organization of the anions when transferred into the water phase. Disintegration of the emulsion droplets (shown by DLS, Fig. 1 e)



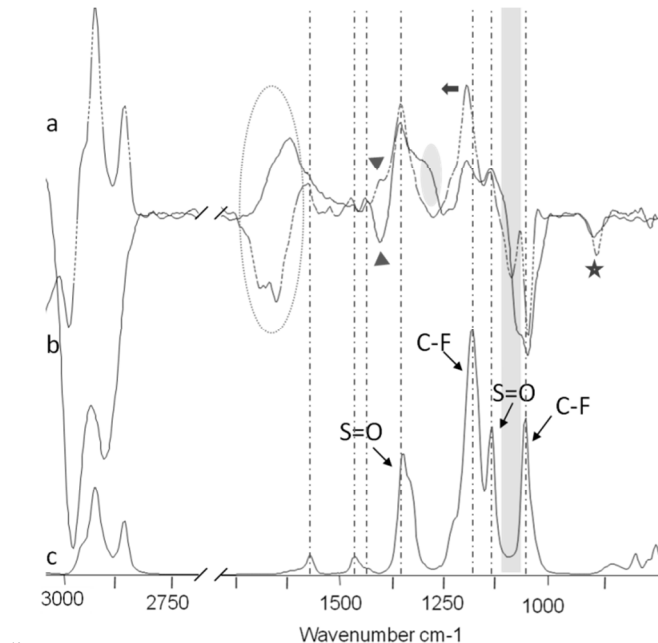
**Fig. 2** FTIR spectra of a) [Ch][NTf2] and b) superimposed spectra of the aqueous phase of [Ch][NTf2]/Na<sub>2</sub>CO<sub>3</sub> biphasic system, measured immediately after its extraction from the biphasic system and following separation from the bulk IL phase for 24 hours.

does not induce any conformational change of the [Ch][NTf2] in aqueous solution (Fig. 2).

#### Salt-induced distinct partitioning of the IL components into aqueous phase - stable IL/W emulsions

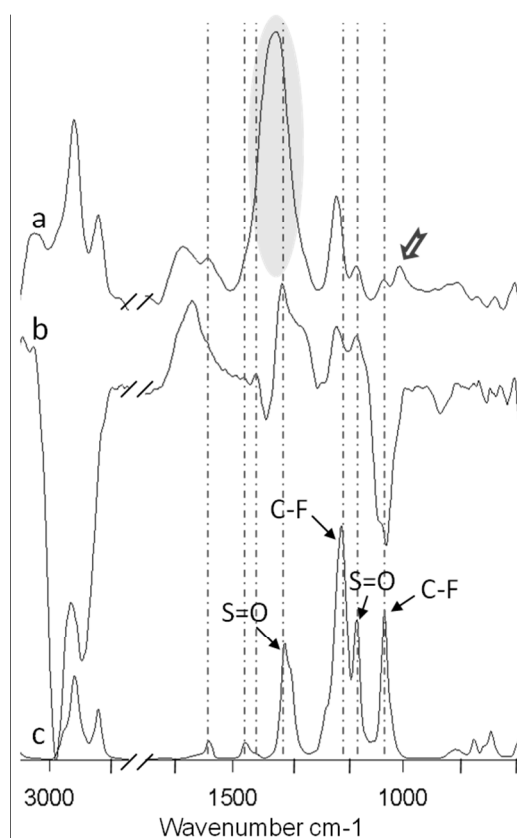
In both [C<sub>12</sub>mim][NTf2]/Na<sub>2</sub>CO<sub>3</sub> and [C<sub>12</sub>mim][NTf2]/Cs<sub>2</sub>CO<sub>3</sub> systems, where relatively stable emulsions are formed, the organization of the IL ions dispersed in the aqueous solution is significantly different from their mutual organization in the neat IL (Fig. 3). As in the case of [Ch][NTf2], spectral features indicate the decrease of the C-F---H-C intramolecular hydrogen bonding (Fig. 3, arrow)<sup>14</sup>, but also a much stronger restriction of the vibrational freedom of the [NTf2]<sup>-</sup> anion (negative C-F peaks at 1057 cm<sup>-1</sup>). The reduced intensity of the pair of C-F and S=O peaks (on the right to 1182 cm<sup>-1</sup>) is associated with expression of new spectral signals in this region (Fig. 3, negative peaks at 1089 cm<sup>-1</sup> corresponding to N-CH<sub>3</sub> vibrations of the imidazolium cation<sup>16</sup> (shaded rectangle) and in a region assigned to C-H vibrations of the imidazolium ring (star)<sup>17</sup>). These spectral features can originate from the vibrations of the IL cation, as they correspond to [C<sub>n</sub>mim]<sup>+</sup> peaks when alkyl-imidazolium cation is combined with simpler anions, for instance monoatomic ions.

