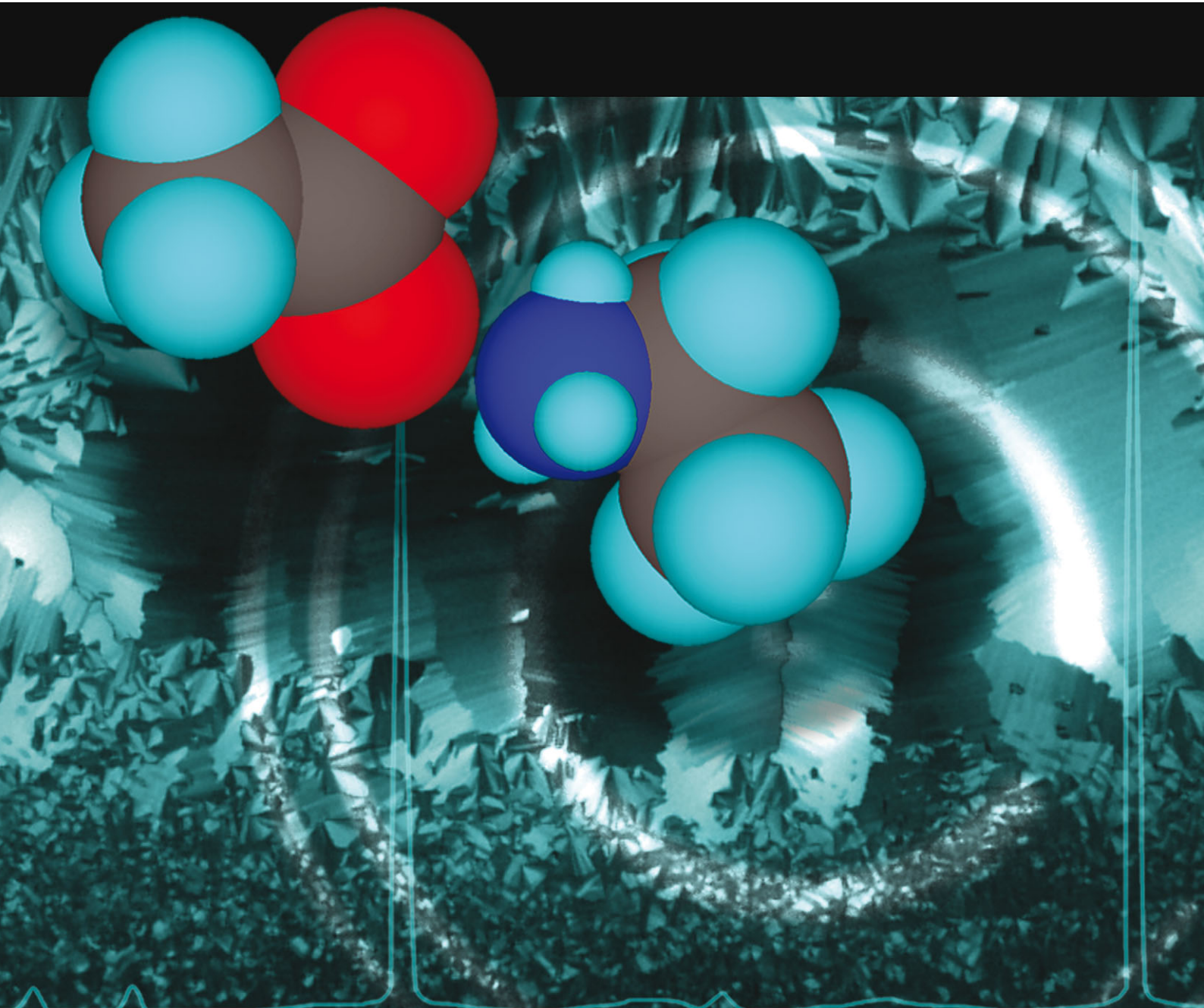


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## Solvent nanostructure, the solvophobic effect and amphiphile self-assembly in ionic liquids

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The ability of ionic liquids (ILs) to support amphiphile self-assembly into a range of mesophase structures has been established as a widespread phenomenon. From the ILs evaluated as self-assembly media, the vast majority have supported some lyotropic liquid crystal phase formation. Many neat ionic liquids have been shown to segregate into polar and non-polar domains to form a nanostructured liquid. A very strong correlation between the nanostructure of the ionic liquid and its characteristics as an amphiphile self-assembly solvent has been found. In this review we discuss ionic liquids as amphiphile self-assembly media, and identify trends that can be used to distinguish which ionic liquids are likely to have good promotion properties as self-assembly media. In particular these trends focus on the nanostructure of neat ionic liquids, their solvent cohesive energy density, and the related solvophobic effect. We forecast that many more ILs will be identified as amphiphile self-assembly solvents in the future.

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### Introduction

Until the last few years there had been a very limited number of solvents which were recognised as capable of promoting amphiphile self-assembly. Prior to 2006 we estimate there to have been 17 known solvents with this ability, of which all but

two were molecular solvents.<sup>1–17</sup> However, this number has been vastly increased since 2006 due mainly to the identification of the widespread ability of ionic liquids (ILs) to be self-assembly media for amphiphiles. Ionic liquids consist of ions and are liquid below 100 °C. For the purpose of this review, amphiphiles are defined as lipids, surfactants and block co-polymers.

It has now been well established that a broad range of ionic liquids are capable of promoting the self-assembly of amphiphiles.<sup>18</sup> In addition, it has recently been shown that many

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small molecular amides likewise are amphiphile self-assembly media.<sup>15</sup> These studies strongly indicate that there are many solvents containing small polar compositional elements which are amphiphile self-assembly media. Of these, the ionic liquids are the largest known class of solvents with the ability to promote amphiphile self-assembly. While to date only a small proportion of ILs have been trialled in this role, it is envisaged that many more will be identified in the future as possessing this ability. It is important to understand what solvent features are important to optimise this property for various amphiphiles and their end-applications.

A solvent characteristic of ionic liquids is that many form a segregated solvent liquid structure containing polar and non-polar domains.<sup>19</sup> This structure can, for example, be dependent on the length of the alkyl chain present on the cation or anion. For imidazolium cations a minimum of three carbons is required in the chain,<sup>20</sup> whereas for alkyl ammonium cations only two carbons is needed.<sup>21</sup>

The ability of an ionic liquid to form a polar and non-polar domain nanostructure is a good measure of how good a solvent it will be for the alkyl component of amphiphiles. Consequently, it has a very strong influence on the ability of amphiphiles to self-assemble in ionic liquids. For example, a simple change in the number of carbons in the alkyl chain on an ionic liquid cation can cause an amphiphile to be either soluble, form lyotropic liquid crystal phases or be insoluble.<sup>22,23</sup>

This review does not include amphiphilic ILs, which have a sufficiently long alkyl chain to undergo self-assembly in water or other solvents. There are many ambiguities in defining classes of ionic liquids, and one of them is defining the alkyl chain length at which an ionic liquid becomes an amphiphilic IL. This is particularly difficult since ILs with chains from two carbons can form phases reminiscent of lyotropic liquid crystal phases in the neat form,<sup>21,24</sup> and ILs with relatively short alkyl chains such as  $C_xMIm BF_4$  where  $x = 6, 8, 10$  have been shown to form micelles in water.<sup>25</sup> For this review we include ILs as the solvent media for amphiphile self-assembly only, and only include amphiphilic ILs if they have been used in an IL. It should also be noted that this review does not consider ionic liquid microemulsions,<sup>26</sup> the use of ionic liquids as amphiphiles in water or organic solvents, or the formation of nanospheres or other particles at an ionic liquid/water(or other) interface. The formation of micelles from ionic liquids as amphiphiles, and the use of ILs as modifiers for more conventional micellar systems has been reviewed by Smirnova *et al.*, and covers the literature up till late 2011.<sup>27</sup> Thermotropic ionic liquids was reviewed by Binnemans<sup>28</sup> up to late 2005 for amphiphilic ionic liquids.

In this review we explore the chemical structures of ionic liquids and identify which structural features lead to good self-assembly media, and which do not. We use these trends to identify which ionic liquids are potentially going to be good self-assembly media. The influence of the nanostructure of the ionic liquids is a focus, and correlated to the amphiphile self-assembly ability of the ionic liquids. There is a large volume of information on amphiphile self-assembly in water and the “hydrophobic effect”. We use this as a reference point

to explore amphiphile self-assembly in ILs and the “solvophobic effect”.

## Hydrophobic effect

There are many theories which address different aspects of the hydrophobic effect. For example macroscopic and microscopic views, different time scales, and different length scales have been considered.<sup>29–32</sup> Here the primary perspective has been to look at the thermodynamics associated with transferring small or large non-polar solutes into water (solvent), and how the formation of aggregates minimises the free energy of the system.

The energetically favourable separation of oil and water is known as the hydrophobic effect. This is the driving force for micellisation and other self-assembly processes of amphiphiles in water, as well as for the separation of oil and water. The Gibbs free energy for aggregation,  $\Delta G_{agg}$ , describes how likely a process is to occur, with negative values indicating a favourable free energy change. This is given by eqn (1), where  $\Delta H_{agg}$  is the enthalpic and  $-T\Delta S_{agg}$  the entropic contributions to the aggregation process, or separation of oil and water, and  $T$  is the temperature.

$$\Delta G_{agg} = \Delta H_{agg} - T\Delta S_{agg} \quad (1)$$

## Solubilising small and large non-polar solutes in water

When hydrophobic solutes are solubilised in water there are two main processes that occur. Firstly a cavity is produced, and then it is filled with the non-polar solute. The energy for cavity formation depends on the number of solvent molecules which have to be displaced in addition to the creation of a solvent–vapour interface.

For small cavities (<1 nm in water) the interfacial energy term is negligible compared to the energy associated with the displacement of solvent molecules. Therefore creating small cavities is dependent on the volume of the cavity,  $v$ , the density of the solvent,  $\rho$ , and fluctuations in the solvent density. For a given solvent, *e.g.* water, the free energy for small cavity formation is proportional to the volume of the cavity (*i.e.* the volume of the non-polar solute).<sup>29,33,34</sup> The water around a small non-polar solute is able to arrange itself so that there are no broken hydrogen bonds, and hence there is little enthalpy change. However, this imposes constraints on the orientations of the water molecules around the non-polar solutes which significantly increases the entropic contribution to the free energy by decreasing the entropy ( $\Delta S$ ) of the system (negative  $\Delta S$ , or positive  $-T\Delta S$ ). This results in a higher density of the water molecules surrounding the non-polar solutes compared to the bulk to maintain all the hydrogen bonds. The degree of water structuring around the non-polar solutes is temperature dependent and decreases with increasing temperature.<sup>35,36</sup>

The original paper by Frank and Evans<sup>37</sup> describes the increased density of the water around the non-polar solutes as being like an ‘iceberg’. Sometimes this has been taken literally in the literature, but generally it is accepted that the water is different around the non-polar solutes with increased density and constrained motion.



Rigid clathrate cages surrounding these nonpolar solutes have been considered by some groups such as Dias *et al.*,<sup>35</sup> though they qualify the use of the term that at room temperature incomplete cages would form which would be more complete with cooler temperatures. For most studies from around room temperature and higher the presence of such rigid structures are considered implausible.<sup>29</sup>

The shape of the non-polar solute does not influence the relationship between the Gibbs free energy of solubilisation,  $\Delta G_{\text{sol}}$ , and the molar volume for small molecular non polar solutes. This holds for branched, unbranched structures or functional groups such as for aliphatic alcohols, aromatic hydrocarbons and alkanes. Solubilising these in water led to a positive hydrophobic Gibbs free energy, which was due to a negative enthalpy and negative entropy for all of them.<sup>33,34</sup> However for polymers with non-polar branched groups the Gibbs free energy for hydration of the polymer cannot be obtained from the sum of them.<sup>36</sup>

The dynamics of the water with higher structure surrounding non-polar solutes has been shown to be slowed compared to bulk water.<sup>32</sup> The steric hindrance of the water being forced into constrained arrangements to maintain hydrogen bonding, sterically hinders a fifth water molecule from getting close so that it can disrupt the tetrahedral structure. It has been proposed that this results in less frequent restructuring, and it occurs in jumps rather than as a continuous process.<sup>32</sup>

For larger cavities (much larger than 1 nm in water) the energy associated with the formation of an interface dominates.<sup>29</sup> Hydrogen bonds need to be broken for water to create the large low-curvature interface for the larger cavities, which leads to a positive enthalpy term. For a large spherical cavity of radius  $R$  the Gibbs free energy for cavity formation,  $\Delta G_{\text{cav}}$ , is given by eqn (2), where  $\gamma$  is the surface tension of the water–air interface (for an empty cavity). The pressure term,  $4/3\pi R^3 p$ , is negligible for cavities on these length scales under standard pressure conditions and can be ignored, leading to eqn (3) which gives a measure of the Gibbs free energy required for cavity formation.<sup>29</sup>

$$\Delta G_{\text{cav}} \approx 4\pi R^2 \gamma + 4/3\pi R^3 p \quad (2)$$

$$\Delta G_{\text{cav}} \approx 4\pi R^2 \gamma \quad (3)$$

The important aspect of the thermodynamics of cavity formation is that there is a length scale dependence. The free energy of cavity formation is proportional to the cavity volume for small cavities, and proportional to area for large cavities. In water small cavities are those with a radius of  $< 1$  nm and large cavities have a radius of at least a few nm.<sup>36</sup>

Filling the cavity with non-polar species can be treated as taking non-polar species from water and moving them to the cavity. The free energy for filling the cavity with alkane chains is dependent on the difference in surface tension between the water–air surface tension and the water–oil surface tension.<sup>29,38</sup>

## Aggregation of non-polar solutes in water

Increasing the number of non-polar solutes present causes it to become energetically favourable for the solutes to

aggregate together. This leads to a favourable entropy contribution since the water molecules are no longer orientationally constrained. The non-polar solutes in aggregates have a decreased entropy (unfavourable), since they are constrained within the aggregate, but this is a much smaller effect compared to the entropy decrease of the water around individual molecules. While no longer orientationally constrained, the water surrounding these larger clusters can no longer maintain the same level of hydrogen bonding as in the bulk, or around individual non-polar molecules. This leads to energetically unfavourable enthalpy from the reduction in the number of hydrogen bonds. This enthalpy term is the dominant contribution to the Gibbs free energy for the non-polar aggregates and is proportional to the area of the aggregates, since it is dependent on the number of hydrogen bonds which need to be broken.<sup>29,36</sup>

A system of  $n$  spherical non-polar solutes with radius,  $r < 1$  nm in water has been used in this section as a simple model system to describe the favourable Gibbs free energy for these solutes to aggregate in water,  $\Delta G_{\text{agg}}$ . Since these solutes have  $r < 1$  nm, the Gibbs free energy,  $\Delta G_{\text{sol}}$ , for solubilising each molecule will be proportional to its molar volume,  $4/3\pi r^3$ , and for  $n$  solutes will be proportional to  $n4/3\pi r^3$ . Therefore there is a linear relationship between  $\Delta G_{\text{sol}}$  and the number of solutes, for solutes as individual molecules. For an aggregate of  $n$  solutes where the aggregate has a radius which is much greater than 1 nm, the Gibbs free energy,  $\Delta G_{\text{agg}}$ , is described by eqn (3), and is proportional to the surface area of the aggregate.

From Fig. 1, it is evident that for a certain amount of non-polar solute in solution it becomes energetically favourable for the solute species to aggregate. The difference between the two curves is the driving force for non-polar aggregation in water for sufficiently large numbers of solute species. It can also be seen from Fig. 1 that the driving force favours larger aggregates.

