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Structural and Physical Aspects of Ionic Liquid Aggregates in Solution

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1. Introduction

Ionic liquids (ILs) are currently defined as liquid organic salts, composed of organic cations and inorganic or organic anions, at or close to room temperature (melting point <100°C) [1], [2]. The liquid state of ILs is thermodynamically favorable due to the large size and conformational flexibility of the ions (headgroup and counterion), leading to small lattice enthalpies and large entropy changes [3], [4]. ILs have negligible vapor pressure, excellent thermal stability, high electrical conductivity, a wide electrochemical window, a strong ability to dissolve many chemicals, and can be easily recycled [5]. The most attractive property of ILs can be effectively "tuned" in the design of the physical, chemical, and biological properties, by simple tailoring the substituent groups which consist of the cation and/or anion. [6]. The most frequently used cations in ILs are alkylammonium, N,N'-dialkylimidazolium, and N-alkylpyridinium cations [7]. Generally, the alkyl chains utilized are methyl, ethyl, butyl, hexyl, octyl, and decyl. A wide range of anions are employed, ranging from simple halides to inorganic anions such as tetrafluoroborate and large organic anions like methane sulfonate, trifluoromethane sulfonate, and bis-(trifluoromethanesulfonyl) amide [8].

Many applications of ILs are closely related to their aggregate formation. It may be expected from the amphiphilicity of ILs that interfacial phenomena play a major role in the behavior of systems which contain ILs. In recent years, most of the investigations in this field have been focused on the formation of IL aggregates in water [9]–[14]. The aggregation behavior of ILs can be modified by changing the alkyl chain length, the type of headgroup, and the nature of the counter-ions [15]–[17]. The structural characteristics of aggregates can be determined by

employing several experimental methods such as conductometry, tensiometry, steady-state fluorescence spectroscopy, isothermal titration calorimetry, small-angle neutron scattering, and nuclear magnetic resonance spectroscopy [18]. Aggregate formations such as micelles, liquid crystals, and microemulsions, depend on the IL structure, solvent, and the conditions of the system being studied like temperature and presence of additives. Whereas that a fine tuning in the aggregation process (e.g., size, morphology and aggregation number) can lead the ILs structures on this systems to different applications.

These characteristics are of great importance from both an academic and technological point of view, since they allow use in synthesis and purification [19], and also as surfactants [20]– [22], lubricants [23], and for nanoparticle coating [24], among other things.

This chapter will illustrate the importance of studying the organization of ILs in solution, and consider the main effects that change this behavior, by reporting the main results obtained and the approaches of these investigations. This chapter includes monocationic and dicationic ILs with different cation, anion, and alkyl chain sizes. The aim of the chapter is to show the influence of: (i) structural effects (length of alkyl chain, polar head, and counter-ion); (ii) temperature effect; and (iii) solvent effect on the aggregation of ILs. We will discuss the influence of these effects on the formation and characterization of IL aggregates through the use of several spectroscopic and non-spectroscopic techniques such as NMR spectroscopy, dynamic light scattering (DLS), fluorescence, conductivity, surface tension, and others.

The data collected for this chapter was selected from a search in the article/reference database *Science Finder*, using "ionic liquid aggregation" as keywords and refining this by requesting "English" language results. The total number of papers found was 597 (between 2002 and 2014). From these papers, studies about IL aggregates in solution that involve water, organic solvents, and water/organic solvent mixtures, including structural effects of the ILs and temperature effect on the aggregation, will be detailed. Due to the wide range of reports, the effect of ionic strength and the addition of surfactants and/or polymers into the system containing IL are not discussed within the scope of this chapter.

2. Effect of the structure of IL aggregation

The idea behind IL aggregation is simple and straightforward. Due to their amphiphilic nature, when IL molecules are dissolved in a solvent the presence of different polarities in their structures causes distortion in the solvent structure, thus increasing the energy in the system. In aqueous solutions, for example, in order to reduce unfavorable interactions, the hydrophobic portion of the IL either directs these interactions to more comfortable interfacial regions (adsorption) or directs them to the inner part of the solution through self-assembly (aggregation) [25], [26].

As a result of aggregation in polar solvents, they can form a structure where all of the nonpolar portion ends are directed toward the core of the aggregates. Aggregation and the aggregate by itself are affected by the complex character of intermolecular interactions between cation/

anion, cation/solvent, and anion/solvent [22], [27], [28]. These interactions consist of hydrogen bonding, as well as coulombic attraction, van der Waals, n-π, and π–π interactions [29]–[31]. Furthermore, aggregation and aggregate features are significantly influenced by structural changes in the IL, such as length and composition of the hydrophobic portion, the nature of the head group, and anion characteristics [22], [27], [32]. Therefore, by varying the chemical structure of ions, it is possible to influence intermolecular interactions and self-organization of ILs, which is important for several applications of ILs.

An extensive number of studies have been performed in order to rationalize the influence of IL chemical structure on aggregate formation [1], [33]–[35]. Although there are divergences in the quantitative estimations from different techniques, the general regularities in the dependence of characteristics on IL structure are well correlated. Among the main parameters obtained, the concentration at which aggregates start to be formed, also known as the critical aggregation concentration (cac), is the most documented one and can be accessed by almost all the techniques. The following may be estimated: the Gibbs free energy of aggregation ($\Delta G°_{agg}$), degree of counter-ion binding (β), the degree of ionization of the aggregate (α) [11], [22], [36], surface activity, (γ_{cac}) and also parameters such as surface tension at the cac, minimum surface area per molecule at the air/aqueous interface (A_{min}), maximum surface excess concentration (Γ_{max}) and standard Gibbs free energy of adsorption ($\Delta G°_{agg}$) can be estimated. Adsorption in the interfaces can also be evaluated through the effectiveness of the surfactant, in order to decrease the surface tension of the solvent (Π_{cac}) and the adsorption efficiency (pC_{20}) — C_{20} is the concentration at which the surface tension of pure solvent is reduced by 20 mNmol^{-1} [27], [31], [37]. The aggregation number (N_{agg}) can also be obtained, usually by fluorescence quenching technique [36], [38].

This overview will discuss the influence of three main features that are related to aggregation in solution: (i) alkyl chain length; (ii) cationic head; and (iii) the nature of the anion. The discussion will take into account not only the cac but also the other parameters mentioned previously, which indicate the stability of aggregates and surface activity of ILs. Each section will cite the main reports in the literature that helped to detail the structural effect on aggregate formation.