Therefore, in systems forming stable emulsions, there is an appreciable loss of mutual association of IL ions upon their transfer into water phase. These IL cation-anion interactions have to be compensated by interaction of individual IL ions with inorganic ions in the aqueous solution. Different water solubility of the IL cation vs. IL anion in combination with inorganic counterions implies that either the IL cation or anion can be present in excess in the aqueous phase. This is in fact supported by the relative changes in the intensity of the spectral signals corresponding to vibrational modes of the IL cation and anion, characteristic for stable IL/W emulsions. Possibility of non-equal partitioning of the components of the hydrophobic IL into the aqueous phase under the action of sodium and caesium salts was



**Fig. 3** FTIR spectra of the aqueous phase of a) [C<sub>12</sub>mim][NTf2]/Cs<sub>2</sub>CO<sub>3</sub>, b) [C<sub>12</sub>mim][NTf2]/Na<sub>2</sub>CO<sub>3</sub> biphasic system and c) neat [C<sub>12</sub>mim][NTf2]. Note that in a) and b) H<sub>2</sub>O spectra was used as a background, therefore negative peaks imply vibration intensity lower than the water vibration in the respective regions. Dashed ellipse indicates vibration of water of hydration of inorganic ions – negative for weakly hydrated caesium and positive for more strongly hydrated sodium.

also confirmed by molecular dynamics simulations<sup>15</sup>. That study<sup>15</sup> showed that in consequence the water phase in the adjacent vicinity of the IL/water interface is not neutral. As emulsion droplets imply the presence of IL/W interfaces of appreciable surface area, the relative excess of one of the IL ions can be detected in our experiments. In the [C<sub>12</sub>mim][NTf2]/Na<sub>2</sub>CO<sub>3</sub> system, all spectral features of the IL cation are represented as negative peaks (Fig. 3 b, the C-H vibrations of alkyl chains (2750 cm<sup>-1</sup>-3000 cm<sup>-1</sup>) and the band corresponding to the imidazolium interaction with inorganic oxy-anion<sup>17</sup>, here CO<sub>3</sub><sup>2-</sup> (triangles)). Therefore it can be concluded that the anions are preferentially extracted to the aqueous phase. On the contrary, in the [C<sub>12</sub>mim][NTf2]/Cs<sub>2</sub>CO<sub>3</sub> system, the intensity of the C-H vibrational modes of the cation is higher with respect to vibrations of the anion, than in neat IL (Fig. 3 a). This suggests that the IL cations are present in excess in the aqueous phase. Such differences in the effect of Na<sub>2</sub>CO<sub>3</sub> versus Cs<sub>2</sub>CO<sub>3</sub> on IL partitioning into the aqueous phase can be explained by considering differences in the hydration properties of the inorganic cations. Cs<sup>+</sup> (of high polarizability and low charge density) interacts with water dipoles in a weaker manner than water with other water molecules, and behaves as a hydrophobic solute, having tendency to partition to non-polar surfaces/phases<sup>18</sup>. It has been recognized that this cation can be extracted from water into the [C<sub>2</sub>mim][NTf2] by a cation-exchange mechanism<sup>19</sup>. Therefore Cs<sup>+</sup> can partition into the IL phase, while IL cations can be transferred into water. Na<sup>+</sup> has stronger affinity for water and its dehydration costs are relatively high. Therefore it will extract IL anions into the aqueous phase, rather than exchange with the IL cations (right-hand broadening of the S=O signal<sup>13</sup> (Fig 3 b, shaded ellipse) suggests S=O---Na