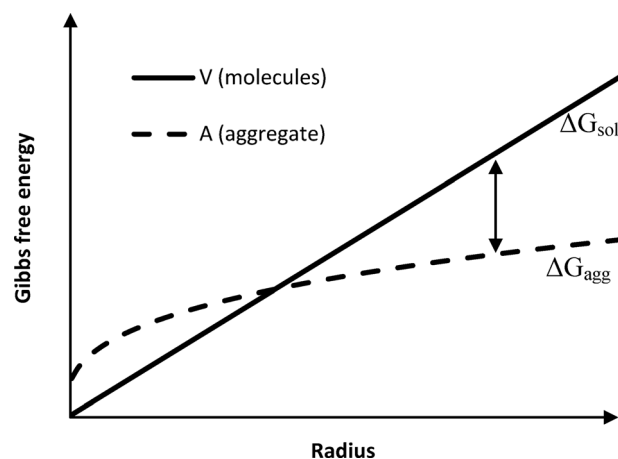


Fig. 1 Representation of the Gibbs free energy for  $n$  solutes as individually solubilised molecules in solution,  $\Delta G_{\text{sol}}$ , (solid line) and for an aggregate of  $n$  non-polar solutes,  $\Delta G_{\text{agg}}$ , (dashed line), as a function of the radius of the aggregate sphere  $n$ -solute would make.

## Hydrophobic effect for the aggregation of amphiphiles

The key difference between the aggregation of amphiphiles and non-polar solutes is the presence of a hydrophilic moiety connected to amphiphiles. This causes an unfavourable entropic term from constraining the hydrophobic portions such that the hydrophilic moieties are external,<sup>29</sup> and a size limitation imposed by keeping the hydrophilic moieties attached, which limits amphiphile clusters to mesoscale lengths.<sup>38</sup> Both of these factors restrict the size of the hydrophobic effect for amphiphiles compared to purely non-polar solutes.

The hydrophobic effect for solubilising amphiphiles in water has frequently treated the non-polar portion of the amphiphile as approximate in behaviour to the analogous non-polar molecule.<sup>29,38</sup> However, for block copolymers with a hydrophobic and hydrophilic block it was reported that the size of the hydrophilic group affected the size of the hydrophobic effect and the solvent conditions.<sup>39</sup>

While non-polar solutes can form aggregates which are not necessarily size limited, the size of amphiphile aggregates and the form of their specific structures may be restricted to depending on a number of factors, chiefly amphiphile shape and concentration. These structures are referred to as lyotropic liquid crystal phases, and a useful method to predict the phase is given by the critical packing parameter, CPP, which is described by eqn (4), where  $\nu$  is the average amphiphile volume,  $a$  is the effective head group area and  $l$  is the effective amphiphile chain length.<sup>40</sup>

$$\text{CPP} = \nu/al \quad (4)$$

The CPP gives an indication of the curvature of the liquid crystal phase, as the initial amphiphile geometrical shape governs the low concentration phase, and then as the amphiphile concentration increases the phase progression generally follows that shown for increasing CPP in Fig. 2.

## Nanostructure of ionic liquids

Within an ionic liquid there are many correlation length scales present between ion pairs which are generally less than 5 Å.

These are due to a variety of cation–anion, anion–anion and cation–cation interactions.<sup>42–44</sup> In this discussion we focus on correlations over larger length scales which generally arise due to alkyl chain segregation. The smaller length scale ion–ion interactions of anion–anion, anion–cation and cation–cation have been reviewed, with a focus on their interactions with solutes.<sup>45,46</sup> Ionic liquids which contain an alkyl chain on their cation or anion can segregate into polar and non-polar domains over an intermediate length scale of typically 8–20 Å. Whether or not this segregation occurs to a sufficient extent to be detectable depends on the type of cation (*e.g.* imidazolium, and primary, secondary and tertiary ammonium) and the length of the alkyl chain.<sup>20,47</sup>

A variety of experimental techniques have been used to show that ionic liquids have aggregated, most likely through segregation into non-polar and polar domains. These include using NMR,<sup>48–51</sup> Raman,<sup>52–55</sup> electrospray ionization mass spectrometry,<sup>56</sup> rheometry,<sup>57</sup> electron paramagnetic resonance,<sup>58</sup> Walden plots based on fluidity and conductivity,<sup>59</sup> molecular probes for polar and non-polar domains<sup>60,61</sup> and magnetic field effects.<sup>62</sup> Scattering techniques provide the most simple and direct measure of the size of the segregated domains. Simulations have been conducted which provides good insight into the degree of segregation and the possible morphology of the domains.<sup>19,63–66</sup> There are several reviews and perspective articles which discuss the nanostructure of ionic liquids.<sup>44,45,47,64,67–71</sup>

There have been a number of studies which have used small and wide angle X-ray scattering (SAXS/WAXS) or small angle neutron scattering (SANS) to get an estimate of the size of the segregated non-polar domains.<sup>47</sup> This involves using Bragg's Law,  $d \approx 2\pi/q_{\text{max}}$ , where  $d$  is the correlation length and  $q_{\text{max}}$  is the peak position at maximum intensity. These scattering techniques show that there is a correlation length which is consistent with the distance between two similarly charged ionic moieties separated by their alkyl chains. For ionic liquids with long alkyl chains (>5–12 carbons) the ionic liquids have been reported to form a smectic *A* phase intermediate between the crystalline and liquid phases, formed through segregation of the alkyl chains.<sup>72,73</sup> Fig. 3a and b shows the size of the segregated non-polar domain which has either been classified as a correlation length, or as a smectic *A* phase, plotted against the number of carbons in the alkyl chain,  $C_x$ , for (a) ILs containing

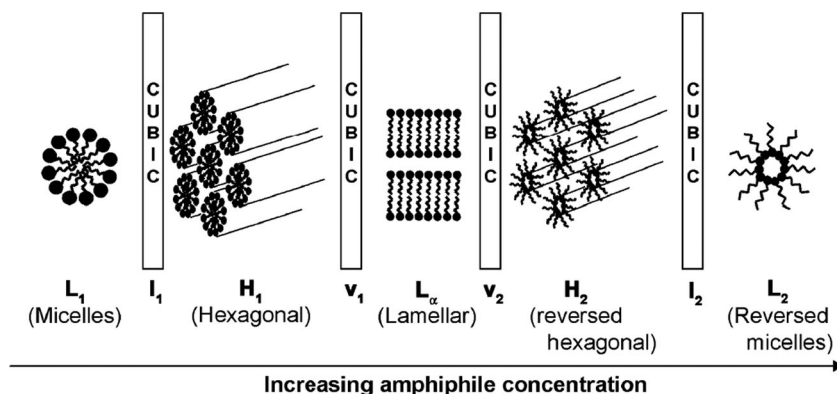
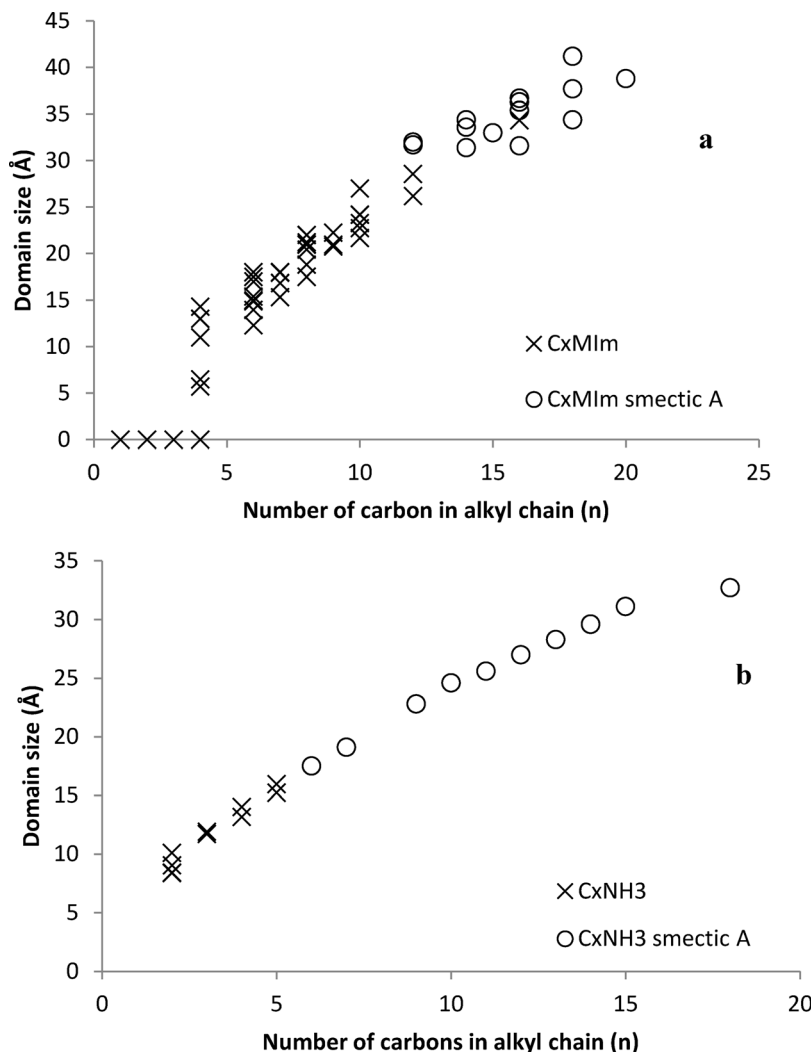


Fig. 2 Liquid crystal phase progression with increasing amphiphile concentration. (From ref. 41 – Reproduced by permission of the PCCP Ownership Board.)



**Fig. 3** Segregated non-polar domain size (correlation length) plotted against the number of carbons in the alkyl chain for ionic liquids containing (a)  $C_x\text{MIm}$  cations which have been classified with a correlation length<sup>20,74,77–84</sup> or as smectic A,<sup>73</sup> (b)  $C_x\text{NH}_3$  cations which have been classified with a correlation length<sup>21,24,75,76</sup> or as smectic A.<sup>72</sup>

a  $C_x\text{MIm}$  cation and (b) ILs containing a  $C_x\text{NH}_3$  cation respectively. It is evident that the trend of the non-polar domain size compared to the length of the alkyl chain is consistent across a wide range of alkyl chain lengths. The ionic liquids with alkyl chains long enough to drive segregation have been considered as forming bicontinuous networks of polar and non-polar domains.<sup>74</sup> The short chained ethylammonium nitrate (EAN) and propylammonium nitrate have been reported to form a  $L_3$ -sponge structure which is bicontinuous.<sup>75,76</sup> In comparison, the presence of a hydroxyl group on the ethyl chain for ethanolammonium nitrate led to small ion clusters.<sup>76</sup>

A similar trend is observed for the nanostructure of nearly all the ionic liquids which have been reported. Fig. 4 shows a plot of the size of the segregated domain against the number of carbons in the longest alkyl chain on the cation, including those which have been classified as smectic A. The data has been sorted by cation (Fig. 4a) and by anion (Fig. 4b) which highlights that both the cation and anion have an influence on

the nanostructure, even though for these ILs it is driven by segregation of the alkyl chains on the cation. It is evident from Fig. 4 that alkyl chains with as few as two carbons are sufficient for some cation moieties to lead to alkyl chain segregation.

There is a strong linear trend which is apparent from Fig. 4. For the ILs with one predominant alkyl chain on the cations ( $C_x\text{MIm}$ ,  $C_x\text{NH}_3$ ,  $C_x\text{Mpiperidinium}$  and  $C_x\text{Mpyrrolidinium}$ ) this trend corresponds to an increase of 1.87 Å per carbon in the alkyl chain. The  $P_{6,6,6,14}$  ionic liquid<sup>85</sup> has a much smaller non-polar size than expected based on a  $C_{14}$  chain, instead corresponding well to what would be expected for a  $C_6$  chain. This suggests that for this cation the three  $C_6$  alkyl chains are governing the size and accommodating the  $C_{14}$  alkyl chain. The dialkyl imidazolium ILs,  $(C_x)_2\text{Im}$  where there are two alkyl chains of the same length have in general a larger nanostructure when compared to their single chained counterparts.

From Fig. 4b, it appears that the anion does influence the nanostructure, though there are insufficient cases where the

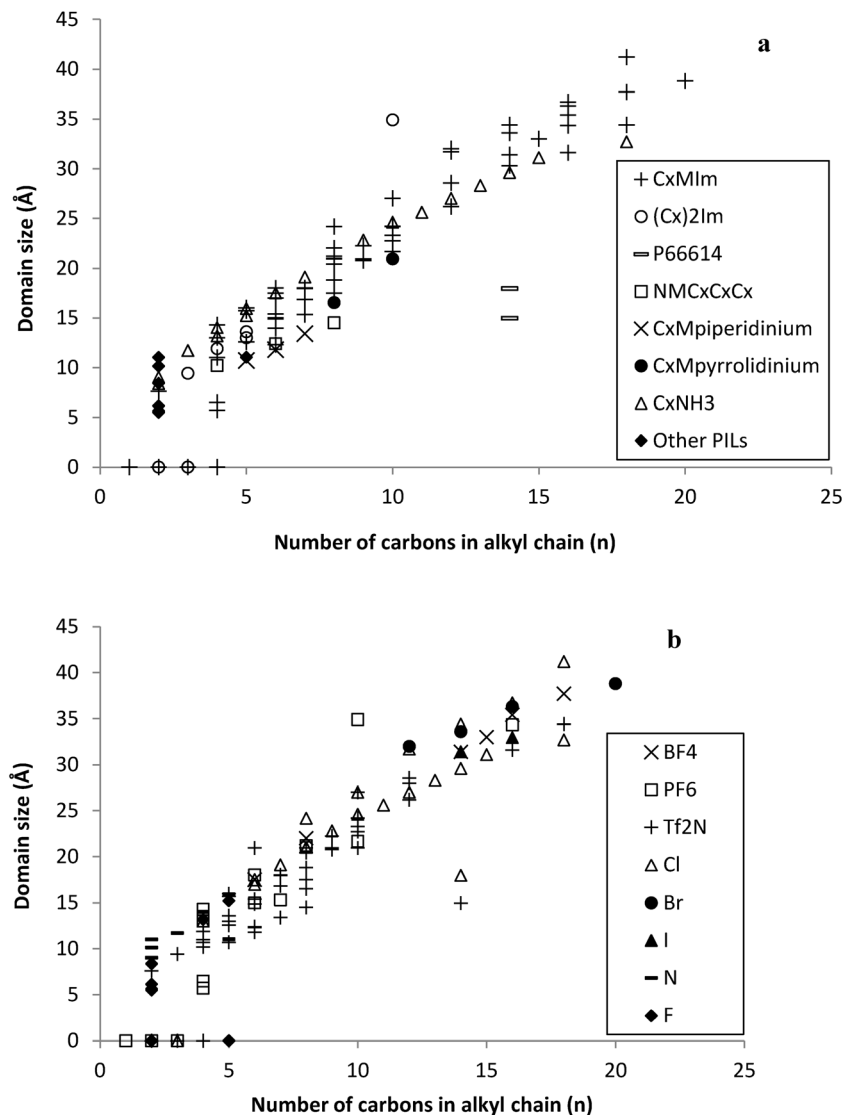


Fig. 4 Segregated non-polar domain size against the number of carbons in the longest alkyl chain on the cation sorted by (a) cation and (b) anion.

cation is the same and the anion varied to provide structure–property correlations. In general, it seems that the Cl anion leads to larger nanostructures than the Tf<sub>2</sub>N anion, which can be most clearly seen for the P<sub>6,6,6,14</sub> cation.