2.1. Effect of cationic alkyl chains

The length of alkyl chains has been reported to be one of the main factors influencing the aggregation behavior of ILs [22], [27], [39]. In aqueous solutions, hydrophobic interactions between ILs and polar solvents are the driving force towards aggregation, due to the increase of entropy and consequently decrease of the free energy of the system [27]. In the aggregate, two types of domains can be observed: (i) one is polar, in which cationic heads and anions arrange in a three-dimensional network supported by strong electrostatic interactions; (ii) in the other domain, alkyl groups aggregate to build nonpolar domains where van der Waals interactions are critical [37], [38], [40]. Generally, some observations can be made about homologous series of ILs. A systematic decrease in cac values with an increase in methylene units in the alkyl chain is observed. The $\Delta G°_{agg}$ tend to become more negative, implying that aggregation comes more easily with the increase of the alkyl chain length, as a direct conse-

quence of the increased hydrophobicity of IL monomers. Significant negative $\Delta G°_{agg}$ values are primarily due to an increase of the entropic contribution, an effect that is common in aggregation processes induced by hydrophobicity of alkyl chains. In aqueous solution, the alkyl chain of the LIs induces a water structure around the chain and this structure breaks down during aggregation, leading to a large entropy increase. The β values increase with an increase in the alkyl chain length, which corresponds to a stronger interaction between anions and aggregates as the alkyl chain's length increases [36], [39]. Furthermore, the surface activity of ILs is improved with an increase in the alkyl chain's length, resulting in smaller γ_{cac} values, and higher Π_{cac} and pC_{20} values.

The organization of an IL as a function of an alkyl chain is similarly affected by the alkyl chain structure. The aggregation behavior of imidazolium-based IL series in aqueous solution has been investigated in independent works [36], [39]. Data related to the conductivities and polarity indexes of pyrene for IL aqueous solutions was determined. The ILs used in both works are [BMIM]Br, [HexMIM]Br, [OctMIM]Br, [DecMIM]Br, [DoDecMIM]Br, [TetDec-MIM]Br and [HexaDecMIM]Br and [BMIM][BF$_4$]. Aggregation was detected for almost all ILs except for [BMIM]Br. These works reported a decrease in cac with an increase in alkyl chain length. The authors related this behavior to a balance between an enhancement of van der Waals interactions by means of alkyl chain-ion inductive force (dielectric polarization) and dispersive interactions. These physicochemical properties depends markedly by the contribution, per (CH$_2$) group, in the alkyl chain of cations. On the other hand, the aggregation number determined by pyrene fluorescence quenching method did not show a tendency for variation in the IL structures for the work performed by Wang et al. [36]. However, in the study reported by Inoue et al. [39] it was observed from conductivity data an increase of aggregation number with the increase in the alkyl chain.

The surface activity and aggregation behavior of the imidazolium-based ILs [BMIM]Br, [HexMIM]Br, [OctMIM]Br, [DecMIM]Br, [DoDecMIM]Br, [TetDecMIM]Br and [HexaDec-MIM]Br and [BMIM]X, [HexMIM]X, and [OctMIM]X (X=Cl, I) were also investigated [32], [41], [42], using surface tension, ^{1}H NMR spectroscopy, and small-angle neutron scattering (SANS). The cac values decrease with the length of the alkyl chain, following the same trend as the work performed by Wang et al. [36] and Inoue et al. [39]. Tensiometric parameters also showed a strong correlation with the structural changes. The decrease in γ_{cac} as the alkyl chain length increased follows the tendency observed for conventional surfactants and indicates better surfactant activity for ILs with longer alkyl chains. This is also corroborated by the Π_{cac} and pC_{20} values, which increased as the alkyl chain length increased. Finally, upon examining the effect of the chain length on the area per IL molecule at the water/air interface (A$_{min}$), it was observed that the A$_{min}$ values systematically increased in the following order: [OctMIM]X < HexMIM]X < [BMIM]X (at 30 °C) and [HexaDecMIM]Br < [TetDecMIM]Br < [DoDecMIM]Br < [DecMIM]Br (at 25 °C), in the studies performed by Vaghela et al. [41] and Dong et al. [32]. Vaghela et al. [41] referred to this behavior as the result of a simple monolayer organization with the alkyl chain oriented toward the water side at the interface for the IL [BMIM]X, while the [HexMIM]X and [OctMIM]X may create more complex and closely packed layers. Similar results were observed by Sastry et al. [38] and Vaghela et al. [41] in a study of the aggregation

of the pyridinium-based ILs [N-BPy]Cl, [N-HexPy]Cl, [N-OctPy]Cl, [N-Oct-2-MePy]Cl, [N-Oct-3-MePy]Cl, and [N-Oct-4-MePy]Cl; and also by Zhao et al. [43] for the pyrrolidinium-based ILs [DoDecMPyrr]Br, [TetDecMPyrr]Br, and [HexaDecMPyrr]Br in aqueous solutions. Improvement in both the surface activity and the A_{min} value was observed with the increase in alkyl chain length, which corroborates with results previously reported. The authors explain this behavior based on the higher hydrophobicity caused by the increased number of methylene units in the alkyl chain. Surface tension data of pyrrolidinium-based ILs showed some peculiarities. No considerable difference was observed in the effectiveness of the surface tension reduction, expressed by the γ_{cac} and Π_{cac} parameters, which is an indication that the structural changes in the alkyl chain did not affect the surface activity of these compounds. On the other hand, the packing at the surface, and the N_{agg} value showed good correlation with the previous works. The increase in the alkyl chain length resulted in better packing at the water/air interface. This result is confirmed by A_{min} and Γ_{max} values and by high aggregation number.

A cationic head bound to a long alkyl chain and a methyl group characterizes most of the studies reported in the literature that investigate the aggregation of imidazolium-based ILs. The change in the methyl group resulting from a long alkyl chain may also play a dominant role, not only in the aggregation behavior and stability of the aggregate, but also in the surface activity of ILs. For better comprehension, in this discussion the size of different alkyl chains bound to imidazolium cationic heads will be represented by *n* and *m*, respectively, as shown in Figure 1.

$$H(H_2C)_n - N \overset{\oplus}{\diamond} N - (CH_2)_m H$$

Figure 1. Representation of cationic head for imidazolium-based dialkyl-substituted IL.