**Fig. 4** FTIR spectra of the aqueous phase of  $[C_{12}mim][NTf_2]/Na_2CO_3$  biphasic system a) agitated by hand-shaking, b) non-agitated and c) spectra of neat  $[C_{12}mim][NTf_2]$ . Note in a) relative increase in the intensity of the C-H vibrations of alkyl groups ( $2750\text{ cm}^{-1}$ - $3000\text{ cm}^{-1}$ ) as well as C-F vibrations of the anion<sup>13</sup> (signals changing from negative to positive) and new features: development of broadband centred at  $1389\text{ cm}^{-1}$  (shaded ellipse) and peak at  $1014\text{ cm}^{-1}$  (arrow). The latter two correspond respectively to imidazolium cation interaction with carbonate anion<sup>17</sup> and S=O interaction with partially dehydrated  $Na^+$  (this signal coincides with S-O---metal cation vibrations in sulphate minerals<sup>20</sup>)

interaction). For electroneutrality preservation, carbonate anions are expected to substitute to some extent  $[NTf_2]^-$  extracted into water. Nevertheless, due to their strong hydration,  $CO_3^{2-}$  are not likely to partition into the IL phase, but rather remain at the IL/water interface. Interestingly, hand-agitation brings about important changes in the pattern of  $[C_{12}mim][NTf_2]$  dispersed and/or dissolved in aqueous solution of  $Na_2CO_3$  (Fig. 4). Mechanical mixing supports extraction of the IL cations into the water phase. This is reflected in the increase in the intensity of alkyl chain C-H vibrations and in appearance of a strong broad peak centred at  $1389\text{ cm}^{-1}$  (Fig. 4 a, shaded ellipse). The latter is attributed to the C-H bending vibration of the  $CH_3$  group, characteristic of the alkyl-imidazolium cations interacting with inorganic oxy-anions<sup>17</sup>, here  $CO_3^{2-}$ . Therefore, with the aid of mechanical agitation, the  $CO_3^{2-}$  anions residing at the interface can extract the IL cations into the aqueous phase. The corresponding spectral feature (broadband around  $1389\text{ cm}^{-1}$ ) is characteristic for all carbonate-bearing systems used in our experiments, including those that do not create emulsions. It appears also in pure water phase in contact with  $[C_{12}mim][NTf_2]$  (this study, data not shown), here suggesting micellar-like organization of the IL cations with their methyl groups, adjacent

to the charged imidazolium ring<sup>21</sup>, exposed to water and long alkyl chains hydrophobically associated.

From the above consideration it can be concluded that the distinctive aspect of spontaneously emulsifying systems is the particular disproportion in the salt-induced IL cation vs. IL anion affinity for the aqueous phase. The different chemical composition, thus structural organization, of the emulsion droplets in comparison with the bulk IL, can account for the stability of these IL/W dispersions (independently of the presence of an excess IL phase). For the  $[Ch][NTf_2]/Na_2CO_3$  system removing of the excess IL layer shifts the equilibrium between the interacting, structurally virtually equal ionic liquid/water interfaces (of the droplets and of the bulk IL phase, Fig. 2) and drives the rearrangement of the system (entropically stabilized Winsor I microemulsion).<sup>12</sup>

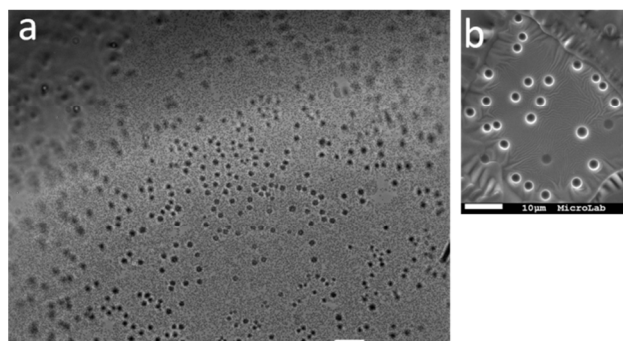
#### Hydration of salt ions and induction of emulsification

Only the combination of the two inorganic ions having strong affinity for water or combination of water-loving ion with the one having affinity for hydrophobic compounds proved to be effective in inducing spontaneous emulsification in our experimental system. Both types of ions assure extraction of the IL ions into the aqueous phase. Hydrophilic ones drag IL ions into water phase by means of electrostatic attraction, while hydrophobic-like exchange with IL ions from water-immiscible phase. Weakly hydrated hydrophilic ions, such as  $K^+$  and  $Cl^-$ , are not effective extractants because of their weaker affinity for water. Yet they are also not effective exchangers for IL ions because of their still prevailing hydrophilic character. This class of ions is designated as negatively hydrated – ions that increase the translational motion of water molecules<sup>22</sup>. Systems containing such ions ( $NaCl$ ,  $KCl$ ,  $K_2CO_3$  and  $CaCl_2$ ) were not prone to induce emulsification, although significant mixing occurred for  $K_2CO_3$  and  $CaCl_2$  in aqueous phase due to the presence of strongly hydrated counterions.