The structure of an ionic liquid can be dramatically reduced through the presence of a hydrophilic group at the end, or near the end, of the alkyl chain. This has been reported using hydroxyl groups,<sup>24,76</sup> methoxy groups<sup>24,65</sup> and ether chains.<sup>86</sup> Whether or not an ionic liquid has segregated into non-polar and polar domains has significant implications on its properties, particularly for how it interacts with solutes. This will be discussed in the following section.

It has also been reported that having alkyl chains present on the anion can lead to segregation of the ionic liquid into polar and non-polar domains.<sup>87–90</sup> A series of ionic liquids containing the EMIm cation have been reported where the ILs with  $x = 4, 6$  or  $8$  were structured according to SAXS/WAXS.<sup>87</sup> More complicated nanostructures have been reported where both the cation and anion can lead to segregation. Guanidinium sulfonate ionic

liquids with alkyl chains on both the cation and anion are reported as co-partitioning to form nanostructures,<sup>89</sup> and similarly for C<sub>x</sub>MIm alkylsulfonate ILs.<sup>91</sup> Ionic liquids containing an alkyl chain on a primary ammonium cation and a fluorocarbon chain on a carboxylate anion led to the IL containing polar, hydrocarbon and fluorocarbon domains.<sup>88</sup>

The formation of segregated phases for neat liquids is not unique to ionic liquids.<sup>92</sup> Primary alcohols form a variety of complex shapes over similar length scales to the ionic liquids,<sup>93–95</sup> as do some amides which have a sufficiently long alkyl chain.<sup>15</sup>

## Effect of nanostructure on ionic liquid–solute interactions

The interaction of ionic liquids with various solutes is complicated and depends on many possible interactions. Depending on the types of cations and anions the ionic liquid may be

hydrophilic or hydrophobic, and able to form weak or strong interactions with a solute, such as hydrogen bonds. In addition, whether or not the solute is polar, non-polar, and/or capable of hydrogen bonding will also have a significant impact on the IL–solute interactions.

The ability of an IL to segregate into polar and non-polar domains has a significant influence on its interactions with solutes. In particular, ILs which do not segregate can be considered as consisting predominately of a polar domain, and as this suggests, are poor solvents for non-polar solutes. Weakly structured ILs are likely to have limited non-polar solute solubility, and ILs which are highly structured are likely to have good non-polar solute solubility. In addition, the polar domain may be solvophobic or solvophilic, depending on the anion.

The early molecular simulation of BMIm PF<sub>6</sub> clearly showed the segregation of ILs into polar and non-polar domains, and the effect of adding the solutes water, methanol, acetonitrile and hexane.<sup>19</sup> This simulation study showed that the specific position of the solute within the ionic liquid was highly dependent on the polarity of the solute. Water was only located in the polar domain, hexane only in the non-polar domain while acetonitrile and methanol interacted with both domains.<sup>19</sup>

Experimental studies have confirmed these findings. Water has been shown to be located in the polar region,<sup>96–101</sup> and the degree of interaction between the IL ions and the water is highly dependent on the anion, where the interaction ranges from significant to the formation of water pools.<sup>96,99–105</sup> The nanostructure of ionic liquids, and other chemical properties associated with the ionic liquid, have been shown to be retained to high levels of added water, with little change.<sup>96–100,105,106</sup> Amphiphilic ILs mixed with water have a strong tendency to form micelles or other liquid crystal phases, which is outside the scope of this review (*e.g.* ref. 107).

Small alcohol solutes are partially located in the polar and partially in the non-polar domains.<sup>108,109</sup> The addition of small *n*-alcohol molecules<sup>105,108–111</sup> and other organic solvents<sup>112</sup> disrupted the IL nanostructure significantly more than water, and has been reported to influence the size of the non-polar domains.<sup>109</sup> The interactions of various organic solutes in BMIm PF<sub>6</sub> has previously been reported based on rotational relaxation spectroscopy, which showed more specific interactions compared to other associated solvents such as glycerol.<sup>113</sup> Non-polar solutes such as hexane and benzene, have been experimentally shown to be only located in the non-polar domain.<sup>109</sup> The octanol–water partition coefficients for ILs has been reported to increase with increasing alkyl chain length, which is consistent with the increasing size of the non-polar domain.<sup>114</sup>

The use of ionic liquids as solvents for the synthesis of a diverse range of nanostructures has been reported.<sup>115,116</sup> The IL can be present as a solvent, an additive, a self-assembly media, an amphiphile (for amphiphilic ILs), and as a template. The presence of nanostructure in ILs with very small alkyl chains enables their use as templates for small pore sizes. The segregated domains in ILs have been used as co-templates with the Pluronic block copolymer, P123, PEO–PPO–PEO ((EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub>) to form hierarchical mesoporous silica in ethylammonium

nitrate (EAN).<sup>116</sup> A bimodal pore distribution was obtained with average sizes of 10 and 45 Å which were due to the EAN and P123, respectively.

The shape of the cation has a significant impact on the nanostructure. For examples, Blesic *et al.*, reported the differences between ILs containing imidazolium and phosphonium type cations, with the former leading to a string like nanostructure, and the latter a more globular type structure.<sup>117</sup> Therefore, the more globular non-polar regions in the phosphonium ILs would be expected to accommodate more non-polar solutes, which was found to be the case in that study.<sup>117</sup> Similarly, *n*-alcohols were miscible in phosphonium ILs, but only partially soluble in imidazolium type ILs.

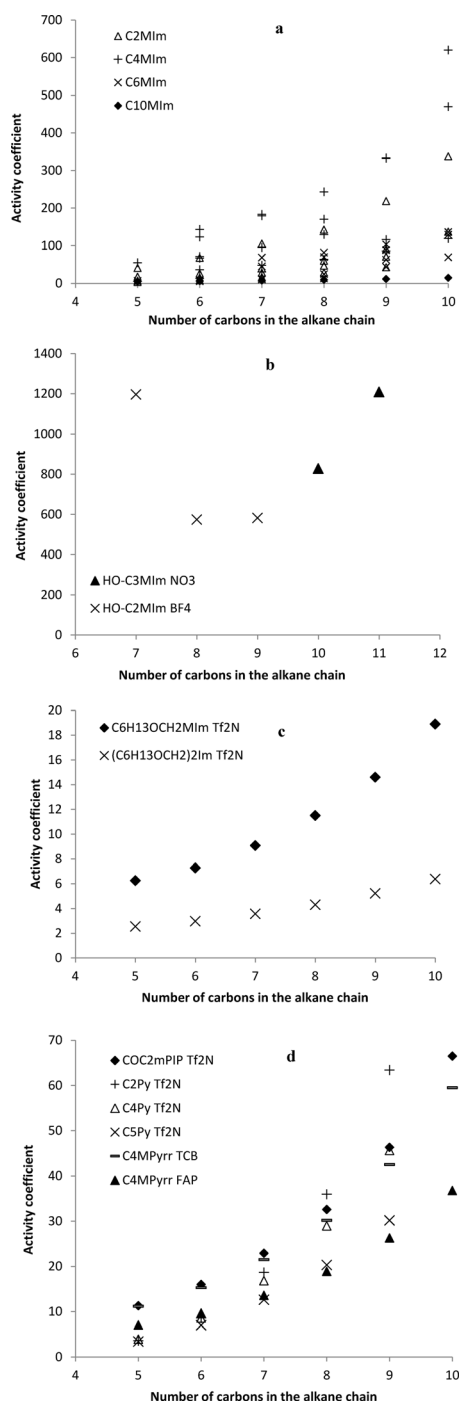
## Non-polar solutes in ionic liquids

The solvophobic effect, like the hydrophobic effect, will be driven by the low solubility of non-polar solutes or portions of solutes in the solvent. Therefore, the interaction of non-polar solutes with an ionic liquid gives an indication of whether there is likely to be an energetically favourable solvophobic effect. The activity coefficient at infinite dilution gives a measure of the interaction between an ionic liquid and a solute, with large activity coefficients corresponding to small solute–solvent interactions. The activity coefficients at infinite dilution for a large range of solutes, between highly non-polar and highly polar in ionic liquids, have been reported.

A small sample of activity coefficients for alkanes from pentane to decane are represented in Fig. 5a for a range of C<sub>x</sub>MIm containing ionic liquids, Fig. 5b and c for ionic liquids with imidazolium cations containing a hydroxyl or methoxy group in the alkyl chain respectively and Fig. 5d for other cyclic IL cations. The measurement temperatures, and references, are given in the figure caption. It is evident from Fig. 5a that there is a strong trend that with increasing alkyl chain length on the imidazolium cation there is greater interaction with the alkyl chain (smaller activity coefficient), and also that with increasing length of the carbon chain of the alkane solute there is less interaction with the IL (larger activity coefficient). This corresponds well to the increase in size of the non-polar segregated domain in the ionic liquid, with larger non-polar alkyl chains more able to interact with the alkyl chain of the solutes. The solubility of carbon dioxide, ethane and butane in C<sub>x</sub>MIm Tf<sub>2</sub>N ILs was shown to increase with increasing *x*, which was attributed to the increase in the non-polar domain sizes.<sup>61</sup> The enthalpies were comparable with increasing *x*, but the entropy became more favourable, hence the increased solubility was due to the size of non-polar domains and not to more favourable interactions between the solutes and the alkyl chains of the ionic liquids. The butane was more soluble than ethane, which due to more negative enthalpies for the solubilisation of butane compared to ethane showed more favourable IL–solute interactions.<sup>61</sup> Therefore, larger non-polar domains are entropically more favourable to non-polar solutes due to providing more variations for the location of the solutes.

It is more difficult to identify trends in the activity coefficients in Fig. 5b or c for imidazolium ILs containing a hydroxyl or methoxy





**Fig. 5** Activity coefficients for the alkanes of pentane to dodecane plotted against the number of carbons in the alkane chain in (a) ILs containing a  $C_2\text{MIm}$ ,<sup>118–121</sup>  $C_4\text{MIm}$ ,<sup>120,122–127</sup>  $C_6\text{MIm}$ <sup>120,124,128–130</sup> or  $C_{10}\text{MIm}$ <sup>131</sup> cation, (b) ILs containing imidazolium cations with hydroxyl groups on the alkyl chains,  $\text{HO-C}_3\text{MIm NO}_3$  (1,2-hydroxypropyl-3-methylimidazolium nitrate)<sup>127</sup> and  $\text{HO-C}_2\text{MIm BF}_4$  (1,2-hydroxyethyl-3-methylimidazolium nitrate),<sup>132</sup> (c) ILs containing imidazolium cations with methoxy groups in the alkyl chain,  $\text{C}_6\text{H}_{13}\text{OCH}_2\text{MIm Tf}_2\text{N}$  (1,3-hexyloxymethyl-imidazolium  $\text{Tf}_2\text{N}$ ),<sup>133</sup>  $(\text{C}_6\text{H}_{13}\text{OCH}_2)_2\text{MIm Tf}_2\text{N}$  (1,3-dihexyloxymethyl-imidazolium  $\text{Tf}_2\text{N}$ )<sup>133</sup> and (d) ILs containing other cyclic cations of  $\text{COC}_2\text{mPIP Tf}_2\text{N}$  (1-(2-methoxyethyl)-1-methylpiperidinium  $\text{Tf}_2\text{N}$ ),<sup>134</sup>  $\text{C}_2\text{Py Tf}_2\text{N}$  (*N*-alkylpyridinium  $\text{Tf}_2\text{N}$ ),<sup>135</sup>  $\text{C}_4\text{MPyrr TCB}$  (1-butyl-1-methylpyrrolidinium tetracyanoborate)<sup>136</sup> and  $\text{C}_4\text{MPyrr FAP}$  (1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate).<sup>137</sup>

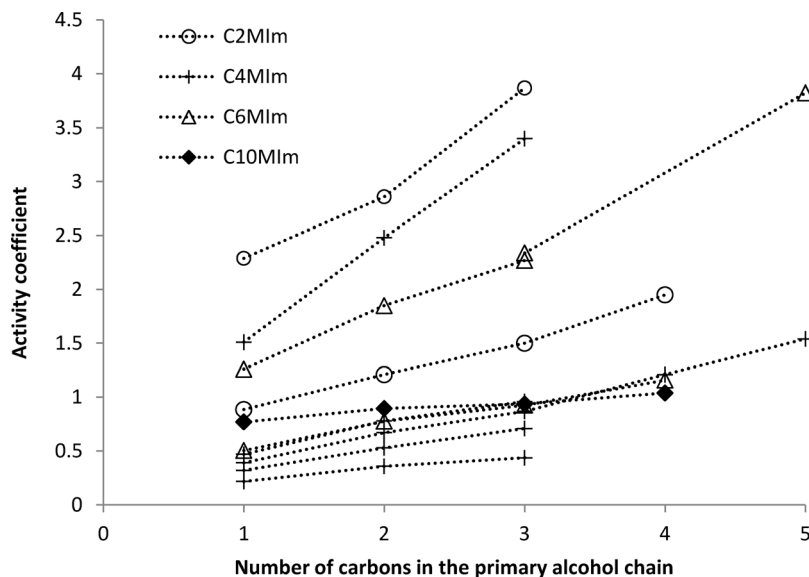
group due to the limited data available. It is expected that the presence of a methoxy or hydroxyl group would decrease the ionic liquids ability to interact with the alkanes, and hence lead to higher activity coefficients. For the  $\text{C}_6\text{H}_{13}\text{OCH}_2\text{MIm Tf}_2\text{N}$  and  $(\text{C}_6\text{H}_{13}\text{OCH}_2)_2\text{Im Tf}_2\text{N}$  ionic liquids the methoxy group is close to the imidazolium ring, ending with a C6 alkyl chain. The activity coefficients for these two ionic liquids were effectively the same as  $\text{C}_6\text{MIm Tf}_2\text{N}$ . In contrast, the  $\text{HO-C}_3\text{MIm NO}_3$  has the hydroxyl group terminating the alkyl chain, which did lead to a higher activity coefficient than expected for a  $\text{C}_3\text{MIm NO}_3$ . Interestingly, the  $\text{HO-C}_2\text{MIm BF}_4$  had unusual behaviour with the activity coefficients decreasing with increasing alkyl chain length of the alkane. The other cyclic ionic liquids, which are shown in Fig. 5d, had increasing activity coefficients with small alkyl chains on the ionic liquid, or with the presence of a methoxy group. The type of cyclic ring appears to have minimal influence, whereas the anion has a significant impact.

For comparison, the activity coefficients for primary alcohols in  $\text{C}_x\text{MIm}$  are given in Fig. 6. These cations were paired with a broad range of anions, and for each IL there was a linear relationship with increasing length of the alkyl chain on the primary alcohol. The values are significantly smaller (about 100 times) for the alcohols compared to the alkanes, which is attributed to greater IL–solute interactions for the alcohols due to hydrogen bonding.