In general, for a homologous series with two long side chains, for a fixed *n* (longer than the methyl group) and a varying *m*, lower cac values may be observed than those for analogous ILs in which *n* is methyl. However, when the length of both alkyl chains varies, it is observed that the longer alkyl chain has the stronger effect, with a smaller cac value [20], [44]. In relation to the thermodynamic properties of aggregates, the $\Delta G°_{agg}$ values are not affected by the insertion of another long alkyl chain, whereas the β values tend to decrease, which indicates a lower charge at the aggregate surface [45]. Surface properties are influenced by insertion of a second alkyl chain in the cationic head. In general, there is an improvement in the surface activity with the increase of alkyl chain length, represented by a decrease in the γ_{cac}, Γ_{max} and N_{agg} while Π_{cac}, pC_{20} and A_{min} values increase. The packing at the surface does not follow the same trend, and the longer the second alkyl chain is, the worse the IL's packing is at the water/air interface, which results in lower Γ_{max} and higher A_{min} values [44].

Liu et al. [44] and Baltazar et al. [20] investigated the aqueous aggregation of diakylimidazolium ILs in two independent works. Liu et al. [44] evaluated the ILs [DoDecMIM]Br, [DoDecEtIM]Br, [DoDecPrIM]Br, and [DoDecBuIM]Br with the dodecyl long chain and the variable

alkyl side chain, while Baltazar et al. [20] varied the length of both alkyl chains. It was found that ILs with one very long and a short chain has a higher cac value than those with two long alkyl chain. This behavior can be confirmed comparing the values of [DoDecBuIM]Br with [HexaDecBuIM]Br. The [HexaDecBuIM]Br has a lower cac value than [DoDecBuIM]Br, which has two long alkyl chains. The lengthening of the alkyl chain resulted in an improvement in tensoative activity. However, longer alkyl chains result in lower packing efficiency at the water/air interface, as observed in the A_{min} and Γ_{max} values. Tariq et al. [45] also investigated the effect of two long alkyl chains on the aggregation behavior of the pyrrolidinium-based ILs [DoDecMPyrr]Br, [DoDecBuPyrr]Br, and [OctBuPyrr]Br. Results with the same patterns as those of Liu et al. [44] and Baltazar et al. [20] were obtained.

Although most of the studies involving the study of alkyl chain effect on IL aggregation have investigated hydrocarbon chains, some works, which will be discussed in this revision, deal with the introduction of polar groups into the alkyl chain. The introduction of polar groups into the alkyl chain connected to the cationic head was also investigated by Garcia et al. [46]. Two series of long chain imidazolium-and pyridinium-based ILs containing an ester functional group in the alkyl side chain were investigated (Figure 2). The aggregation behavior of the ILs under investigation followed the same pattern as those already discussed. Even in the presence of the ester group, aggregation was favored and surface activity improved with the increase in alkyl chain length for both imidazolium-and pyridinium-based ILs. The enhancement of pC_{20} and Π_{cac} show the increase of the surfactant properties with the lengthening of the IL's alkyl chain, while both γ_{cac} and A_{min} decrease. The decrease of A_{min} corresponds to a better packing at water/air surface.

n = 6, 8, 10, 12, 14   n = 6, 8, 10, 12, 14
(a)   (b)

Figure 2. Structure of (a) imidazolium-and (b) pyridinium-based ILs studied by Garcia et al. [46].

The effect of a polar group on one of the alkyl chains connected to the imidazolium head was investigated by Liu et al. [47]. They studied the aggregation and surfactant activity of the hydroxyl-functionalized IL [EtOHDoDecIM]Cl in aqueous solution. The results obtained can be compared with those already published by the same author [44] with an alkyl (ethyl and dodecyl) group connected to each nitrogen in the imidazolium ring. It was possible to observe that the insertion of a polar group did not influence the aggregation behavior and surface properties. Some differences were observed in the parameters related to the packing at the air/water surface; for example, lower $\Gamma_{máx}$ and higher A_{min} values of hydroxyl-functionalized ILs. The authors state that interactions between the hydroxyl group and water molecules are responsible for increasing the area around the molecule on the surface. A second cac (cac$_2$) was

reported and the N_{agg} for the first (cac_1) and second (cac_2) aggregation was calculated. An increase in monomer units within the aggregate was observed, from cac_1 to cac_2, and it is suggested that the second cac emerges from an improvement in the aggregate organization in solution.

Li et al. [34] evaluated the aggregation and adsorption behavior of [HexaDecHyPrIM]Br in aqueous solution. The cac obtained for [HexaDecHyPrIM]Br is similar to [HexaDecMIM]Br, showing the predominant effect of the longest alkyl chain on the aggregation. A lower β value was obtained, which might be caused by an increase in electrostatic repulsions between the hydrophilic heads of adjacent IL molecules. Both the factors related to the hydrophilic head-group size and electrostatic repulsion in [HexaDecHyPrIM]Br aggregates lead to looser packing of ILs. Water molecules may more easily penetrate the looser micelles resulting in a higher I_1/I_3 ratios and smaller N_{agg} value. Shi et al. [29] evaluated the aggregation behavior of [DecPhMIM]Br, [DoDecPhMIM]Br, and [TetDecPhMIM]Br in aqueous solutions and showed that the introduction of the 2,4,6-trimethylphenyl group into an imidazolium head favors aggregation, due to the more delocalized charge of the cationic head, which reduces the electrostatic repulsion of the head group. The authors mention a reduction in the steric hindrance of head groups caused by the occurrence of ππ interactions among the adjacent 2,4,6-trimethylphenyl groups, which allows dense arrangement of these IL molecules at the air/water interface.

Besides the substitution at positions 1 and 3 in the imidazolium ring, the insertion of a methyl group at position 2 was also performed and the aggregation behavior of the IL was investigated (Figure 3) [48].

Figure 3. Structure of IL

Figueira-Gonzalez et al. [48] observed two cac values, which were related to a morphological change in the aggregates. The data obtained for β was correlated to a formation of spherical micelles in accordance with cac_1, and with the transition to cylindrical micelles in accordance with cac_2. Results obtained from fluorescence spectroscopy, fluorescence anisotropy, and chemical NMR were used to investigate the change in the morphology — the results were consistent with the sphere-to-cylinder transition. Moreover, at higher concentrations, a new conformational change from cylindrical micelles to bilayer aggregates was proposed, based on the analysis of diffusion coefficients obtained by diffusion-ordered NMR spectroscopy (DOSY).