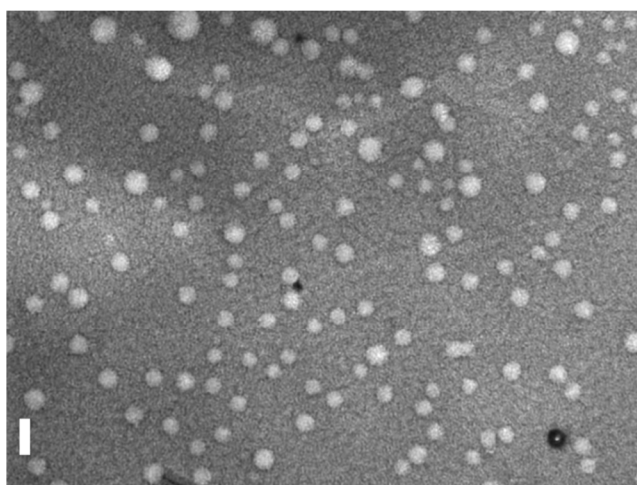
Increasing the concentration of  $Na_2CO_3$  to 1 M hampers spontaneous emulsification. This can be understood by considering salting out effect (competition for water of hydration) of inorganic ions on ILs due to the recognized switchover between electrostatic (promoting salting in) and hydration forces on increasing ionic strength of aqueous solution<sup>23, 24</sup>. This trend, initial solubilisation of hydrophobic ILs followed by decrease in their solubility on increasing salt concentration, is in agreement with previous findings<sup>25</sup>.

#### Mechanism of spontaneous emulsification and its application for solids templating

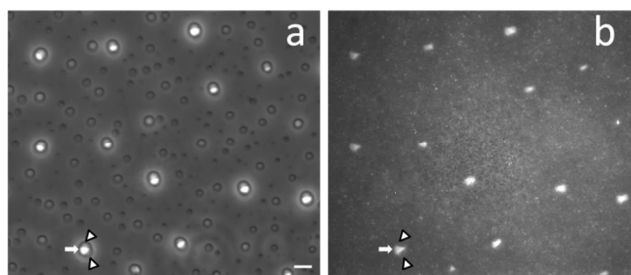
In order to spontaneously create nanoscale droplets, a surfactant having a specific affinity to the oil/nonpolar component has to be present in the aqueous phase.<sup>1</sup> But there is no surfactant dissolved in water in our experimental system. Nevertheless, the ions constituting the water-immiscible ILs used in our work, when combined with our inorganic counterions, are soluble in water and exert surface activity. Hydrophilic inorganic ions interact with the IL cations and anions at the IL/water interface and tend to extract those into the aqueous phase. This can induce a transient negative liquid/liquid interfacial tension and spontaneously generate nano-sized droplets<sup>1, 11</sup>. At the same time, the IL component having a stronger affinity to the aqueous phase,



**Fig. 5** a) Optical microscopy image of a porous film formed by the evaporation of 40mg/ml aqueous solution of Lysozyme deposited on the top of a neat [C<sub>12</sub>mim][NTf<sub>2</sub>] layer. b) Scanning electron microscopy (SEM) image showing smooth edges and uniform size of the pores. Scale bar: 10μm