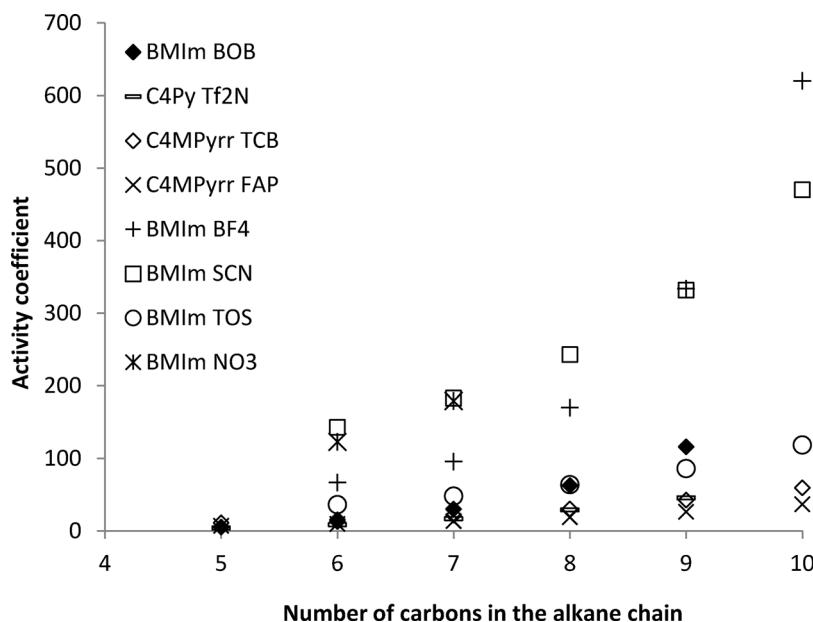
The anion clearly has a strong influence on the interaction of the ionic liquid with alkanes, and hence on the activity coefficients. To further explore this, the activity coefficients for alkanes in ionic liquids containing a butyl alkyl chain are provided in Fig. 7. Assuming that anions have a greater influence than the differences between the cations then it can be inferred that the IL–alkane interactions are weaker for  $\text{BF}_4$ ,  $\text{SCN}$  and  $\text{NO}_3$ , intermediate for  $\text{BOB}$  and  $\text{TOS}$  and stronger for  $\text{FAP}$ ,  $\text{TCB}$ ,  $\text{Tf}_2\text{N}$ . While there is limited data to compare, it appears that there is a trend that small hydrophilic anions lead to weak interactions with alkanes, whereas larger and more hydrophobic anions lead to greater interactions.

For the ionic liquids to exhibit a high solvophobic effect we would anticipate that they would require a low interaction with the alkanes, which would lead to a good driving force for the segregation of the alkane from the ionic liquid. Of the ionic liquids in Fig. 5 and 6 we are only aware of  $\text{BMIm BF}_4$  which has been reported as capable of supporting amphiphile self-assembly. It has a low interaction with alkanes, as reflected in high activity coefficients. In addition, the activity coefficient appears to increase at a far greater rate than most of the ionic liquids, which may lead to significantly weak interactions for chain lengths of typical amphiphiles. While not included in the figures, the activity coefficients for  $\text{P}_{6,6,6,14}(\text{C}_2\text{F}_5)_3\text{P}$  had the lowest activity coefficients, and hence greatest interaction with the ionic liquid. Hence it is likely to have a very weak solvophobic effect.

A few trends can be identified, based on these activity coefficients, for chemical structural features of ionic liquids which are likely to lead to weak interactions with alkanes, and hence more likely to have a large solvophobic effect. These include short alkyl chains, the presence of hydroxyls terminating the alkyl chains, and small hydrophilic anions.



**Fig. 6** Activity coefficients for primary alcohols from methanol to 1-hexanol plotted against number of carbons in ILs containing a  $C_2MIm$ ,<sup>118,120,121</sup>  $C_4MIm$ ,<sup>120,122–127</sup>  $C_6MIm$ <sup>120,124,128–130</sup> or  $C_{10}MIm$ <sup>131</sup> cation. The dotted lines connect the data for each specific IL.



**Fig. 7** Activity coefficients for alkanes in ionic liquids with a C4 alkyl chain, BMIm BOB (1-butyl-methylimidazolium bis(oxalato)borate),<sup>120</sup>  $C_4Py Tf_2N$  (*N*-alkylpyridinium  $Tf_2N$ ),<sup>135</sup>  $C_4MPyrr TCB$  (1-butyl-1-methylpyrrolidinium tetracyanoborate)<sup>136</sup> and  $C_4MPyrr FAP$  (1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate),<sup>137</sup> BMIm  $BF_4$ ,<sup>124</sup> BMIm SCN (BMIm thiocyanate),<sup>125</sup> BMIm TOS (BMIm tosylate)<sup>126</sup> and BMIm  $NO_3$ .<sup>127</sup>

In water, an important component of the hydrophobic effect is associated with the thermodynamics of the transfer of non-polar solutes into water, the Gibbs free energy,  $\Delta G_{sol}$ , is positive, indicating it is an unfavourable process along with negative enthalpy ( $\Delta H$ ) and negative entropy ( $\Delta S$ ).<sup>138,139</sup> The thermodynamics for non-polar solutes in select ionic liquids has a similar behaviour.  $\Delta G_{sol}$  associated with transferring *n*-alkanes into ionic liquids containing a  $C_xMIm$  cation has been reported as possessing a large positive value, which indicates weak solute–IL interactions.<sup>137</sup> For the addition of

alcohols the Gibbs free energy tends to be positive, but smaller than for the alkanes.<sup>118,134,136</sup> The Gibbs free energy increases with increasing chain length on the *n*-alkane solute or alcohol. The addition of alkanes has a negative entropic contribution.<sup>118,134,136</sup> In contrast the addition of alcohols leads to high positive excess entropies which indicates that hydrogen bonds are breaking.<sup>118,134,136</sup> The enthalpies on addition of alkanes or alcohols increases with increasing carbon chain length and are positive, indicating weak solvent–solute interactions.<sup>118,134,136</sup> The greater interactions for the IL with the alcohols in comparison

to the alkanes can be attributed to their ability to hydrogen bond. The transfer of small non-polar gases into the protic ionic liquid EAN was reported in 1981 and showed similar behaviour between EAN and water, with a lower Gibbs free energy for transferring non-polar gases into EAN compared to water.<sup>138</sup> The thermodynamic properties associated with dissolving methane, ethane or butane were similar in behaviour in EAN compared to water. The interaction of smaller non-polar solutes in  $C_n\text{Mim Tf}_2\text{N}$  ionic liquids has been investigated using ethane and butane as probes.<sup>61</sup> As expected, it was found that the solubilities of these gases increased with increasing alkyl chain length on the cation, and that the non-polar solutes resided in the segregated non-polar region of the IL. The thermodynamics associated with these small non-polar solutes in EAN and  $C_x\text{Mim Tf}_2\text{N}$  ILs were similar to those associated with the larger non-polar solutes in the ILs discussed above, in that the enthalpy and entropy terms were both negative.

## Ionic liquids as amphiphile self-assembly media

The ability of a solvent to support amphiphile self-assembly is an unusual property, but not limited to water. The solvophobic effect is considered analogous to the hydrophobic effect, and is the more general description for the aggregation of alkyl groups in a solvent. There have been a number of non-aqueous molecular polar solvents which have been reported as amphiphile self-assembly solvents. These include the small glycol solvents of glycerol,<sup>1-4</sup> ethylene glycol,<sup>1,5,6</sup> 1,3-propanediol,<sup>2</sup> 1,2-propanediol,<sup>2</sup> 1,4-butanediol,<sup>2</sup> 1,3-butanediol,<sup>2</sup> small amides consisting of formamide,<sup>1-4,6-15</sup> *N*-methylformamide,<sup>4,15</sup> *N*-methylacetamide,<sup>7</sup> *N,N*-dimethylformamide,<sup>2,4,6-8,15</sup> *N*-ethylformamide,<sup>15</sup> *N*-pentylformamide,<sup>15</sup> *N*-(2-hydroxyethyl)acetamide,<sup>15</sup> *N*-tetrabutylformamide,<sup>15</sup> *N,N*-diethylacetamide,<sup>15</sup> and other solvents including hydrazine,<sup>7,8</sup> *N*-methylsydnone,<sup>16,17</sup> dimethyl sulfoxide,<sup>6,7</sup> formic acid,<sup>2</sup> 2-aminoethanol,<sup>2</sup> 1-amino-2-propanol,<sup>2</sup> 2-mercaptoethanol,<sup>2</sup> ethylene diamine<sup>2</sup> and acetonitrile.<sup>6</sup>

In addition to the molecular solvents it has been well established that many ionic liquids and molten salts share this ability. This was first reported in the late 1960's for the molten salt pyridinium chloride,<sup>140-144</sup> and in the early 1980's for the protic ionic liquid ethylammonium nitrate (EAN).<sup>145-147</sup> Since then it has been reported that at least 37 protic ionic liquids (PILs) with an ammonium head group are amphiphile self-assembly media,<sup>148-150</sup> with EAN being the most commonly reported PIL.<sup>148-154</sup> In addition at least 11 aprotic ionic liquids (AILs) have been reported as amphiphile self-assembly solvents, consisting of BMIm BF<sub>4</sub>,<sup>152,155-166</sup> BMIm Cl,<sup>167</sup> BMIm PF<sub>6</sub>,<sup>156,160,165-173</sup> BMIm Tf<sub>2</sub>N,<sup>156,174</sup> EMIm Tf<sub>2</sub>N,<sup>168,175,176</sup> EMIm EtSO<sub>4</sub>,<sup>152</sup> EOMIm Br,<sup>177,178</sup> MOMIm Br,<sup>177,178</sup> bis(2-hydroxyethyl)dimethylammonium methane sulfonate [BHEDA] [MeSO<sub>3</sub>],<sup>152,179</sup> 1-butyl-1-methylpyrrolidinium dicyanamide [BMPyr][DCA],<sup>152</sup> 1-allyl-MIm Cl,<sup>180</sup> and C<sub>6</sub>MIm BF<sub>4</sub> + EMIm BF<sub>4</sub> mixed-IL system.<sup>23,181</sup>

Previously reviews have been published on the self-assembly of amphiphiles in non-aqueous molecular solvents<sup>182</sup> and in ionic liquids.<sup>18,27,166,183</sup> These reviews provide specific details about the ionic liquids and surfactants which have been reported, and the lyotropic liquid crystal phases which have been observed up to early 2008. All the main lyotropic liquid crystal phases which are found in aqueous systems have been reported in ionic liquids including micellar, cubic micellar, normal bicontinuous cubic, normal hexagonal, lamellar, inverse hexagonal, inverse bicontinuous cubic and inverse micellar.

The solubility and self-assembly of various polymers in ILs has been previously reviewed.<sup>184</sup> It was shown that the Lewis basicities of the anions were important for the solubilities of the polymers. For some of the polymers, the ILs appeared to have increased structure surrounding the polymer, similar to water around non-polar species.

The majority of the ionic liquids evaluated as amphiphile self-assembly media have this property, though not necessarily with all the surfactants in the investigation. Therefore, while only a small fraction of the number of possible ionic liquids have been reported as being self-assembly media, we can extrapolate that many more will be found to possess this ability. A focus of this review is in identifying what are the key chemical structural features and physico-chemical properties which are likely to lead to ionic liquids being good amphiphile self-assembly media.

## Solvent cohesion

A very important solvent feature for a solvent to be an amphiphile self-assembly media is a high cohesive energy density.

**Table 1** Gordon parameters of molecular solvents capable of supporting amphiphile self-assembly

Molecular solvent	<i>G</i> value (J m <sup>-3</sup> )
Water	2.743 <sup>185</sup>
	2.750 <sup>17</sup>
Formamide	1.50 <sup>185</sup>
	1.70 <sup>17</sup>
Ethylene glycol	1.20 <sup>185</sup>
Glycerol	1.51 <sup>186</sup>
Hydrazine	2.1 <sup>185</sup>
<i>N</i> -Methylformamide	1.01 <sup>15</sup>
<i>N</i> -Ethylformamide	0.84 <sup>15</sup>
<i>N</i> -Pentylformamide	0.59 <sup>15</sup>
<i>N</i> -(2-Hydroxyethyl)acetamide	1.16 <sup>15</sup>
<i>N,N</i> -Diethylacetamide	0.64 <sup>15</sup>
<i>N,N</i> -Dimethylformamide	0.91 <sup>15</sup>
<i>N-tert</i> -Butylformamide	0.53 <sup>15</sup>
1,3-Propanediol	1.18 <sup>2,187</sup>
3-Methylsydnone	1.4 <sup>185</sup>
1,2-Propanediol	0.91 <sup>2,187</sup>
1,4-Butanediol	1.06 <sup>2,187</sup>
1,3-Butanediol	0.87 <sup>2,187</sup>
<i>N</i> -Methylacetamide	0.73 <sup>187,188</sup>
Dimethylsulfoxide	1.03 <sup>187,189</sup>
Formic acid	1.14 <sup>2,187</sup>
2-Aminoethanol	1.47 <sup>2,187</sup>
1-Amino-2-propanol	0.85 <sup>2,187</sup>
2-Mercaptoethanol	0.98 <sup>2,187</sup>
Ethylenediamine	1.06 <sup>2,187</sup>
Acetonitrile	0.76 <sup>187,189</sup>