2.2. Effect of cationic head

The influence of cationic head structural characteristics has also been investigated. There are two opposing effects that make the understanding of this effect very complex. Repulsive interactions due to the positive charge, and hydration and steric hindrance among cationic moieties in solution are anti-aggregation effects. Attractive interactions arising from a need to minimize hydrocarbon/water contacts favor aggregation [22]. As seen in the alkyl chain effect, the hydrophobicity of cationic heads also plays an important role, favoring aggregation in aqueous solutions [31], [49]. In the same way, the binding strength between cations and anions has an influence on the aggregate stabilization, by reducing the repulsive interaction among head groups with the increase in β [22], [31], [49].

Galgano et al. [31] investigated the aggregation of ILs with different head groups and with the same alkyl chain and anionic moiety (Cl⁻). The influence of the cationic head was observed and it was determined that the aggregation is favored in the following order: Pyridinium [N-HexaDecPy][Cl] < Imidazolium [HexaDecMIM][Cl] < Ammonium [PentDecAEtBzMe$_2$][Cl]. The decrease in the ionization degree (α) and N$_{agg}$ for [PentDecAEtBzMe$_2$][Cl] showed that aggregates formed by this surfactant are stabilized more by counter-ions and they have better packing.

Wang et al. [22] investigated the effect of cationic ring types on the aggregation of ILs in aqueous solutions. It was found that cac and $\Delta G°_{agg}$ decrease in the following order: Pyrrolidinium [OctMPyrr]Br > Imidazolium [OctMIM]Br > Pyridinium [N-Oct-4-MePy] Br. This indicates that the pyridinium head has a higher ability to form aggregates. However, there are no substantial differences between the values obtained for different cationic heads. The reason is based on the similar hydrophobic characteristic of the cations under investigation. The authors observed that the van der Waals volumes of cationic rings (167, 150, and 144 Å^3 for [BMPyrr], [BMIM], and [N-BPy], respectively), assume an important role in the aggregation process, in which smaller values are related to a more favorable aggregation. The increase in the van der Waals volumes indicates an increase in steric hindrance, which corroborates with the increase in cac. The results for ionization degree of the aggregates (α) demonstrated that anionic counter-ions are less bound to the surface of [OctMPyrr] than [BMIM] and [N-Oct-4-MePy].

2.3. Counter-ion effects

In this discussion, the counter-ion will be considered to be the ion on the surface of the aggregate, which can be both an anion and a cation. The role of the counter-ion can result in significant alterations in the IL aggregation and aggregate stability. As previously mentioned, aggregation is a result of the hydrophobic effect of alkyl chains, which leads to aggregation through attempting to minimize the exposure of the alkyl chain to water, and repulsive interactions among cationic head groups. The counter-ions play a key role in reducing the repulsive headgroup interactions through adsorption on the aggregate surface, thereby lowering the cac values [11], [22]. In the cationic aggregates, the foremost characteristics of the anions are their size, hydrated radius, polarizability, hydrophobicity, and bulkiness [22], [41]. All parameters are related and anions with high polarizability will also have high hydropho-

bicity and a lower hydrated radius. Anions with higher polarizability are more bound at the aggregate surface and decrease the electrostatic repulsion between the head groups of the ILs, thus increasing the tendency toward aggregation [22].

2.3.1. Anionic counter-ion effect

In general, the reports about IL aggregation evaluate cationic head with long alkyl chains and relatively small anions (when compared to the cation size). Strongly hydrated ions such as chloride are partially screened by the surrounding polar water molecules and, therefore, are less effective at reducing the repulsion between the cations when they are absorbed in the surface and do not stabilize the aggregate properly [50]. On the other hand, anions such as BF_4^- and PF_6^-, besides giving a higher overall hydrophobicity to the IL, also tend to promote better stabilization of aggregates [50]. The effect of anions is observed in the cac, $\Delta G°_{agg}$, and β values. Anions with higher hydrophobicity tend to decrease the cac and $\Delta G°_{agg}$ values and increase the β values [22], [41], [50].

Wang et al. [22] studied the effect of anions on the aggregate formation of the ILs [OctMIM]X (X=$CH_3CO_2^-$, Br^-, Cl^-, NO_3^-, $CF_3CO_2^-$) in aqueous solution. The aggregation of ILs with different anions followed the Hofmeister series [51], [52]. The increase in the hydrophobicity and decrease in hydration radius caused a decrease in the cac and $\Delta G°_{agg}$ values. It was observed that a more hydrophobic IL leads to lower α values, which indicates a higher concentration of anions on the surface and better stabilization of the aggregate. The aggregates were found to be spherical and the anions had a weak effect on the morphology. On the other hand, the effect of the anion on the size and N_{agg} indicates that the increment in the hydrophobicity of anionic moieties causes an increase in size, with a consequent increase in the number of monomers in the aggregate (N_{agg}).

Vaghela et al. [41] evaluated the surface activity and aggregation behavior in water of the imidazolium-based ILs [BMIM]X, [HexMIM]X, and [OctMIM]X with different anions (X=Cl^-, Br^-, I^-). Among the ILs with the same cationic structure but with different anions, an reduction in the cac and $\Delta G°_{agg}$ values was observed, in the following order: $Cl^- < Br^- < I^-$. This behavior was explained based on the relative hydrophobicity and binding capacity of three different halides to a cation. The more hydrophobic, the more attached the anions are at the surfaces.

The influence of anions on pyridinium-based aggregation in aqueous solution was studied by Bandrés et al. [50]. The results of [N-Bu-3-MePy] cation with BF_4^- and $N(CN)_2^-$ anions were compared with data obtained by Singh et al. [11] in a previous work with the same cation and the Cl^- anion. The authors observed that by changing the anion in the IL, the cac decreases in the following order: [N-Bu-3-MePy][Cl] > [N-Bu-3-MePy][N(CN)₂] ≈ [N-Bu-3-MePy][BF₄]. The most important difference between the chloride and tetrafluoroborate or dicyanamide anions was reported to be related to their size. The bigger the anion structure, the smaller the hydration radius and the greater the hydrophobicity, which implies that tetrafluoroborate or dicyana-mide make aggregation easier. Higher β values were observed in the ILs with $N(CN)_2^-$ and BF_4^- anions, which indicates a decrease in the charge repulsion between the cations when they are absorbed at the aggregate's surface.