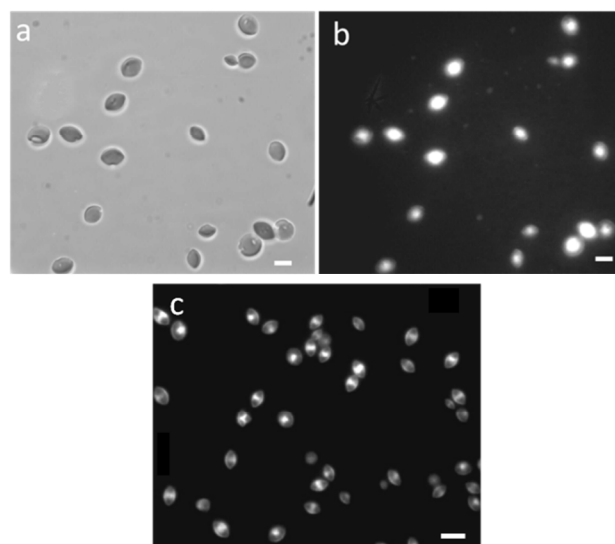


**Fig. 6** Optical microscopy image of BaSO<sub>4</sub> nanocrystals deposited at a IL/water interface. The BaSO<sub>4</sub> were precipitated by adding a BaCl<sub>2</sub> solution to the aqueous phase of a biphasic system composed of [Ch][NTf<sub>2</sub>] and solution of Na<sub>2</sub>SO<sub>4</sub>. The organization of the nanoparticles into disks repeats the deformation of the interface that can be induced by inorganic ions pulling the IL components into the aqueous phase. Scale bar: 10μm



**Fig. 7** Bright field a) and fluorescence b) microscopy images capturing the mechanism of development of hollow-core crystals and showing IL droplets (arrow) encapsulated inside of the crystalline CaCO<sub>3</sub> shells (triangles). IL cores are intrinsically fluorescent while solid shells are invisible upon excitation with UV light. Scale bar: 10μm

when diffusing out of the IL phase (extracted by hydrophilic or exchanged with hydrophobic ion), can drag with it the less

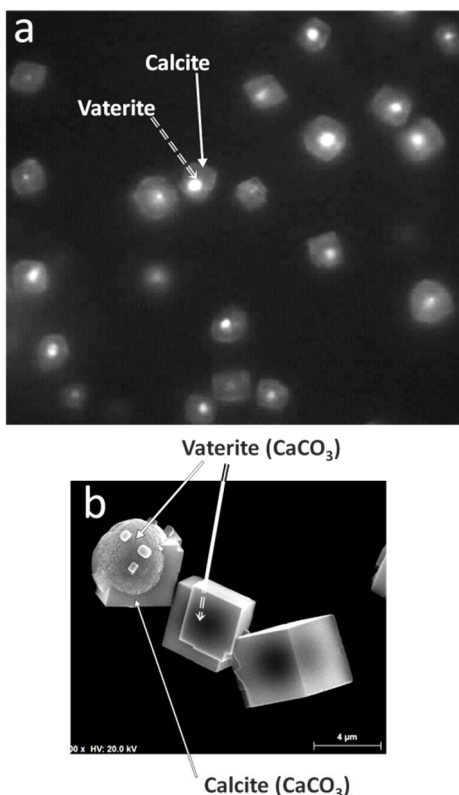


**Fig. 8** Bright field a) and fluorescence b) and c) microscopy images of vaterite (CaCO<sub>3</sub>) microcrystals grown by the evaporation of the aqueous phase (AP) of [C<sub>12</sub>mim][NTf<sub>2</sub>]/water biphasic system containing 5 mM Na<sub>2</sub>CO<sub>3</sub> (hand-mixed with the IL) and 5 mM CaCl<sub>2</sub> (added to the mixture and equilibrated for several hours before the extraction of the AP). Particle fluorescence in b) is due to the incorporation of the IL ions, which show intrinsic fluorescence. Image c) shows vaterite microparticles loaded with a fluorescent dye (the dye clearly penetrates into the particles interior)

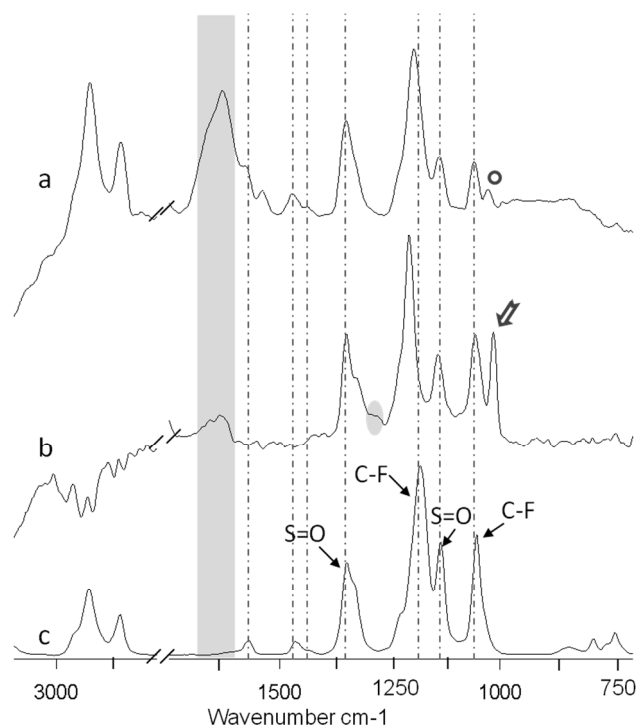
hydrophilic component that becomes stranded in water and nucleates into micrometer-sized droplets.<sup>1,2</sup> These larger droplets are unstable over time (DLS measurements indicate nanoscale character of the dispersions), but their emergence can be captured e.g. by films recording the shape of the emulsifying interface (Fig. 5 and 6) or by crystals that grow by encompassing emulsion droplets (Fig. 7). The spontaneous formation of the emulsion droplets can be also supported by the electrochemical instability<sup>26</sup> of the IL/W interface. The instability is likely to be induced by the non-equal distribution of the ions at both the aqueous and organic side of the interface, resulting in a potential difference between those. Such scenario is in fact supported by our observations that suggest accumulation of charge (excess of anions or cations) at the IL/W droplets. Vanishing of the emulsification at higher concentration of the supporting electrolyte is also in line with the features of the process induced by electrochemical instability.