Table 2 Gordon parameters of ionic liquids

Ionic liquid	G value (J m <sup>-3</sup> )
[Me(EG) <sub>2</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	0.534 (25) <sup>190</sup>
[C <sub>1</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	0.583 (25) <sup>190</sup>
[C <sub>2</sub> C <sub>1</sub> Im][BF <sub>4</sub> ]	1.004 (25) <sup>190</sup>
	1.006 (25) <sup>191,192</sup>
	1.013 (24) <sup>193</sup>
[C <sub>2</sub> C <sub>1</sub> Im][EtSO <sub>4</sub> ]	0.846 (25) <sup>152,191a</sup>
[C <sub>2</sub> C <sub>1</sub> Im][FAP]	0.510 (25) <sup>194</sup>
[C <sub>2</sub> C <sub>1</sub> Im][NPF <sub>2</sub> ]	0.502 (24) <sup>193</sup>
[C <sub>2</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	0.613 (25) <sup>191a</sup>
	0.598 (24) <sup>193</sup>
	0.552 (25) <sup>190a</sup>
[C <sub>3</sub> C <sub>1</sub> Im][BF <sub>4</sub> ]	0.920 (24) <sup>193</sup>
[C <sub>3</sub> C <sub>1</sub> Im][Glu]	1.006 (25) <sup>195</sup>
[C <sub>3</sub> C <sub>1</sub> Im][NO <sub>3</sub> ]	1.008 (24) <sup>193</sup>
[C <sub>3</sub> C <sub>1</sub> Im][NPF <sub>2</sub> ]	0.478 (24) <sup>193</sup>
[C <sub>3</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	0.552 (24) <sup>193</sup>
[C <sub>4</sub> C <sub>1</sub> Im][BF <sub>4</sub> ]	0.818 (24) <sup>193</sup>
	0.815 (25) <sup>191a</sup>
[C <sub>4</sub> C <sub>1</sub> Im][NO <sub>3</sub> ]	0.904 (24) <sup>193</sup>
[C <sub>4</sub> C <sub>1</sub> Im][NPF <sub>2</sub> ]	0.453 (24) <sup>193</sup>
[C <sub>4</sub> C <sub>1</sub> Im][Cl]	0.885 (25) <sup>196,197a</sup>
[C <sub>4</sub> C <sub>1</sub> Im][FAP]	0.457 (25) <sup>194</sup>
[C <sub>4</sub> C <sub>1</sub> Im][PF <sub>6</sub> ]	0.824 (25) <sup>191a</sup>
[C <sub>4</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	0.463 (25) <sup>190</sup>
[C <sub>4</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	0.526 (24) <sup>193</sup>
[C <sub>5</sub> (C <sub>1</sub> Im) <sub>2</sub> ][NPF <sub>2</sub> ]	0.446 (24) <sup>193</sup>
[C <sub>5</sub> (C <sub>1</sub> Im) <sub>2</sub> ][Tf <sub>2</sub> N]	0.523 (24) <sup>193</sup>
[C <sub>5</sub> C <sub>1</sub> Im][BF <sub>4</sub> ]	0.726 (24) <sup>193</sup>
[C <sub>5</sub> C <sub>1</sub> Im][NO <sub>3</sub> ]	0.743 (24) <sup>193</sup>
[C <sub>5</sub> C <sub>1</sub> Im][NPF <sub>2</sub> ]	0.437 (24) <sup>193</sup>
[C <sub>5</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	0.503 (24) <sup>193</sup>
[C <sub>6</sub> (C <sub>1</sub> Im) <sub>2</sub> ][NPF <sub>2</sub> ]	0.438 (24) <sup>193</sup>
[C <sub>6</sub> (C <sub>1</sub> Im) <sub>2</sub> ][Tf <sub>2</sub> N]	0.510 (24) <sup>193</sup>
[C <sub>6</sub> C <sub>1</sub> Im][BF <sub>4</sub> ]	0.654 (24) <sup>193</sup>
[C <sub>6</sub> C <sub>1</sub> Im][Cl]	0.722 (25) <sup>196,197a</sup>
[C <sub>6</sub> C <sub>1</sub> Im][FAP]	0.431 (25) <sup>194</sup>
[C <sub>6</sub> C <sub>1</sub> Im][NO <sub>3</sub> ]	0.674 (24) <sup>193</sup>
[C <sub>6</sub> C <sub>1</sub> Im][NPF <sub>2</sub> ]	0.419 (24) <sup>193</sup>
[C <sub>6</sub> C <sub>1</sub> Im][PF <sub>6</sub> ]	0.626 (20,25) <sup>67,198a,b</sup>
[C <sub>6</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	0.438 (25) <sup>190</sup>
	0.491 (24) <sup>193</sup>
	0.490 (24) <sup>193</sup>
[C <sub>8</sub> (C <sub>1</sub> Im) <sub>2</sub> ][Tf <sub>2</sub> N]	0.480 (40,20) <sup>191b</sup>
[C <sub>8</sub> C <sub>1</sub> Im][BF <sub>4</sub> ]	0.414 (25) <sup>190</sup>
[C <sub>8</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	0.430 (25) <sup>199,200</sup>
[C <sub>8</sub> C <sub>1</sub> Im][TCB]	0.565 (25) <sup>190</sup>
[C <sub>8</sub> C <sub>1</sub> Im][BF <sub>4</sub> ]	0.485 (25) <sup>190</sup>
[C <sub>8</sub> C <sub>1</sub> Im][FAP]	0.402 (25) <sup>190</sup>
[C <sub>8</sub> C <sub>1</sub> Im][MeOSO <sub>3</sub> ]	0.462 (25) <sup>190</sup>
[C <sub>8</sub> C <sub>1</sub> Im][NO <sub>3</sub> ]	0.535 (25) <sup>190</sup>
[C <sub>8</sub> C <sub>1</sub> Im][PF <sub>2</sub> N]	0.372 (25) <sup>190</sup>
[C <sub>8</sub> C <sub>1</sub> Im][PF <sub>6</sub> ]	0.499 (25) <sup>190</sup>
[C <sub>8</sub> C <sub>1</sub> Im][TfO]	0.425 (25) <sup>190</sup>
[C <sub>8</sub> C <sub>1</sub> Im][Br]	0.512 (25) <sup>190</sup>
[C <sub>8</sub> C <sub>1</sub> Im][Cl]	0.505 (25) <sup>190</sup>
[C <sub>8</sub> C <sub>1</sub> Im][I]	0.521 (25) <sup>190</sup>
[C <sub>9</sub> (C <sub>1</sub> Im) <sub>2</sub> ][BF <sub>4</sub> ]	0.635 (24) <sup>193</sup>
[C <sub>9</sub> (C <sub>1</sub> Im) <sub>2</sub> ][NPF <sub>2</sub> ]	0.418 (24) <sup>193</sup>
[C <sub>9</sub> (C <sub>1</sub> Im) <sub>2</sub> ][Tf <sub>2</sub> N]	0.480 (24) <sup>193</sup>
[C <sub>10</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	0.402 (25) <sup>190</sup>
[C <sub>10</sub> (C <sub>1</sub> Im) <sub>2</sub> ][BF <sub>4</sub> ]	0.606 (24) <sup>193</sup>
[C <sub>10</sub> (C <sub>1</sub> Im) <sub>2</sub> ][NPF <sub>2</sub> ]	0.410 (24) <sup>193</sup>
[C <sub>10</sub> (C <sub>1</sub> Im) <sub>2</sub> ][Tf <sub>2</sub> N]	0.469 (24) <sup>193</sup>
[C <sub>12</sub> (C <sub>1</sub> Im) <sub>2</sub> ][BF <sub>4</sub> ]	0.563 (24) <sup>193</sup>
[C <sub>12</sub> (C <sub>1</sub> Im) <sub>2</sub> ][NPF <sub>2</sub> ]	0.396 (24) <sup>193</sup>
[C <sub>12</sub> (C <sub>1</sub> Im) <sub>2</sub> ][Tf <sub>2</sub> N]	0.451 (24) <sup>193</sup>
[C <sub>12</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	0.396 (25) <sup>190</sup>
[P <sub>6,6,6,14</sub> ][FAP]	0.308 (25) <sup>198</sup>
[C <sub>4</sub> C <sub>1</sub> Pyrr][Tf <sub>2</sub> N]	0.481 (25) <sup>190</sup>
[C <sub>2</sub> Pyrr][Tf <sub>2</sub> N]	0.592 (25) <sup>201</sup>

Table 2 (continued)

Ionic liquid	G value (J m <sup>-3</sup> )
[C <sub>4</sub> Pyrr][Tf <sub>2</sub> N]	0.507 (25) <sup>201</sup>
[C <sub>5</sub> Pyrr][Tf <sub>2</sub> N]	0.484 (25) <sup>201</sup>
[C <sub>1</sub> NH <sub>3</sub> ][Formate]	1.041 (27) <sup>149</sup>
[C <sub>2</sub> NH <sub>3</sub> ][Formate]	0.997 (25) <sup>150</sup>
[C <sub>2</sub> NH <sub>3</sub> ][HSO <sub>3</sub> ]	1.540 (25) <sup>150</sup>
[C <sub>2</sub> NH <sub>3</sub> ][NO <sub>3</sub> ]	1.060 (27) <sup>149</sup>
	1.3 (25) <sup>185</sup>
[C <sub>2</sub> NH <sub>3</sub> ][formate]	0.867 (27) <sup>149</sup>
[C <sub>2</sub> NH <sub>3</sub> ][butyrate]	0.576 (27) <sup>149</sup>
[C <sub>2</sub> NH <sub>3</sub> ][glycolate]	1.056 (27) <sup>149</sup>
[C <sub>2</sub> NH <sub>3</sub> ][lactate]	0.793 (27) <sup>149</sup>
[C <sub>2</sub> NH <sub>3</sub> ][propionate]	0.644 (27) <sup>149</sup>
[C <sub>2</sub> NH <sub>3</sub> ][HSO <sub>3</sub> ]	1.215 (27) <sup>149</sup>
[OHC <sub>2</sub> NH <sub>3</sub> ][acetate]	1.099 (27) <sup>149</sup>
[OHC <sub>2</sub> NH <sub>3</sub> ][formate]	1.448 (27) <sup>149</sup>
[OHC <sub>2</sub> NH <sub>3</sub> ][HSO <sub>3</sub> ]	1.698 (25) <sup>150</sup>
[OHC <sub>2</sub> NH <sub>3</sub> ][lactate]	1.149 (27) <sup>149</sup>
[OHC <sub>2</sub> NH <sub>3</sub> ][NO <sub>3</sub> ]	1.097 (27) <sup>149</sup>
[(C <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> ][formate]	0.775 (25) <sup>150</sup>
[(C <sub>2</sub> ) <sub>3</sub> NH][formate]	0.812 (25) <sup>150</sup>
[(OHC <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> ][formate]	1.185 (25) <sup>150</sup>
[C <sub>4</sub> NH <sub>3</sub> ][formate]	0.669 (27) <sup>149</sup>
[C <sub>5</sub> NH <sub>3</sub> ][formate]	0.614 (27) <sup>149</sup>
[(C <sub>1</sub> -O-C <sub>2</sub> )NH <sub>3</sub> ][formate]	0.891 (25) <sup>150</sup>
[(C <sub>1</sub> (C <sub>1</sub> C <sub>2</sub> )NH <sub>3</sub> ][formate]	0.629 (27) <sup>149</sup>
[(C <sub>2</sub> (C <sub>1</sub> C <sub>2</sub> )NH <sub>3</sub> ][formate]	0.596 (27) <sup>149</sup>
[C <sub>1</sub> (OH)C <sub>2</sub> NH <sub>3</sub> ][formate]	0.977 (27) <sup>149</sup>
[(OH-C <sub>2</sub> -O-C <sub>2</sub> )NH <sub>3</sub> ][formate]	1.032 (25) <sup>150</sup>
[(OH-C <sub>2</sub> -O-C <sub>2</sub> )NH <sub>3</sub> ][HSO <sub>3</sub> ]	1.094 (25) <sup>150</sup>
[(OH-C <sub>2</sub> -O-C <sub>2</sub> )NH <sub>3</sub> ][NO <sub>3</sub> ]	1.223 (25) <sup>150</sup>
[(OH-C <sub>2</sub> -O-C <sub>2</sub> )NH <sub>3</sub> ][TFA]	0.733 (25) <sup>150</sup>
[Alanine ethyl ester][formate]	0.586 (23) <sup>202</sup>
[Alanine ethyl ester][glycolate]	0.874 (23) <sup>202</sup>
[Alanine ethyl ester][NO <sub>3</sub> ]	0.927 (23) <sup>202</sup>
[Alanine methyl ester][glycolate]	0.978 (23) <sup>202</sup>
[Glycine ethyl ester][formate]	0.728 (23) <sup>202</sup>
[Glycine ethyl ester][lactate]	0.804 (23) <sup>202</sup>
[Proline methyl ester][acetate]	0.523 (23) <sup>202</sup>
[Proline methyl ester][formate]	0.565 (23) <sup>202</sup>
[Proline methyl ester][glycolate]	0.651 (23) <sup>202</sup>
[Proline methyl ester][lactate]	0.541 (23) <sup>202</sup>
[Proline methyl ester][NO <sub>3</sub> ]	0.991 (23) <sup>202</sup>

<sup>a</sup> References in that reference. <sup>b</sup> Temperatures of (surface tension, density). Pyr = pyridinium. Pyrr = pyrrolidinium.

In water it leads to the increased structure around small non-polar solutes to maintain hydrogen bonds, and to the high water-oil surface tension for the interface surrounding non-polar clusters. Both of these are an integral component of the hydrophobic effect.

The cohesive energy density of a solvent can be described in a number of different ways. A useful measure for discussions involving water, non-aqueous molecular solvents and ionic liquids is to use the Gordon parameter.<sup>18,139</sup> The Gordon parameter is given by eqn (5), where  $\gamma_{LV}$  is the air-liquid surface tension and  $V_m$  is the molar volume. Table 1 contains a summary of the Gordon parameters for molecular solvents which have been reported as amphiphile self-assembly media. Table 2 contains a summary of Gordon parameters for ionic liquids where the surface tension and density have been reported. It should be noted that not all the ionic liquids in Table 2 have been reported as amphiphile self-assembly media and most appear not to have been trialled.



$$G = \gamma_{LV}/(V_m^{1/3}) \quad (5)$$

High solvent cohesive densities are frequently associated with solvents which are capable of forming a hydrogen-bond network. There has been significant literature on whether or not the solvent is required to form a hydrogen-bond network in order to promote amphiphile self-assembly. Studies by Evans *et al.*<sup>185</sup> into aprotic solvents such as 3-methylsydnone found no evidence of amphiphile aggregation which led the group to the conclusion that a protic solvent was required. However, since then 3-methylsydnone has been shown to have self-assembly ability and hence a network of hydrogen bonding is not a requisite property.<sup>16,17</sup> Cassel *et al.* reported on the self-assembly in the aprotic 3-methylsydnone and commented that the discrepancy between studies is due to the Krafft temperature being solvent and surfactant dependent, and hence higher temperatures were required to observe amphiphile self-assembly in 3-methylsydnone.<sup>17</sup> It has been suggested that in aprotic ionic liquids there is an ionic network, instead of a hydrogen bonded network, and thus they are still structured around surfactant alkyl chains.<sup>157</sup> There are a significant number of aprotic polar solvents which are known self-assembly media, as listed in Table 1, in addition to the aprotic ionic liquids.

It has been argued that the Gordon parameter is a better indication of a solvent's solvophobic effect, as measured by the Gibbs energy of micellisation,  $\Delta G_{mic}$ , than the polarity or dielectric constant.<sup>203</sup> The cohesive energy density reflects a solvent's ability to solubilise an amphiphile aligned with the extent of intermolecular forces required to overcome the solvent-solvent interactions.

The relationship of the Gordon parameter to the size of the segregated domain is shown in Fig. 8a. The ionic liquids on the figure are sorted by those which have been reported as amphiphile self-assembly media, those which have been shown to not support amphiphile self-assembly, and those which have not had an evaluation reported. It should be noted that the ILs reported as not supporting amphiphile self-assembly may subsequently be found to do so with amphiphiles other than the ones trialled, perhaps using longer chained amphiphiles, or at higher temperatures. There is a scarcity of ILs where both the size of the segregated non-polar domain and the density (for the Gordon parameter) have been reported, and what is readily available has been provided in Fig. 8a. To extend this data set, in Fig. 8b the Gordon Parameter is plotted against the number of carbons in the longest alkyl chain on the IL. From Fig. 8 there is an evident trend where the Gordon Parameter decreases with increasing size of the non-polar segregated domain, or with increasing alkyl chain length. The highest reported Gordon parameter for an IL is  $1.448 \text{ J m}^{-3}$  for ethanolammonium formate.<sup>149</sup> The smallest Gordon parameter reported for an IL which supports amphiphile self-assembly is  $0.576 \text{ J m}^{-3}$  for ethylammonium butyrate.<sup>204</sup> It appears that most ILs fall within this range of Gordon parameters, and hence it is forecast that many more ILs will be identified as amphiphile self-assembly solvents in the future, dependent on trialling a broad range of amphiphiles and temperatures.

Gordon Parameters are calculated based on the surface tension and density of the solvent. Therefore the Gordon Parameters will be dependent on the experimental technique used to measure the surface tension or density, the temperature, and the water concentration and other impurities in the IL. For example, the broad range of reported IL surface tension values can be seen in the review by Tariq *et al.*<sup>196</sup>

## Amphiphile micellisation in ionic liquids

The formation of micelles comprising self-assembled amphiphiles has been reported in a variety of ionic liquids. The critical micelle concentration (CMC) is the minimum amphiphile concentration for micelles to form in the solution, and is a good way to get an indication of the solvophobic interaction.

The CMCs for the non-ionic alkyl polyoxyethylene surfactants,  $C_{12}E_m$ , in ionic liquids and molecular solvents are shown in Fig. 9. The most prominent feature from Fig. 9 is the two orders of magnitude difference between the CMC values in the ILs or molecular solvents compared to water. This huge difference is due to the weaker solvophobic interaction in these solvents compared to the hydrophobic effect in water. To a large extent this is due to the higher hydrocarbon solubility in the ILs, which reflects the significant proportion of alkyl chains present in the solvent, which in turn lead to non-polar domains.