2.3.2. Cationic counter-ion effect

Although most reports in the literature consider cationic aggregates with anions as counterions, there are also studies in which anions with long alkyl chains are investigated, thus playing a more important role in the aggregation [10], [37], [53]. In this case, the anion acts as a surfactant moiety of the IL and aggregation will mainly be influenced by its structural features of anion, following the trend observed for cationic structure already discussed in the previous sections (see Section 2.1 and 2.2). The cationic moiety is then considered to be the counter-ion and will work in the same way that anions do for cationic aggregates.

Rao et al. [10] investigated the effect of cationic counter-ions on anionic aggregates in aqueous solution with amino acid-based ILs (AAILs). The ILs hydrophobicity was the primary factor influencing aggregation behavior. It was observed that the cac, β, and $\Delta G°_{agg}$ values increase in the following order: GluPrELS < ValPrELS < ProPrELS < AlaPrELS < GlyPrELS. The surface activity of the ILs was also influenced by the hydrophobicity of the cationic moiety, showing the same behavior previously described for anionic counter-ions. The increases in the hydrophobicity of amino acid-based cationic moieties lead to higher Π_{cac}, pC_{20}, and A_{min} values and lower γ_{cac} values. The aggregation number and aggregate size of the AAILs were found to depend on the structure of cationic amino acid-based counter-ions. AAILs with bigger cationic moieties formed larger aggregates, but with a lower aggregation number.

Anouti et al. [9] investigated the aggregation behavior of the imidazolium and pyrrolidinium alkycarboxylate protic ILs, ([IM][AlkylCO$_2$] and [Pyr][AlkylCO$_2$]), as a function of alkylcarboxylate chain length (Alkyl=Pent, Hex, Hep, Oct). The effect of the alkyl chain length on the anionic moiety was the same as that observed for cationic aggregates. Decreases in the cac were detected for both groups of ILs, with an increase in the anionic alkyl chain length (n). Furthermore, the surface activity was also improved, with higher hydrophobicity being caused by longer alkyl chains. The sulfate ILs, with pyrrolidium as cationic counter-ions, showed superior surface activity and favored aggregation more than for imidazolium cations. The cac, ΔG^0_{cac} and α values were lower for pyrrolidinium, which means that aggregates are formed easily and are stabler for these IL than for those with imidazolium cations. In general, ILs with a pyrrolidium cationic moiety presented lower cac and γ_{cac} values and higher Π_{cac} values, and also displayed the best surface activity. Finally, the best packing at the air/water surface was found for imidazolium ILs based, probably due to the lower electrostatic repulsion caused by this cation in relation to pyrrolidium ones.

In the examples used previously, ILs composed of a cationic and an anionic moiety were investigated in terms of the structural effect on aggregation and surface activity properties. However, Liu et al. [54] investigated the opposite charges on the same molecule through surface tension and fluorescence, and the results obtained were compared with another zwitterionic IL [DoDecIMCH$_2$COO]. Large A_{min} and cac/C_{20} values were attributed to a carboxymethyl imidazolium group in the [DoDecIMCH$_2$COO] molecule. The steric effect was shown to be more prominent in aggregation than in adsorption at the air-solution interface for [DoDecIMCH$_2$COO] triggered by larger head groups.

Finally, Blesic et al. [53] investigated anionic and cationic alkyl-chain effects on self-aggregation in aqueous solutions for ILs denominated as catanionic surfactants (Figure 4). To determine aggregation parameters and surface activity, fluorescence spectroscopy and interfacial tension measurements were used. ILs with relatively small methylsulfonate anions (n=8, 10, and 12; and m=1) showed similar behavior to conventional single-chain ILs. A decrease in the cac was observed with the increase in the length of the cationic alkyl chain. However, when both the cation and the anion have a long alkyl chain (n=4 and 8; and m=4 and 8), lower cac values and better surface activity were found when compared with those corresponding to the cationic analogues. It was found that the presence of a hydrophobic chain in both the cationic and anionic moiety of the IL works synergistically to favor aggregation and improve the tensoative properties.

$$\left[H_3C-N \overset{\frown}{\underset{\oplus}{}} N-(CH_2)_nH \right] \quad [(CH_2)_mSO_3]^-$$

Figure 4. Structure of catanionic surfactant ILs.

2.4. Aggregation of dicationic ILs

Besides the length and introduction of functional groups, a new cationic head can be introduced at the end portion of an alkyl chain in the ILs. This new class of ILs is denominated dicationic or gemini. These ILs consist of a hydrophobic chain connected to each of the polar head groups, which are covalently attached through a spacer group, as schematically represented in Figure 5. Reports investigating the influence of structural changes in the aggregation and surface activity properties of dicationic ILs approach both the structure of the spacer group and the hydrocarbon chain connected to the cationic head [20], [55], [56]. In general, it is observed that dicationic ILs have lower cac values, higher adsorption efficiency and surface activity than analogous monocationic ILs [20], [57]. Among the dicationic ILs, the effect of a spacer group has been evaluated and it was found that for a cationic head connected to an alkyl chain with invariable m, the length increase of spacer groups (higher n values) leads to a decrease in the aggregation trend and surface properties [58]. A cationic head with a fixed spacer group and variable alkyl chain length (increase in m values) favors aggregation, following the same trend as that observed for monocationic ILs [57].

$$H_m(H_2C) - \overset{\ominus}{\underset{\oplus}{}} \overset{\ominus}{\underset{n}{}} \overset{}{\underset{\oplus}{}} - (CH_2)_mH$$

Figure 5. Schematically representation of dicationic IL where n is the spacer group and m are alkyl chain with variable length.