The encapsulation of IL droplets by inorganic crystalline shells (Fig.7) suggested a possible route for the creation of core/shell structures with potential functionality. The spontaneous emulsification of the [C<sub>12</sub>mim][NTf<sub>2</sub>]/Na<sub>2</sub>CO<sub>3</sub> system was used to form fluorescent vaterite (CaCO<sub>3</sub>) microcrystals with hollow cores and permeable walls (Fig.8). We successfully loaded the microparticles that can find applications as carrier and delivery systems with the pH- dependent dissolution of the CaCO<sub>3</sub> enabling pH-controlled target release. Fluorescence can either track the load or add photoresponsive properties to other materials. The chemically uniform, but structurally composite, CaCO<sub>3</sub> crystals with spherical and fluorescent vaterite cores and rhombohedral calcitic shells (Fig. 9) were grown starting from the Ca<sup>2+</sup> ions complexed with [NTf<sub>2</sub>]<sup>-</sup> in the aqueous phase of IL/W biphasic system (as indicated by FTIR measurements (Fig. 10)).

To the best of our knowledge, such composite CaCO<sub>3</sub> crystals in



**Fig. 9** a) Fluorescence microscopy and b) SEM image of composite CaCO<sub>3</sub> crystals grown by mixing aqueous phases of [C<sub>12</sub>mim][NTf<sub>2</sub>]/Na<sub>2</sub>CO<sub>3</sub> with [C<sub>12</sub>mim][NTf<sub>2</sub>]/CaCl<sub>2</sub> (concentration of inorganic salts = 10 mM). The prerequisite for the formation of composite crystals was the use of CaCl<sub>2</sub> aqueous solution in which Ca<sup>2+</sup> ions were preferentially solvated by the IL ions

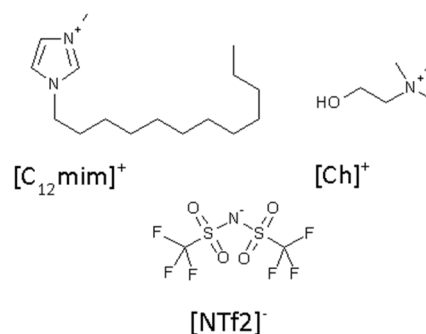


**Fig. 10** FTIR spectra of a) freshly prepared and b) equilibrated for several weeks aqueous phase of the [C<sub>12</sub>mim][NTf<sub>2</sub>]/CaCl<sub>2</sub> and c) neat [C<sub>12</sub>mim][NTf<sub>2</sub>]. Note in b) vanishing of the absorption in a region corresponding to the water of hydration of the inorganic cation (centred around 1632 cm<sup>-1</sup>, shaded rectangle), together with the development of a new spectral feature on the right side of the S=O peak<sup>13</sup> (shaded ellipse) and appearance of a new peak at 1014 cm<sup>-1</sup> (arrow) that can be assigned to S=O---Ca interactions<sup>20</sup>. In a) peak in the latter region appears at higher wavenumber (1025 cm<sup>-1</sup>) and can result from imidazolium cation vibrations, expressed when [NTf<sub>2</sub><sup>-</sup>] absorptions in this part of the spectra become suppressed. The new spectral features in b) therefore indicate substantial dehydration of Ca<sup>2+</sup> and its preferential solvation by the IL ions.

which vaterite (thermodynamically unstable polymorph) coexists in an aqueous solution with calcite in one structure (with no signs of recrystallization) are being reported for the first time. Both the structural heterogeneity and the added fluorescence of the cores (due to the incorporation of the IL molecules) make those core/shell crystals potentially highly attractive for advanced photonic applications.