Ionic liquids which have no segregated non-polar domains, or only a weak structure, have very poor solubility with these  $C_nE_m$  surfactants to the extent that it is not possible to dissolve enough to reach the CMC. Consequently they remain below the Krafft boundary, which is the "solubility boundary of surfactants".<sup>205</sup> This has been reported for  $C_{12}E_6$  being immiscible in  $C_2\text{Mim BF}_4$ ,<sup>23</sup> and for  $C_{12}E_m$  ( $m = 3-8$ ) in the protic ionic liquids ethanolammonium formate, pentanolammonium formate, pentanolammonium nitrate and ethylammonium formate.<sup>22</sup> In contrast, if the ionic liquids have a large, well structured non-polar domain then the solubility of the  $C_nE_m$  surfactants is too high, which leads to a weak solvophobic interaction and no micelle formation. This has been reported for  $C_{12}E_6$  in  $C_6\text{Mim BF}_4$ ,<sup>23</sup>  $C_{14}E_8$  in  $C_4\text{Mim Tf}_2\text{N}$ ,<sup>156</sup> and  $C_{12}E_m$  ( $m = 3-8$ ) in protic ionic liquids butylammonium nitrate, propylammonium nitrate, pentylammonium formate and pentylammonium nitrate.<sup>22</sup>

Consequently, whether or not ionic liquids have a non-polar segregated domain, and how large and structured it is, has a significant impact on whether  $C_nE_m$  surfactants will form micelles in an ionic liquid. The solvophobic effect can be optimised through mixing ILs to obtain a suitable hydrocarbon solubility. For example,  $C_{12}E_6$  in  $C_2\text{Mim BF}_4$  is immiscible, and no micelles detected in  $C_6\text{Mim BF}_4$ , however the mixture of  $C_2\text{Mim BF}_4$  with  $C_6\text{Mim BF}_4$  enabled micelle formation.<sup>23</sup> It appears that for ILs with a  $C_x\text{Mim}$  cation that the optimal chain length for micelle formation of  $C_nE_m$  surfactants is around  $x = 4$ . A similar phenomenon was observed for protic ionic liquids, with micelles being detected in those with a comparable degree of nanostructure to  $\text{BMim BF}_4$ , namely butylammonium formate, diethylammonium formate, ethanolammonium nitrate, triethylammonium formate and propylammonium nitrate.<sup>22</sup>

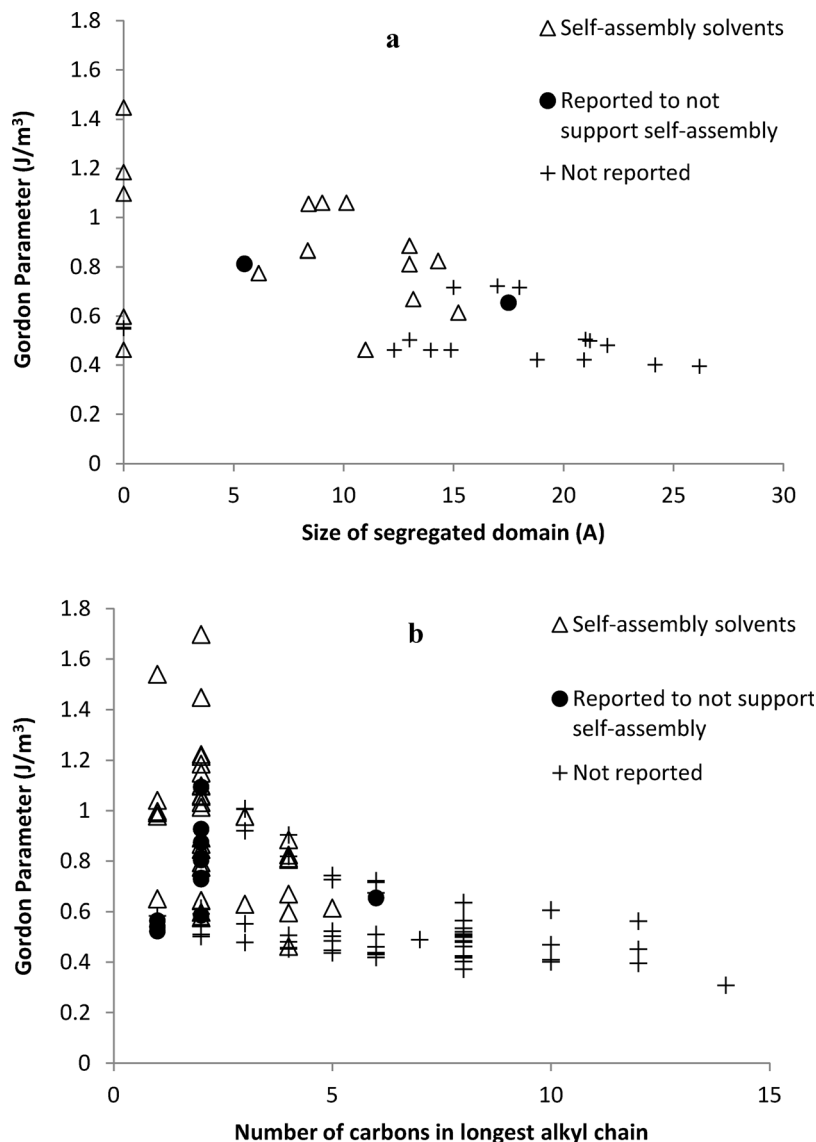


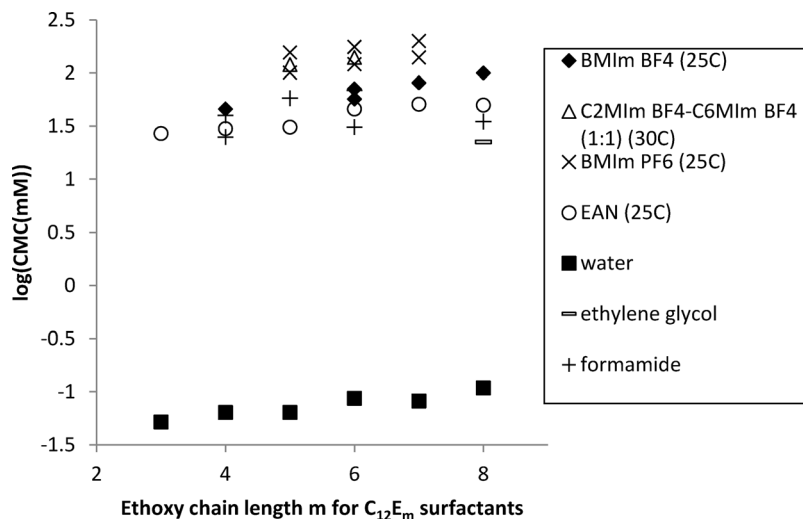
Fig. 8 (a) Gordon parameter ( $G$ ) versus size of segregated non-polar domain for ILs. (b)  $G$  versus number of carbons in alkyl chain of ILs.

The interaction of ionic amphiphiles in ILs is complicated by the electrostatic shielding of the amphiphile headgroups. This effect favours the micellisation process, and thus decreases the CMC. The CMCs of  $C_x$ TAB amphiphiles in ionic liquids are shown in Fig. 10, along with water and other molecular solvents for comparison. It is apparent that the CMC in water is generally lower than in the ILs, but by a much smaller amount than for the non-ionic amphiphiles shown in Fig. 9. Therefore for the  $C_x$ TAB amphiphiles the CMC increase due to the lower hydrocarbon solubility in the ILs is similar to the CMC decrease due to the electrostatic shielding. The CMC of the molecular solvents is similar to that of most of the ILs. For all the ILs and the molecular solvents the CMCs decrease with increasing amphiphile alkyl chain length due to the greater solvophobic interaction.

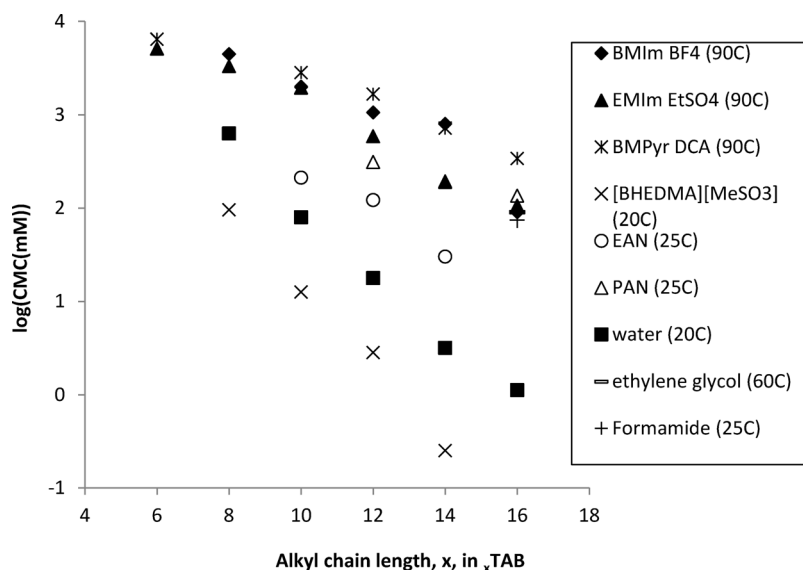
Competitive counter-ion exchange is also an important consideration if the self-assembled surfactant has a different counter-ion to those present in the IL.<sup>18,149</sup>

As can be seen from Fig. 10, the CMC increased with increasing non-polar domain size for propylammonium nitrate compared to ethylammonium nitrate,<sup>146,206</sup> and somewhat for EMIm EtSO<sub>4</sub> compared to BMIm BF<sub>4</sub>.<sup>152</sup> It is expected that [BHEDA][MeSO<sub>3</sub>], which has the structure (OH-C<sub>2</sub>)<sub>2</sub>(C<sub>1</sub>)<sub>2</sub>N C<sub>1</sub>SO<sub>3</sub>, would not form segregated non-polar domains, which is consistent with its low CMC values, which interestingly are about six times smaller than those in water.<sup>152</sup>

The CMC's of ionic amphiphiles in EAN are shown in Fig. 11, along with comparison values for water. It is evident that the CMC's are consistently higher in EAN than in water, similar to what was observed for  $C_x$ TAB amphiphiles shown in Fig. 10. The CMC's for propylammonium nitrate were reported for  $C_x$ PyrCl and these have been included in Fig. 11, and as expected the CMC's are higher in PAN, which we attribute predominantly to the higher hydrocarbon solubility due to the larger non-polar domain. The CMC's of  $C_x$ MIm Br varied



**Fig. 9** Log(CMC) of  $C_{12}E_m$  amphiphiles in ionic liquids plotted against  $m$  for  $C_4MIm BF_4$ ,<sup>156,157</sup>  $C_2MIm BF_4$ - $C_6MIm BF_4$  (1 : 1),<sup>23</sup>  $C_4MIm PF_6$ ,<sup>171</sup> and EAN.<sup>22</sup> The molecular solvents of water, ethylene glycol and formamide were included for comparison and references are given within ref. 22.



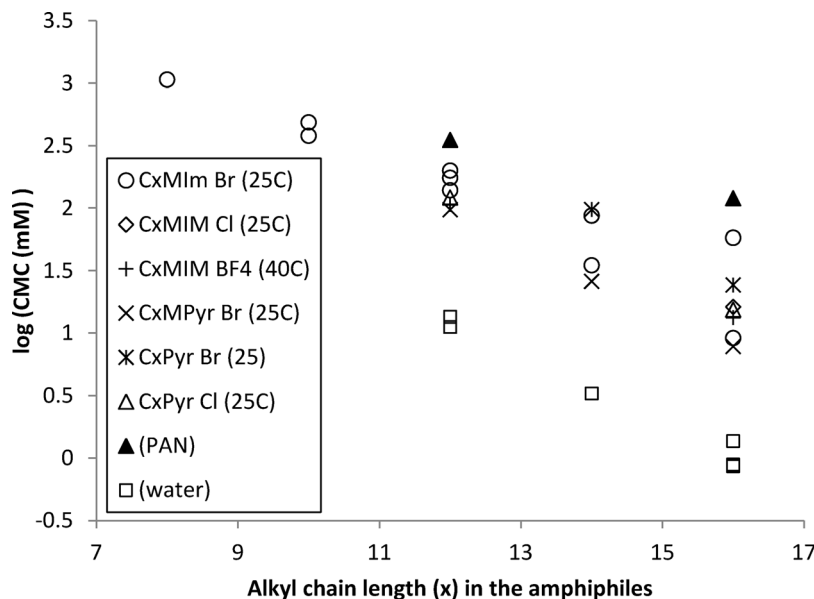
**Fig. 10** Log(CMC) of  $C_xTAB$  surfactants plotted against the number of carbons ( $x$ ) in the surfactant in BMIm BF<sub>4</sub>,<sup>152</sup> EMIm EtSO<sub>4</sub>,<sup>152</sup> BMPyr DCA (1-butyl-1-methylpyrrolidinium dicyanamide),<sup>152</sup> BHEDA MeSO<sub>3</sub> (bis(2-hydroxyethyl)dimethylammonium methanesulfonate),<sup>152</sup> EAN,<sup>146,206</sup> PAN<sup>206</sup> and water.<sup>152</sup> Other molecular solvents have been included for comparison  $C_{16}TAB$  and the references are given in ref. 7. (Note: the PAN values were converted from mol kg<sup>-1</sup> using a density estimate of 1.2 g ml<sup>-1</sup>.)

substantially in different publications, and for  $x = 16$  the CMC values differ by a factor greater than six, though the data was reported under the same conditions. This highlights the importance of reporting the water content, and any other impurities, present in the ILs. The CMC of the  $C_{12}MIm$  Br amphiphile in various molecular solvents has also been reported, where the CMC went formamide > dimethylformamide > acetonitrile > DMSO > water, and no micelles were formed in ethylene glycol.<sup>6</sup>

The anion also has a significant influence on the ability of the IL to support amphiphile self-assembly, which can be seen for the comparison of the hydrophilic and hydrophobic BMIm BF<sub>4</sub> and BMIm PF<sub>6</sub>. Investigations of these two ILs with non-ionic surfactants have shown that the solvophobic interaction

is weaker in BMIm PF<sub>6</sub>,<sup>171</sup> and it was suggested this might be due to a weaker interaction between the BMIm cation and the PF<sub>6</sub> anion, though from Table 2 it is evident that these two ILs have similar Gordon parameters for solvent cohesive energy density.

The Hofmeister series describes the effect of specific salts on aqueous colloidal systems, and many others. This series is related to how kosmotropic or chaotropic the salt ions are. Kosmotropic ions have a low polarisability and remain strongly hydrated, whereas chaotropic ions are highly polarisable, and hence can minimise energy by being located at an interface through redistributing their charge to remain within the bulk aqueous phase. Chaotropic ions tend to increase hydrocarbon



**Fig. 11** Log(CMC) of ionic amphiphiles in EAN plotted against the number of carbons in the alkyl chain of the surfactant (AmlL) for  $C_x$ MIm Br,<sup>207–209</sup>  $C_x$ MIm Cl,<sup>210</sup>  $C_x$ MIm BF<sub>4</sub>,<sup>209,210</sup>  $C_x$ MPyr Br,<sup>162</sup>  $C_x$ Pyr Br,<sup>146,147</sup>  $C_x$ Pyr Cl.<sup>206</sup> For comparison, ionic amphiphiles in water have been included for  $C_x$ MIm Cl,<sup>210</sup>  $C_x$ MIm BF<sub>4</sub>,<sup>210</sup>  $C_x$ MPyr Br<sup>211</sup> and  $C_x$ Pyr Cl.<sup>206</sup> Similarly, the CMC of  $C_x$ Pyr Cl in PAN has been included and denoted PAN.<sup>206</sup> Many of these amphiphiles are amphiphilic ILs.

solubility through locating at the aqueous–oil interface, and hence decrease the solvophobic effect in water. In contrast, kosmotropic ions favour aggregation of hydrocarbons in aqueous phases.<sup>212</sup> In the Hofmeister series, the PF<sub>6</sub><sup>−</sup> anion is more chaotropic than BF<sub>4</sub><sup>−</sup>, which may be contributing to the weaker solvophobic effect in BMIm PF<sub>6</sub> compared to BMIm BF<sub>4</sub>. However, it is not known how transferable the Hofmeister series will be to ions within ionic liquids compared to aqueous systems.