Ao et al. [58] studied the aggregation behavior for the gemini IL [Bis-AlkylDoDecIM]Br$_2$ with different spacer lengths. Fluorescence measurements showed that there is an increase in the micropolarity of the aggregates and a decrease in N$_{agg}$ as the spacer length increases. The increase in the micropolarity can be explained by considering that the longer the spacer, the more distant the hydrophilic heads will be. According to Ao et al. [58] this would result in a less tightly packing of the palisade layer, and lead more water molecules to exist in the palisade layer of the gemini ILs aggregates. The decrease in N$_{agg}$ is justified based on the conformation of longer spacers which remain in extended conformation, thus allowing them to aggregate relatively loosely and form smaller aggregates. These results also corroborate with the lower β and higher $\Delta G°_{agg}$ values for ILs with longer spacer groups, which indicates lower stability for these aggregates. In a second work, Ao et al. [57] investigated the aggregation of the gemini IL [Bis-BuAlkIM]Br$_2$ with a fixed spacer group and variable alkyl chain (Alk=Dec, DoDec, TetDec) in aqueous solution. A decrease in the cac value was observed with the increase in the alkyl chain length, following the same aggregation characteristic of analogous monocationic ILs. Surface tension results indicated an increase in the tensoative activity with the increase in the alkyl chain length. On the other hand, the packing ability at the air/water surface is lost with an increase in the alkyl chain length, which is demonstrated by a higher A$_{min}$ value for the IL [Bis-BuTetDecIM]Br$_2$. Zhang et al. [59] investigated the aggregation of gemini pyrrolidine-based ILs in aqueous solution and they showed the same aggregation behavior as that previously described by Ao et al. [57] for gemini imidazolium ILs. These results suggest that changing the alkyl chains and the head groups of the ILs can significantly change the surface activity of the ILs and the aggregation process for dicationic ILs, as it does for analogous monocationic ILs.

2.5. Temperature effect on the IL aggregation

The aggregation behavior of long-chain ILs is generally investigated at room temperature by different techniques, which have been previously mentioned. The main physicochemical properties of ILs determined experimentally are cac, , γ_{cac}, pC$_{20}$, Π_{cac}, Γ_{max}, $\Delta G°_{agg}$ and equilibrium constant of aggregation process (K$_a$) [60]. Studies seeking thermodynamic parameters and the driving force of the IL aggregation process (enthalpic or entropic in nature) within a defined range of temperatures have been reported in the literature [61]. From thermodynamics data — such as enthalpy ($\Delta H°_{agg}$), entropy ($\Delta S°_{agg}$) and $\Delta G°_{agg}$, at various temperatures — it is possible to suggest the mechanism of IL aggregate formation. The relationship between thermodynamic parameters determined at several temperatures allows determination of the contribution of the hydrophobic effect (van der Waals interactions) and electrostatic repulsion between ionic portions of the IL structures [62], [63]. Studies are being conducted in order to rationalize how the enthalpy, entropy, and standard Gibbs free energy of IL aggregation changes with temperature. Some works have shown thermodynamic parameters for ILs with several cations and/or sizes of the alkyl chains [10], [31], [64]. The temperature of the system was found to influence the self-assembly of ILs in solutions. An increase in temperature provides more energy to the system and, consequently, intermolecular interactions may be broken. An increase in the cac, α value, and the surface activity of the ILs is observed, and, therefore, less closely packed aggregates are expected [34].

During the aggregation, the hydrocarbon chain of the IL monomer moves from the solvent media to the aggregate core. This process is expected to be exothermic and governed primarily by the entropy gain associated with the hydrophobic ILs being transferred from the solvent environment to the aggregate interior. However, some ILs have demonstrated distinct tendencies in the features associated with thermodynamic analysis [18]. Thus, this section will detail the literature reports that help to understand the temperature effect on aggregate formation.

Inoue et al. [39] studied the aggregate formation of the long-chain imidazolium ILs [DoDec-MIM]Br, [TetDecMIM]Br, and [HexaDecMIM]Br in aqueous solution, through electrical conductivity measurements. The data demonstrate that the cac increases with an increase in temperature (20°C–40°C), whereas the β value decreases. The thermodynamic parameters indicate that the entropic term ($-T\Delta S°_{agg}$) plays an important role at low temperatures, whereas the $\Delta H°_{agg}$ contribution becomes dominant at higher temperatures (exothermic process). In other words, the aggregation process for long-chain imidazolium ILs is entropy driven at low temperature, while enthalpy driven at high temperature, and this behavior coincide with micelle formation of conventional long-chained surfactants.

Shi et al. [29] evaluated the aggregation behavior of [DecPhMIM]Br, [DoDecPhMIM]Br, and [TetDecPhMIM]Br in aqueous solutions at temperatures between 25°C and 45°C. In the range of temperatures investigated, the values of $\Delta G°_{agg}$ for the three ILs are negative. The $\Delta G°_{agg}$ values were determined and $\Delta H°_{agg}$ was seen to be the main contributor. This fact suggests that the aggregate formation process for these ILs is enthalpy-driven. This behavior was attributed to the strong electrostatic self-repulsion of the headgroups and the counter-ions, as well as the π-π interactions arising from 2,4,6-trimethylphenyl group introduced into the headgroup, since it is known that the enthalpy change of aggregation is mainly a result of hydrophobic and electrostatic interactions [63], [65]. The β value for these ILs is rather low, thus the contribution of electrostatic interactions should be exothermic.

Shi et al. [62] also studied the aggregation behavior of the ILs [DecPhMIM]Br, [DoDecPh-MIM]Br, and [TetDecPhMIM]Br in another IL, [BMIM][BF$_4$], in the same temperature range. They showed that the cac values of ILs increase with the increase in temperature. For all of the ILs, $\Delta H°_{agg}$ was the main contributor to a large negative $\Delta G°_{agg}$ in the temperature range investigated. Therefore, the aggregates of [DecPhMIM]Br, [DoDecPhMIM]Br, and [TetDecPh-MIM]Br in [BMIM][BF$_4$] are enthalpy-driven, similar to the behavior noted in aqueous systems [29]. In the aggregation process, which is exothermic, the hydrocarbon chain of the IL monomer moves from the IL media to the aggregate core. The [BMIM] cation strongly interacts with the cations of the long chain ILs and this interaction increases the electrostatic repulsion between the polar groups. Meanwhile, the effect of π-π interactions between the adjacent aryl groups may be a reason for the large $\Delta H°_{agg}$ observed in this study. Furthermore, it was found that by increasing the alkyl chain length, the entropic term becomes more pronounced. The cac values of ILs in [BMIM][BF$_4$] is much higher than that in water suggesting that the aggregation process is more favorable in aqueous system due to the weak solvophobic effect in IL.