## Experiments

Milli-Q water or aqueous solutions of inorganic salts were gently placed over the layer of a water-immiscible ionic liquid (IL), 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [C<sub>12</sub>mim][NTf<sub>2</sub>] or 2-hydroxyethyltrimethylammonium bis(trifluoromethyl sulfonyl)imide [Ch][NTf<sub>2</sub>]<sup>10</sup> (200 μl of IL + aqueous phase up to 2 ml of final volume) or b) were mixed by hand-shaking with [C<sub>12</sub>mim][NTf<sub>2</sub>] (IL: aq. phase = 2 : 40 or 2 : 18 (v/v)) and let to equilibrate for several days. All experiments were performed at room temperature. The structures of ILs are presented in Scheme 1. Types and concentrations of inorganic salts used in combination with particular IL are given in Table 1.



**Scheme 1.** Structures of the ionic liquid ions

Aqueous phases of IL/W biphasic systems were analysed by dynamic light scattering (DLS) in order to verify possible assembly of solutes (ILs and inorganic ions) into objects of defined apparent hydrodynamic radius, referred in this work as emulsion droplets of a given size. DLS measurements were performed with the use of a Zetasizer Nano ZS from Malvern Instruments. The instrument measures the scattering information at 173°. The autocorrelation function (expressing the rate of fluctuation of the intensity of scattered light over time) is used by DLS software to calculate particle size based on the relationship of the latter with the Brownian motion of the particles. Example

Table 1 Concentration of aqueous solutions of inorganic salts used to create biphasic systems with respective ionic liquids

	[C <sub>12</sub> mim][NTf <sub>2</sub> ]	[Ch][NTf <sub>2</sub> ]
Na <sub>2</sub> CO <sub>3</sub>	0.01 M <sup>a</sup> ; 1 M	0.01 M <sup>a</sup>
5 Cs <sub>2</sub> CO <sub>3</sub>	0.01 M	
K <sub>2</sub> CO <sub>3</sub>	0.01 M	
NaCl	0.01 M; 0.02 M	
KCl	0.01 M; 1 M	
CaCl <sub>2</sub>	0.005 M; 0.01 M <sup>a</sup>	0.01 M <sup>a</sup>

10 a) conditions for which mechanical agitation was applied in addition to gentle contacting of the two phases

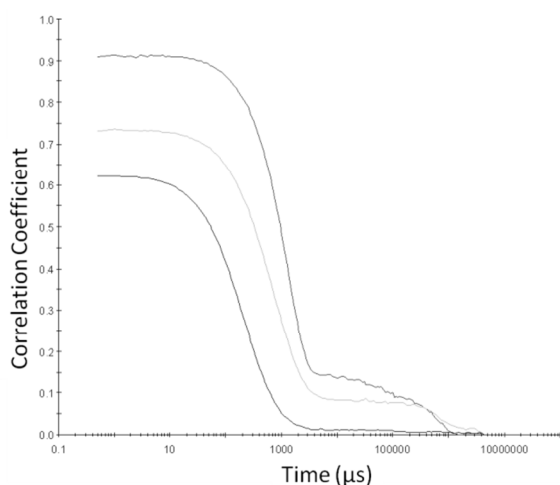


Fig. 11 DLS raw correlation data for (from top to bottom)

15 [C<sub>12</sub>mim][NTf<sub>2</sub>]/Cs<sub>2</sub>CO<sub>3</sub> matured separately from the IL phase for two days and [C<sub>12</sub>mim][NTf<sub>2</sub>]/Cs<sub>2</sub>CO<sub>3</sub> and [C<sub>12</sub>mim][NTf<sub>2</sub>]/Na<sub>2</sub>CO<sub>3</sub> aqueous phases just separated from the IL phase.

of raw autocorrelation function generated in our experiments is shown in Fig. 11. Polidispersity index (PDI) is a measure of the width of the particle size distribution. PDI scale ranges to 1 and PDI < 0.1 is usually referred as monodisperse. Calculations for this parameter are defined in the ISO standard document 13321:1996 E. All DLS measurements were performed at least in triplicate and the reported parameters (size and PDI) are averages calculated from multiple measurements of different samples at given experimental conditions.