Micellisation studies with a series of related amphiphiles with various alkyl chain lengths can be used to obtain the contribution of the polar heads and CH<sub>2</sub> groups to the micellisation. Plots of log(CMC) vs. the number of CH<sub>2</sub> groups in the amphiphile alkyl chain generally provide a linear graph where the intercept represents the head group and terminal CH<sub>3</sub> contribution and the gradient the contribution per CH<sub>2</sub> group. This behaviour can be described by eqn (6), where *A* is the head group and terminal CH<sub>3</sub> contribution, *B* the contribution per CH<sub>2</sub> group and *n<sub>c</sub>* the number of CH<sub>2</sub> carbons.<sup>17,206</sup>

$$\log(\text{CMC}) = A - Bn_c \quad (6)$$

The parameter *A* gives a measure of the solvent–head group interaction, with smaller values leading to lower CMC values. For parameter *B*, larger values indicate a stronger solvophobic interaction. A summary of the *A* and *B* values for various IL–amphiphile systems is provided in Table 3. As mentioned in the table, there are quite a few systems where the analysis is based on only two data points.

In general, it can be seen that the values of *B* are smaller in the ILs than in water, for the same amphiphile, which is consistent with generally a lower solvophobic interaction in the ILs. The exception is for  $C_x$ TAB in [BHEDA][MeSO<sub>3</sub>] which

has a value for *B* of 0.42 compared to  $C_x$ TAB in water with *B* of 0.33. The longer chained PAN compared to EAN had significantly smaller *B* values, indicating the much weaker solvophobic interaction in PAN which is consistent with it having higher hydrocarbon solubility through the longer alkyl group on the ammonium cation.

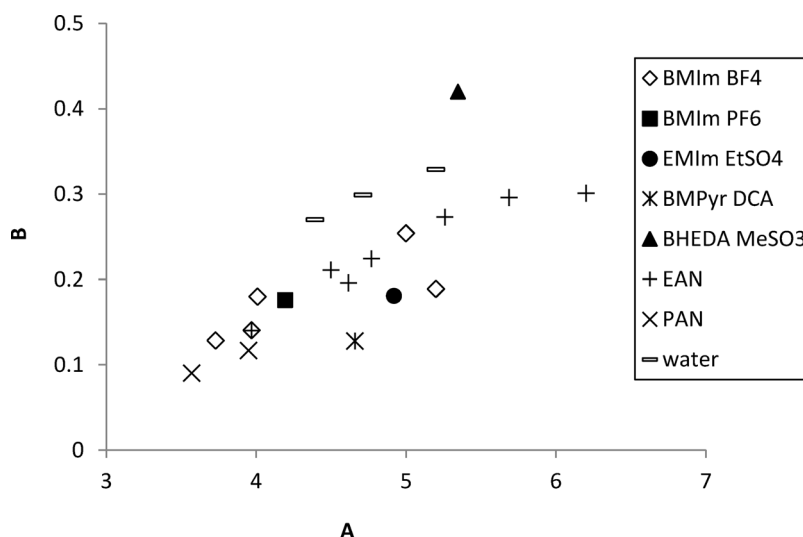
The *B* values for water were effectively constant, ranging from 0.28 to 0.33. In contrast, the values for *B* displayed a greater variation for the ILs, with for example BMIm BF<sub>4</sub> having *B* values between 0.14 to 0.25. This range could be due to the IL cation behaving as a co-surfactant and influencing the alkyl chain segregation of the amphiphile to a greater or lesser extent depending on the IL–head group interaction. There was no appreciable difference between the ionic and non-ionic amphiphiles in the ILs which is as expected due to the ionic nature of the ILs shielding headgroup repulsion of the ionic amphiphiles.

There is a consistent correlation present between *A* and *B*, with increasing *A* values associated with increasing *B* values, as shown in Fig. 12 therefore, solvents with a strong solvophobic interaction (large *B* values) have little or no ability to interact with the alkyl chains of the amphiphile, but instead can strongly interact with the head group of the amphiphile, for example water. For solvents with a small hydrocarbon portion, such as EAN, there is greater hydrocarbon solubility (weaker solvophobic effect, and smaller *B* values), and consequently a slightly reduced headgroup interaction, and therefore a smaller *A* value. The effect of increasing the hydrocarbon portion of the solvent further is evident for PAN, where the values of *A* and *B* are both quite small indicating considerable interaction between the solvent and the amphiphile chains, and a significantly reduced interaction between the solvent and the amphiphile head group.



**Table 3** Contributions to the CMC of the headgroups and terminal CH<sub>3</sub>, *A*, and the CH<sub>2</sub> moiety in the amphiphile alkyl chains, *B*. Temperatures at 25 °C unless otherwise indicated

Amphiphile	Solvent	<i>A</i>	<i>B</i>	Ref.
C <sub>x</sub> TAB	[BMIm][BF <sub>4</sub> ] (90 °C)	5.2	0.19	152
C <sub>x</sub> TAB	[EMIm][EtSO <sub>4</sub> ] (90 °C)	4.9	0.18	152
C <sub>x</sub> TAB	[BMPyr][DCA] (90 °C)	4.7	0.13	152
C <sub>x</sub> TAB	[BHEDMA][MeSO <sub>3</sub> ] (20 °C)	5.3	0.42	152
C <sub>x</sub> TAB	EAN	4.5	0.21	206
C <sub>x</sub> TAB	PAN	3.6	0.09	206
C <sub>x</sub> TAB	Water	5.2	0.33	152, 206
C <sub>x</sub> MIm Br	EAN	4.6	0.20	209
		4.0	0.14	207
		5.7	0.30	208
C <sub>x</sub> MIm Br	BMIm BF <sub>4</sub>	4.0	0.14	207
C <sub>x</sub> MPyrBr	EAN	5.3	0.27	211
C <sub>x</sub> MPyrBr	Water	4.7	0.30	211
C <sub>x</sub> Pyr Br	EAN	6.2	0.30 <sup>a</sup>	147
C <sub>x</sub> Pyr Cl	EAN	4.8	0.22 <sup>a</sup>	206
C <sub>x</sub> Pyr Cl	PAN	3.9	0.12 <sup>a</sup>	206
C <sub>x</sub> Pyr Cl	Water	4.4	0.28 <sup>a</sup>	206
1-(2,4,6-Trimethylphenyl)-3-C <sub>x</sub> Im Br	BMIm BF <sub>4</sub>	3.7	0.13	162
C <sub>x</sub> E <sub>8</sub>	BMIm BF <sub>4</sub>	5.0	0.25	156
C <sub>x</sub> E <sub>6</sub>	BMIm BF <sub>4</sub>	4.0	0.18 <sup>a</sup>	157, 158
C <sub>x</sub> E <sub>6</sub>	BMIm PF <sub>6</sub>	4.2	0.18	171

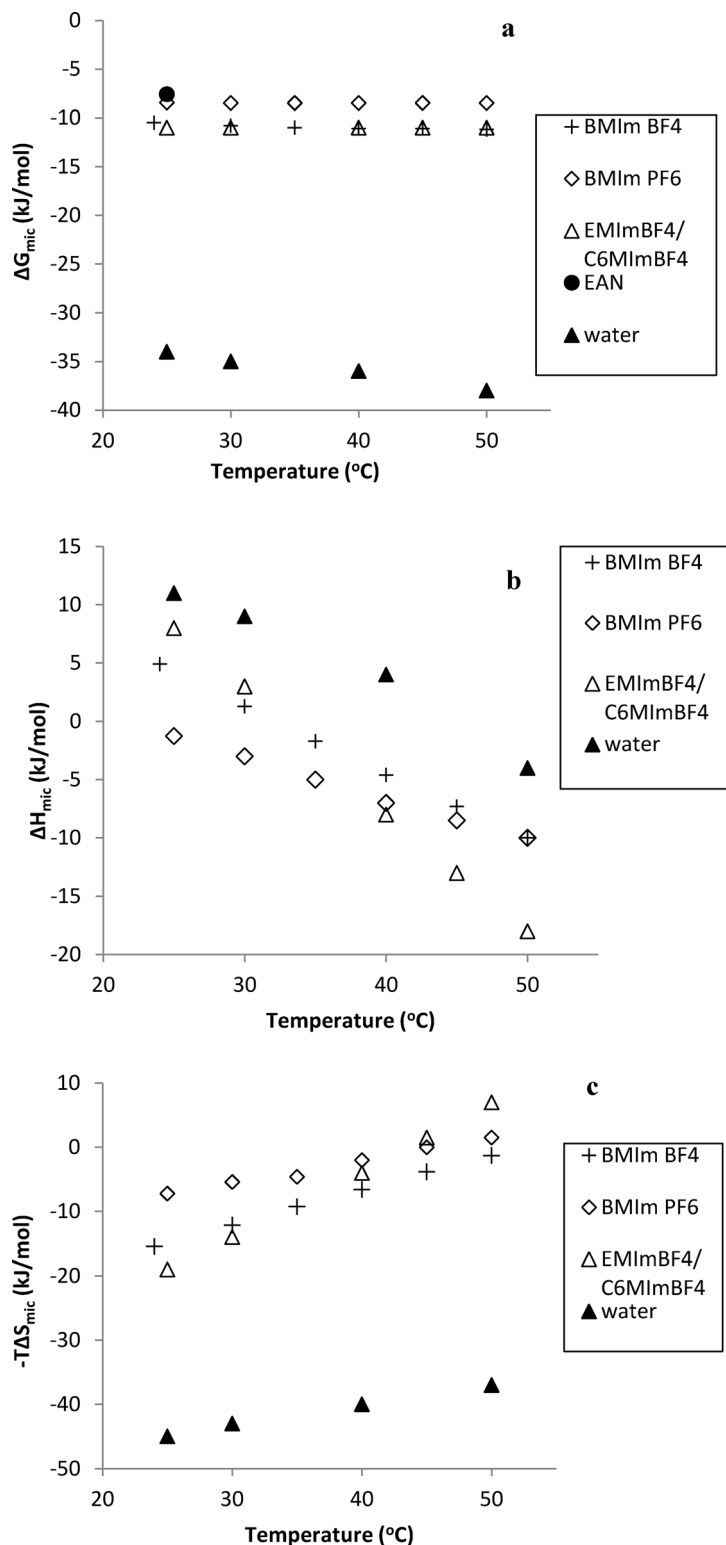
<sup>a</sup> Only two data points.**Fig. 12** Correlation of *B* and *A* for micellisation of various amphiphiles in ILs and water. BMIm BF<sub>4</sub>,<sup>152,156–158,162,207</sup> BMIm PF<sub>6</sub>,<sup>171</sup> EMIm EtSO<sub>4</sub>,<sup>152</sup> BMPyr DCA,<sup>152</sup> BHEDA MeSO<sub>3</sub>,<sup>152</sup> EAN,<sup>147,162,206–209</sup> PAN<sup>206</sup> and water.<sup>152,162,206</sup>

For a series of betaines in water, formamide and 3-methylsydnone the contribution per CH<sub>2</sub> group was between  $-0.29$  and  $-0.33$ ,<sup>17</sup> which was virtually the same for all three solvents, while the contribution per head groups varied significantly. This implies that the solvophobic interaction between the solvents and the alkyl chains were comparable in these solvents.

The Gibbs free energies, enthalpy and entropic contribution for C<sub>12</sub>E<sub>6</sub> micellisation in some ILs and water are shown in Fig. 13. The thermodynamics associated with micelle formation of the Gibbs free energy,  $\Delta G_{\text{mic}}$ , enthalpy,  $\Delta H_{\text{mic}}$ , and entropy,  $\Delta S_{\text{mic}}$ , have the same trends in ionic liquids as in water. With increasing temperature  $\Delta H_{\text{mic}}$  decreases and the entropic

contribution,  $-T\Delta S_{\text{mic}}$ , increases. These two terms compensate for each other such that  $\Delta G_{\text{mic}}$  is relatively independent of temperature. The magnitude of these three terms, and where the entropic and enthalpic contributions change between favourable and unfavourable is different between the ionic liquids as well as in comparison to water. The  $\Delta G_{\text{mic}}$  can be described by eqn (7). Combining eqn (6) and (7) gives that  $\Delta G_{\text{mic}} = -2.3 RT(A - Bn_c)$ . Therefore, for a given alkyl chain length the  $\Delta G_{\text{mic}}$  can be calculated from *A* and *B*. From Fig. 11 for any *n<sub>c</sub>* value it is clear that the  $\Delta G_{\text{mic}}$  in water is significantly smaller than in EAN, and that EAN is smaller than PAN.

$$\Delta G_{\text{mic}} = -2.3 RT \log (\text{CMC}) \quad (7)$$



**Fig. 13** Thermodynamic parameters associated with micellisation of  $\text{C}_{12}\text{E}_6$  in BmIm  $\text{BF}_4$ ,<sup>157</sup> EMIm  $\text{BF}_4/\text{C}_6\text{MImBF}_4$  (7 : 3 molar ratio),<sup>23</sup> EAN<sup>22</sup> and water<sup>213</sup> of (a)  $\Delta G_{mic}$ , (b)  $\Delta H_{mic}$  and (c)  $-T\Delta S_{mic}$ . The thermodynamic parameters associated with micellisation of  $\text{C}_{12}\text{E}_5$  BmIm  $\text{PF}_6$ <sup>171</sup> have also been included.

The Gibbs free energy describes how energetically favourable the micellisation process is, and hence gives a measure of the solvophobic interaction. It is evident from Fig. 13a that there is a very large difference in  $\Delta G_{mic}$  values between

micellisation in ionic liquids and in water, which highlights that the ILs in the figure have a much weaker solvophobic effect compared to the hydrophobic effect. As mentioned in the caption for Fig. 13, the thermodynamic quantities for

micellisation in BMIm PF<sub>6</sub> are for C<sub>12</sub>E<sub>5</sub> instead of C<sub>12</sub>E<sub>6</sub>. The  $\Delta G_{\text{mic}}$  of C<sub>12</sub>E<sub>m</sub> surfactants in BMIm BF<sub>4</sub> has been reported as becoming less negative with increasing *m* (for *m* = 6, 7, 8), and hence it can be inferred that there is a weaker solvophobic effect in BMIm PF<sub>6</sub> compared to BMIm BF<sub>4</sub> for C<sub>12</sub>E<sub>m</sub> surfactants.

The entropic contribution was significantly more favourable in water. In water, the water molecules arrange themselves around individual amphiphile alkyl chains to prevent hydrogen bonds breaking, and this configuration constraint is entropically unfavourable. When micelles are formed, the water is no longer constrained, and the difference in energy between these two situations is the entropic contribution which favours micellisation at low temperatures. We envisage that in the ILs there will be completely different arrangements of the IL solvent species around the individual alkyl chains, and hence the entropy associated with this structuring will be very different to that in water. The entropic contribution was similar for all of these ILs, which is as expected due to the similar nature of their cations. The alkyl moiety on the ILs means that the IL ions can be arranged far more favourably near the alkyl chains of the amphiphiles.

To form a sufficiently large cavity in the solvent for the micelle requires some interaction between solvent molecules to be disrupted. In water and protic ILs these may be hydrogen bonds, and in aprotic ILs these may be van der Waal interactions. The magnitude of  $\Delta H$  was comparable for the ILs and water, though the water had consistently higher values, which is expected for hydrogen bonds compared to van der Waal interactions, and with the higher Gordon parameter of water. The enthalpy change with temperature differed for the ILs and for water. Over the temperature range of 25–50 °C the enthalpy contribution was always negative for C<sub>12</sub>E<sub>5</sub> in BMIm PF<sub>6</sub>.