Li et al. [34] studied the long-chain IL [HexaDecHyPrIM]Br from the natural amino acid alanine and focused their attention on the adsorption and aggregation behaviors of this IL in aqueous

solution. The temperature dependence of [HexaDecHyPrIM]Br was evaluated by surface tension and conductivity at temperatures between 25°C and 50°C. The cac values increase with the increase in temperature, whereas the surface tension at the cac (γ_{cac}) follows the opposite trend. The cac values plotted as a function of temperature demonstrate a U-shaped curve with a minimum around 25°C. The surface behavior is similar to the ILs without alanine moiety [39]. The adsorption efficiency of the IL at the air-water interface (pC_{20}) improves with the increase in temperature. The higher temperature resulted in a greater minimum area occupied by a single surfactant molecule at the air-water interface (A_{min}) and a lower maximum surface excess concentration (Γ_{max}). According to the authors, this may be due to increased molecular motion at higher temperatures, which enables the adsorption of fewer molecules at the interface. The tendency is in accordance with the decreased effectiveness of the IL to lower the surface tension, observed through the Π_{cac} data, with the increase in temperature. The thermodynamic analysis resulted in negative $\Delta G°_{agg}$ values, which suggests that the aggregation process is spontaneous. The $\Delta H°_{agg}$ decreases with the increase in temperature and becomes negative at 30°C, indicating that the aggregate formation process is endothermic at lower temperatures and exothermic at higher temperatures. Furthermore, the $-T\Delta S°_{agg}$ value increases with the increase in temperature, contributing much to negative $\Delta G°_{agg}$ values. Thus, the aggregation of alanine-based ILs was proven to be entropy-driven.

Ao, et al. (2008), studied the thermodynamic properties of the aggregation of two Gemini ILs in aqueous solution at 15°C–35°C: [Bis-AlkylDoDecIM]Br$_2$ with different spacer lengths [58]; and [Bis-BuAlkIM]Br$_2$ with different lateral alkyl chain lengths [57]. The negative $\Delta G°_{agg}$ values for [Bis-EtDoDecIM]Br$_2$, [Bis-BuDoDecIM]Br$_2$, [Bis-BuDecIM]Br$_2$, and [Bis-BuTetDecIM] are mainly due to the large positive value of $\Delta S°_{agg}$. Therefore, the aggregation process is governed primarily by the entropy gain associated with it (aggregation is entropy-driven). On the other hand, the aggregate formation process of [Bis-HexDoDecIM]Br$_2$ is enthalpy-driven at lower temperatures, but entropy-driven at higher temperatures. The β values of ILs with different spacer lengths decrease with the increase in temperature. Thus, the authors state that the aggregates of these ILs would be smaller at higher temperatures. The authors confirmed this fact by DLS, which showed that the apparent hydrodynamic radius of [Bis-HexDoDe-cIM]Br$_2$ decreases from 4.0 nm at 25°C to 2.5 nm at 35°C. This result is in accordance with the results reported by Pal et al. [64] who used SANS when studying similar IL aggregates in aqueous solution at 30°C–70°C. Furthermore, the increase in the temperature results in a decrease of the aggregation number. Conversely, for the corresponding monomeric IL, the aggregate formation process is entropy-driven at low temperatures and enthalpy-driven at high temperatures [39].

Zhang et al. [59] investigated the aggregation behavior in aqueous solution of gemini pyrro-lidine-based ILs [Bis-BuAlkPyrr]Br$_2$, where Alk=Dec, DoDec, TetDec). The temperature dependence in the aggregation process was investigated by electrical conductivity in the temperature range of 25°C–45°C. The cac values increase with the increase in temperature. The negative $\Delta G°_{agg}$ value suggests that the aggregation process is a spontaneous process. The values increase with an increase in the hydrophobic chain length, which proves that the increase in alkyl chain length is favorable to the aggregation of the IL in solution. The negative

ΔG°_{agg} values are mainly contributed to by ΔH°_{agg} within the range of temperatures investigated, which suggests that the aggregation of [Bis-BuAlkPyrr]Br$_2$ in aqueous solution is enthalpy-driven. This behavior is different to the corresponding monocationic ILs, [AlkMPyrr]Br, which have entropy-driven aggregate formation at low temperatures and enthalpy-driven formation at high temperatures [43]. On the other hand, the aggregation of dicationic IL with imidazolium head groups [Bis-BuAlkMIM]Br$_2$ is an entropy-driven process for all the temperatures investigated [57]. These results suggest that changing the structure and the head groups of the ILs can significantly change the surface activity of the ILs and the driving forces of the aggregation process. For the authors, the driving force for the entropy-driven process is the tendency of the hydrophobic group to transfer from the solvent to the interior of the aggregate, while the enthalpy-driven process is probably a result of the increase in the degree of hydration for the hydrophilic head groups.

Tariq et al. [45] studied the self-aggregation properties of three pyrrolidinium-based ILs — [DoDecMPyrr]Br, [DoDecBuPyrr]Br, and [OctBuPyrr]Br — in aqueous solution. The aggregation enthalpies were measured at three different temperatures (15°C, 25°C and 50°C) using isothermal titration calorimetry (ITC) measurements. The focus of this study was to determine the driving force of aggregation. The gradual breakdown of the hydrogen-bonded network of liquid water when the temperature increases (resulting in an increase in entropy) leads to enthalpy-driven aggregation at higher temperatures, whereas entropy-driven processes will usually dominate at lower temperatures. The enthalpy of aggregation of [DoDecMPyrr]Br and [DoDecBuPyrr]Br is positive at lower temperatures and becomes negative at higher temperatures. Higher ΔH°_{agg} values for [DoDecBuPyrr]Br in comparison with [DoDecMPyrr]Br indicated stronger interactions between the alkyl chains in the first case. On the other hand, the enthalpy of aggregation decreases and approaches zero at around 50°C for [OctBuPyrr]Br, meaning that both contributions to the enthalpy are equally important; that is, the disruption of the structural organization of the water molecules around the hydrophilic and hydrophobic domains of the IL surfactant, and the restoring of the hydrogen-bond structure of water when the aggregate is formed.