Fourier transform infrared attenuated total reflectance (FTIR - ATR) spectroscopy was used to access information about conformation and interaction of solutes in aqueous phases of the biphasic systems. Measurements were performed on a IFS-66/S FTIR spectrometer from Bruker (Bruker Daltonics, MA, USA) using a single reflection ATR cell (DuraDisk). Acquisition was accomplished in the DTGS-detection mode using an accumulation rate of 258 scans at a resolution of 8 cm<sup>-1</sup> at room temperature in the spectral range of 4000–600 cm<sup>-1</sup> and was processed using the Opus software package (Bruker) with a wavenumber accuracy of 0.1 cm<sup>-1</sup>. As the aqueous phases were analyzed, Milli-Q water was scanned as a background spectra.

## 40 Conclusions

To the best of our knowledge, this work shows for the first time the spontaneous formation of nanoscale IL/W emulsions in a

basically two-component system consisting of an aqueous solution of inorganic salt and a water-immiscible IL. This phenomena highlights the unique versatility of the ILs – here the individual compartments of the IL have the characteristics of an oil (in their initial configuration) or of a surfactant (when combined with the aqueous inorganic ions). The emulsions are spontaneously formed under the action of low concentration of inorganic salts that promote non-equal partitioning of the IL cation and anion into the aqueous phase.

## Acknowledgments

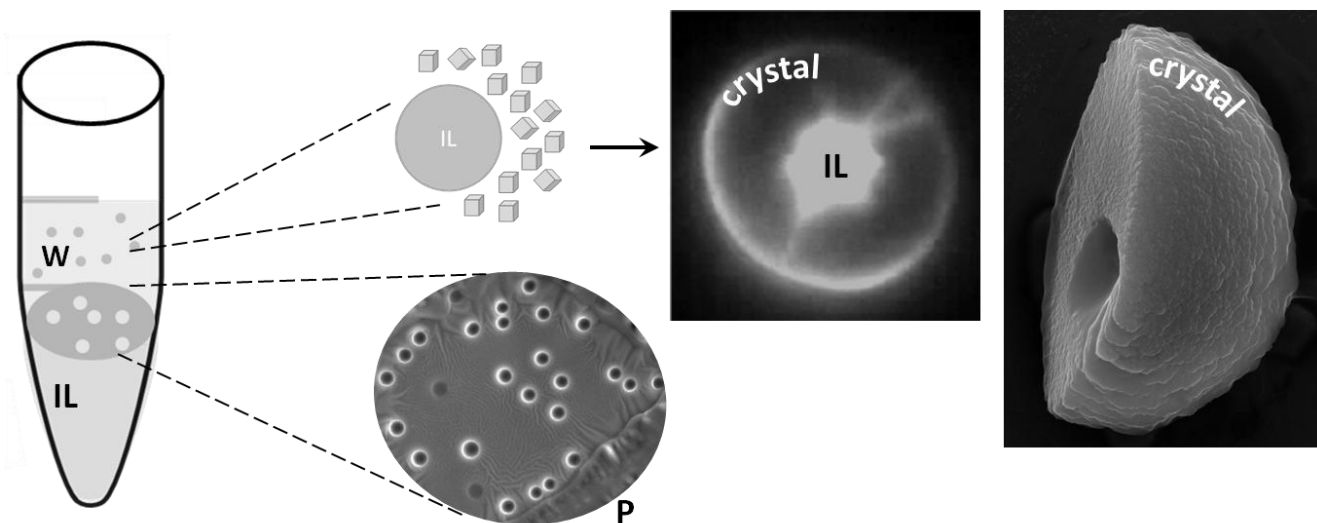
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## 60 Notes and references

- <sup>a</sup>Instituto de Tecnologia Química e Biológica, [www.itqb.unl.pt](http://www.itqb.unl.pt), Universidade Nova de Lisboa, Av. da República, 2780-157 Oeiras, Portugal. Fax: +351 - 21 4411 277; Tel: +351 - 21 4469 413 / 441; E-mail: [magda@itqb.unl.pt](mailto:magda@itqb.unl.pt), [luis.rebelo@itqb.unl.pt](mailto:luis.rebelo@itqb.unl.pt)
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Spontaneous emulsification in ionic liquid/water system (IL/W) imprinted in porous film (P) at the liquid/liquid interface and in crystalline shells encapsulating IL droplets.