The  $\Delta G_{\text{mic}}$  of C<sub>x</sub>TAB amphiphiles in EAN, PAN and water are shown in Fig. 14. It is evident that the solvophobic interaction follows water > EAN > PAN, which matches well to the length of the IL alkyl chain, and the hydrocarbon solubility. There is much smaller relative difference between  $\Delta G_{\text{mic}}$  for the ILs and water for the micellisation of C<sub>x</sub>TAB compared to that of C<sub>12</sub>E<sub>6</sub> shown in Fig. 13a. This is because of the excellent

electrostatic shielding of the head group charges of the ionic C<sub>x</sub>TAB by the ionic liquids. This favours the micellisation process, but does not occur to the same extent in water (unless a salt is present) or for non-ionic amphiphiles. As the alkyl chain length, *x*, increases the micellisation process becomes energetically more favourable. This effect is greatest for water, with smaller changes in  $\Delta G_{\text{mic}}$  for EAN and PAN with increasing *x*.

The CMC Krafft point is the intersection of the CMC vs. temperature trajectory with the Krafft boundary, with micellar solutions only occurring at temperatures above the CMC Krafft point.<sup>205</sup> The Krafft points have been reported for a series of C<sub>n</sub>TAB amphiphiles in a variety of ionic liquids, EMIm EtSO<sub>3</sub>, BHEDA MeSO<sub>3</sub>, BMIm BF<sub>4</sub>, BMPyr DCA and EAN, and were shown to be significantly greater in the ILs compared to in water, for all except for BHEDA MeSO<sub>3</sub>.<sup>152</sup> This increase is predominantly due to the greater number of counter ions present in the IL systems, which are known to cause an increase in Krafft points in aqueous systems through electrostatic shielding enabling the neat surfactant phase to be retained to higher temperatures. For BHEDA MeSO<sub>3</sub> the Krafft point was less than room temperature, and markedly lower than the other ILs. The BHEDA cation contains two ethanol chains on the ammonium ion, and it was proposed that these are behaving like alcohols in aqueous systems.<sup>152</sup> In aqueous systems, the addition of alcohols lowers the Krafft point through the alcohols co-partitioning with the amphiphiles forming a mixed micelle.<sup>214</sup>

The Gibbs adsorption equation<sup>215</sup> can be used to determine the surface excess concentration,  $\Gamma_{\text{max}}$ , of amphiphiles at the air/liquid interface, as shown in eqn (8). This uses the gradient of the surface tension at concentrations just below the CMC. The minimum molecular area,  $A_{\text{min}}$ , of the amphiphile at the air–liquid interface can then be calculated from eqn (9).

$$\Gamma_{\text{max}} = -\frac{1}{2.303RT} \left( \frac{d\gamma}{d \log[C_{12}E_n]} \right) \quad (8)$$

$$A_{\text{min}} = \frac{10^{20}}{N_A \Gamma_{\text{max}}} \quad (9)$$

For a specific amphiphile, smaller  $A_{\text{min}}$  values can be attributed to a stronger solvophobic interaction, and *vice versa*. This is as the relative strength of the solvophobic interaction increases there is a larger packing density of the amphiphiles at the interface. The  $A_{\text{min}}$  values for cationic amphiphiles in various ionic liquids and water are represented in Fig. 15, against the number of carbons in the amphiphile alkyl chain. The values for the head group areas of ionic surfactants in all the ILs are comparable to water with the notable exception of PAN where the values are more than 5 times larger, which is attributed to the weaker solvophobic interaction in PAN.<sup>206</sup> C<sub>x</sub>TAB, C<sub>x</sub>PyrCl and C<sub>x</sub>TACl all had comparable values for the same value of *x* in the same IL, which shows the solvophobic interaction is primarily dependent on the alkyl chain length.<sup>206</sup>

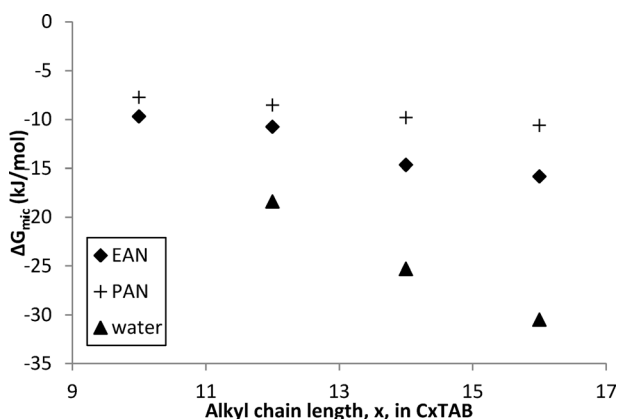
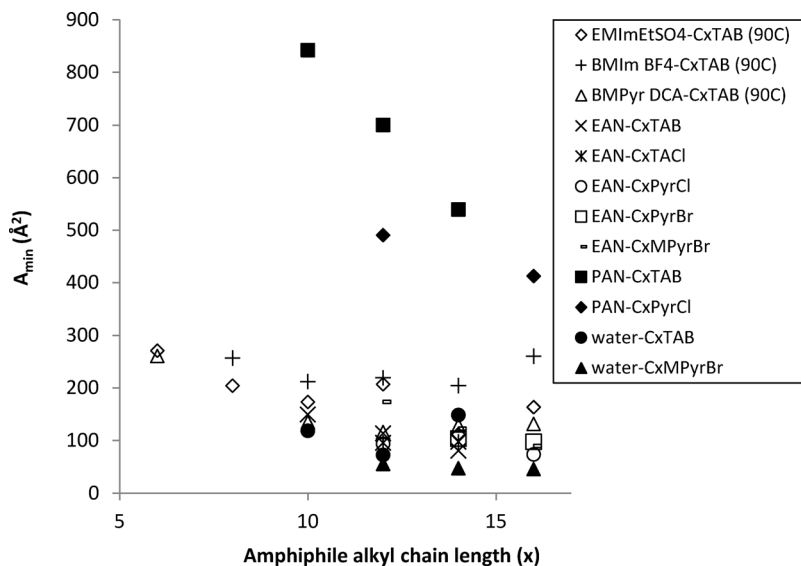


Fig. 14  $\Delta G_{\text{mic}}$  of C<sub>x</sub>TAB amphiphiles in EAN, PAN and water.<sup>206</sup>



**Fig. 15** Minimum amphiphile molecular packing area at the air/liquid interface,  $A_{\min}$ , for ionic amphiphiles in EMIm EtSO<sub>4</sub>,<sup>152</sup> BMIm BF<sub>4</sub>,<sup>152</sup> BMPyr DCA,<sup>152</sup> EAN,<sup>147,206,211</sup> PAN<sup>206</sup> and water<sup>206,211</sup> against alkyl chain length of the amphiphile. All temperatures are at 25 °C unless otherwise stated.

The components shape and ionic nature of the IL will affect the effective headgroup area. The ILs with longer alkyl chains on the cations, such as propylammonium and BMIm, are anticipated to behave to some extent as co-surfactants and thus increase the effective head group area, which can be seen in Fig. 15.<sup>149</sup> For ionic surfactants the ionic nature of ILs will lead to shielding of the head group charges, which will decrease the effective head group area. This can be observed in Fig. 15, where the ionic amphiphiles have comparable  $A_{\min}$  values in the ILs and in water, despite the weaker solvophobic interaction in the ILs.

## Lytotropic liquid crystals

The formation of lyotropic liquid crystal mesophases, other than micellar, have also been reported in neat ionic liquids.<sup>18</sup> These have predominantly involved the use of EAN,<sup>145,148–150,154,206,208,210,216–222</sup> and other protic ionic liquids.<sup>148–150,202,206,219,223</sup> The only studies that we are aware of which use the more conventional aprotic ILs as the solvent have used BMIm BF<sub>4</sub><sup>164</sup> or BMIm PF<sub>6</sub>.<sup>169</sup>

The solvophobic effect has a strong correlation with the diversity of lyotropic liquid crystal phases supported and the thermal ranges of these phases. For example, (CH<sub>3</sub>(CH<sub>2</sub>)<sub>17</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>*n*</sub>OH, *n* ≈ 10) (Brij 97) in water forms micellar, normal hexagonal and lamellar phases. In EAN it forms normal hexagonal and micellar phases, while only micelles are formed in BMIm BF<sub>6</sub>, BMIm BF<sub>4</sub>, pyrrolidinium nitrate and ethylammonium butyrate.<sup>154</sup> This series strongly follows the cohesive energy density of these solvents with water > EAN > the other ILs in this study.

The ionic liquids which have a sufficiently long alkyl chain to segregate into polar and non-polar domains and be nanostructured in the neat form, are likely to behave to some extent

as co-surfactants when amphiphiles are added, and thus will modify the lyotropic liquid crystal phases. An example of this behaviour was reported for CTAB in a range of PILs.<sup>149</sup> The mesophase behaviour could be sorted into two categories of either just a lamellar phase, or hexagonal, cubic and lamellar phases. The PILs which only supported the lamellar phase were those with longer alkyl chains.<sup>149</sup> In general, greater phase diversity has been observed for PILs which are not nanostructured in the neat ionic liquid form.<sup>148–150</sup>

## Concluding remarks

It has become widely recognised that many ionic liquids are capable of supporting amphiphile self-assembly. To a large extent, work to date has focussed on the formation of micellar phases in ILs, with investigations of more concentrated amphiphile phases being mainly conducted with protic ionic liquids, predominantly EAN. Consequently, ILs represent a highly tailorable class of solvents which can be modified to achieve specific lyotropic liquid crystalline behaviour, and solvent properties for different amphiphile end-applications.

In this review we have highlighted the importance of cohesive energy density as a solvent property to describe the solvophobic effect, where the cohesive energy density can be usefully described by the Gordon parameter for ILs. All of these ILs had lower Gordon values than water, which indicates a weaker solvophobic effect compared to the hydrophobic effect. However, there are unique benefits which can be obtained using ILs such as being non-aqueous, and in some cases being non-volatile, and possessing good thermal stability.

The ability of neat ILs to form a segregated nanostructure of polar and non-polar domains has been widely reported where a minimum alkyl chain containing 2–5 carbons is required



depending on the ions. As the size of the non-polar domain in the IL increases, the hydrocarbon solubility increases, the Gordon value decreases, and hence there is a weaker solvophobic effect. While this effect is more associated with the length of the alkyl chain and the van der Waals interactions between the IL and the amphiphile alkyl chain, the use of IL nanostructure is a useful tool for determining which IL may be a suitable choice for a specific amphiphile and the desired lyotropic liquid crystal phase. A secondary effect of an alkyl chain being present on the IL is that it enables the IL to behave as a co-surfactant and hence will modify the lyotropic liquid crystal mesophases. Using the nanostructure is also an excellent way of accounting for the effect of added polar groups on the alkyl chains. For example, ethylammonium nitrate (EAN) and its hydroxyl containing counterpart ethanolammonium nitrate (EOAN) could be expected to have similar properties as amphiphile self-assembly media due to both sharing many chemical features, including an ethyl alkyl chain. However, EAN is nanostructured and is an excellent self-assembly media, whereas EOAN has no discernible nanostructure, and such poor hydrocarbon solubility that often the CMC cannot be reached at low to intermediate amphiphile concentrations.<sup>22</sup>

There is an apparent 'optimal' degree of hydrocarbon solubility, or nanostructure, in the IL for it to be a good amphiphile self-assembly media. This is particularly well shown by Inoue *et al.* who studied non-ionic surfactants in mixtures of EMIm BF<sub>4</sub> and C<sub>6</sub>MIm BF<sub>4</sub>.<sup>23</sup> The surfactant had insufficient solubility in the neat EMIm BF<sub>4</sub> to reach the CMC, whereas in the longer chained IL C<sub>6</sub>MIm BF<sub>4</sub> the solubility was too high and no micelles formed. However, the mixture of these two ILs enabled micelle formation. Similarly, non-ionic amphiphiles in a range of protic ionic liquids clearly showed that the ability of the PIL to support micelle formation was dependent on the hydrocarbon solubility, which was simply described by the nanostructure of the PIL.<sup>22</sup> PILs with no, or very little nanostructure had insufficient solubility of the amphiphile, whereas PILs which had large, well defined non-polar regions were too good a solvent for the amphiphile and no micelles formed. For these PILs with alkyl ammonium cations the optimal PIL was observed to be the most commonly studied PIL, EAN.

A review of the synthesis of inorganic materials from ILs has shown that it is possible for the ILs to be used as the solvent, template and reactant, when metal ions are incorporated into the IL.<sup>224</sup> While this review focussed on amphiphilic ILs the same behaviour is possible for more conventional shorter chained ILs which are nanostructured. For example, bimodal hierarchically porous silica has been synthesised in EAN with the block copolymer P123, where micropores were templated from the non-polar domains present in the EAN and mesopores were templated from the P123 mesophase structure.<sup>116</sup>

## Abbreviations

IL	Ionic liquid
PIL	Protic ionic liquid

AmIL	Amphiphilic ionic liquid
$\Delta G_{cav}$	Gibbs free energy for cavity formation
$\Delta G_{sol}$	Gibbs free energy for solubilising a solute
$\Delta G_{agg}$	Gibbs free energy for aggregation
$\Delta G_{mic}$	Gibbs free energy for micelle formation
$\Delta H$	Enthalpy
$\Delta S$	Entropy
CPP	Critical packing parameter
EAN	Ethylammonium nitrate
PAN	Propylammonium nitrate
P <sub>6,6,6,14</sub>	Trihexyl(tetradecyl)phosphonium
C <sub>x</sub> MIm	1-C <sub>x</sub> -3-methylimidazolium
C <sub>x</sub> NH <sub>3</sub>	Alkyl <sub>x</sub> ammonium
BMIm	1-Butyl-3-methylimidazolium
EMIm	1-Ethyl-3-methylimidazolium
HO-C <sub>3</sub> MIm	1,2-Hydroxypropyl-3-methylimidazolium
HO-C <sub>2</sub> MIm	1,2-Hydroxyethyl-3-methylimidazolium
C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> MIm	1,3-Hexyloxymethyl-imidazolium
(C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> ) <sub>2</sub> MIm	1,3-Dihexyloxymethyl-imidazolium
COC <sub>2</sub> mPIP	1-(2-Methoxyethyl)-1-methylpiperidinium
BMPyrr	1-Butyl-1-methylpyrrolidinium
BHEDA	Bis(2-hydroxyethyl)dimethylammonium
MOMIm	1-Methoxymethyl-3-methylimidazolium
EOMIm	1-(2-Methoxyethyl)-3-methylimidazolium
Pyr	Pyridinium
Pyrr	Pyrrolidinium
NO <sub>3</sub>	Nitrate
BF <sub>4</sub>	Tetrafluoroborate
PF <sub>6</sub>	Hexafluorophosphate
Tf <sub>2</sub> N	Bis(trifluoromethanesulfonyl)imide
TCB	Tetracyanoborate
FAP	Tris(pentafluoroethyl)trifluorophosphate
BOB	Bis(oxalato)borate
TOS	Tosylate
SCN	Thiocyanate
MeSO <sub>3</sub>	Methane sulfonate
EtSO <sub>4</sub>	Ethylsulfate
DCA	Dicyanamide
NPF <sub>2</sub>	Bis(perfluoroethylsulfonyl)amide
Glu	Glutamate
TfO	Triflate (trifluoromethanesulfonate)
P123	Pluronic block copolymer (EO) <sub>20</sub> (PO) <sub>70</sub> (EO) <sub>20</sub>
C <sub>n</sub> E <sub>m</sub>	Polyoxyethylene alkyl ether, C <sub>n</sub> H <sub>2n+1</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>m</sub> OH
C <sub>x</sub> TAB	Alkyltrimethylammonium bromide
CTAB	C16TAB, hexadecyltrimethylammonium bromide
Brij 97	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>17</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>n</sub> OH, n ≈ 10

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