Rao et al. [10] investigated the thermodynamic parameters of self-aggregation, in aqueous solution and at different temperatures (25°C, 35°C, and 45°C), for the following AAILs: GlyPrELS, AlaPrELS, ProPrELS, ValPrELS, and GluPrELS. The cac increases with temperature for all the ILs except for GlyPrELS. A significant negative ΔG°_{agg} value was observed, which indicates a spontaneous aggregation of the AAILs. These values become more negative for ILs that have larger counter-ions. During the aggregation process, the endothermic "breaking" in the network of water molecules ordered around the nonpolar tails of AAILs is greater than the subsequent exothermic association of the molecules, thus leading to the positive entropy. Furthermore, the size and the hydration of the counter-ions are also responsible for the variation in the thermodynamic parameters. The larger and more hydrophobic AAILs, such as GluPrELS, have very high ΔS°_{agg} values when compared with GlyPrELS which is smaller both in size and degree of hydrophobicity. The aggregation of AAILSs are driven by entropic contribution in the temperature range evaluated.

Galgano et al. [31] investigated the micellar properties of [HexaDecMIM]Cl and [N-HexaDec-Py]Cl and compared the data with [HDaEtBzDMA]] which had been investigated by Shimizu et al. [65]. They showed that cac and values of ILs increase with increase of temperature, while N_{agg} decrease. The enthalpies of aggregation, $\Delta H°_{agg}$, were obtained directly by conductivity measurements and ITC. Aggregate formation is entropy-driven at: all studied temperatures (15°C–75°C) for [HexaDecMIM]Cl; up to 65°C for [N-HexaDecPy]Cl; and up to 55°C for [HDaEtBzDMA]. All these data can be rationalized by considering hydrogen-bonding between the head-ions of the monomers in the aggregate. The authors considered that which distinguishes imidazole-based surface active ionic liquids (SAILs) from the other conventional cationic ILs ([N-HexaDecPy]Cl and [HDaEtBzDMA]) to be the strong hydrogen-bonding between the counter-ion and the relatively acidic H2 of the imidazolium ring.

The thermodynamic parameters of the ILs [BMIM]X, [HexMIM]X, and [OctMIM]X (X=Cl⁻, Br⁻, and I⁻) in water at temperatures between 25°C and 40°C was investigated by Vaghela et al. [66]. The $\Delta G°_{agg}$ value was negative and the values increased from [BMIM]X to [HexMIM]X and again to [OctMIM]X. The enthalpies of aggregation are small but negative. For the [HexMIM]X and [OctMIM]X, the large positive entropy values indicate that the aggregation is an entropy-driven process in which the hydrophobic forces are predominant.

2.6. The solvent effect on IL aggregation

Solvents play a decisive role in controlling the aggregation characteristics of ILs. Organic solvents have high cohesive energies and considerable hydrogen-bonding capability [67]; therefore, aggregation studies of ILs in mixed solvents are of fundamental and practical importance. Mixtures of IL solutions usually form mixed micelles that frequently exhibit characteristic properties which are remarkably different from those of the individual component aggregates [68].

There are three important factors to be examined when considering the effect of the solvent on the aggregation parameters: the dipolarity/polarizability parameter (π^*), the solvophobic parameter (Sp), and the Gordon parameter (G). The dipolarity/polarizability parameter measures the non-specific parts of the van der Waals interactions between solvents and solutes; for example, dispersive, inductive, and electrostatic interactions [69]–[72].

Another important characteristic of an organic solvent is the solvophobic parameter, which is equal to the $\Delta G°$ of hydrocarbon transfer from a gaseous phase to a given solvent. This parameter can be used for comparative estimation of the intensity of the interaction between the alkyl chains of an IL and a solvent. A high Sp value indicates a weaker solvent–hydrocarbon interaction and, therefore, a stronger tendency of a system to aggregate. Thus, the aggregation behavior of ILs can be regulated by selecting a solvent with an optimal Sp value for a given problem that is of importance for practical applications. Two aspects of view: (i) the changes of driving forces and (ii) the structure of aggregate could be considered to explain the influences of solvent in the aggregate formation. There is a large number of reports about IL aggregation in water (binary systems) compared to reports on organic solvents or organic solvents/aqueous solutions (ternary systems) [73]–[76]. The cac values of the ILs in different organic-solvent systems tend to increase when increasing the content of the organic additive

in solution, with few exceptions. When increasing the organic solvent content in water, the dielectric constant of the mixture is lowered, which results in an increase in the electrostatic forces of the ionic head groups in the IL aggregate [77]. Additionally, the hydrophobic interactions between the hydrophobic groups of the IL aggregate are gradually reduced, hence the aggregation potential decreases. Both effects justify the higher cac values obtained when increasing the organic solvent content. This section will detail the main reports in the literature that help to elucidate the solvent effect on aggregate formation in ILs.

Through conductivity measurements, He et al. [61] studied the effect that the addition of ethylene glycol (EG) had on the aggregation of the mixture of [HexaDecMIM]Br and [N-HexaDecPy]Br. The cac values of the binary mixtures are between the cac values of the individual surfactants and increase with volume percentage of EG and the mole fraction of [TetDecMIM]Br. The $\Delta G°_{agg}$ values were negative, illustrating that the aggregation process is spontaneous. The $\Delta G°_{agg}$ increase with the increasing in percentage of EG indicating that the process of micellization becomes less spontaneous. The $\Delta H°_{agg}$ and $\Delta S°_{agg}$ values gradually decreased with the concentration of cosolvent. The authors concluded that the aggregation is an entropy-driven process in pure water, whereas the formation of aggregates is enthalpy-driven in the aqueous solution of EG.

Feng et al. [78] investigated the effect of solvents — including acetonitrile, ethylene glycol, N,N-dimethylformamide, formamide, and dimethylsulfoxide solvents — on the aggregation behavior of [DoDecMIM]Br. The study showed that the solvophobic effect and the hydrogen-bonding interaction between the IL anion and the solvents are the main factors affecting the aggregation of ILs in non-aqueous solvents. In aprotic solvent, the cac values increase with the decrease in solvophobic parameters, which indicates that the aggregation of ILs is dominated by the interactions between the alkyl chains of the IL and the solvents. However, in protic solvents, the hydrogen-bonding interactions between the IL anions and the solvents have to be considered. In general, it is found that the aggregation of ILs in non-aqueous solvents can be controlled and regulated by solvent properties. The cac values of [DoDecMIM]Br in non-aqueous solvents are all higher than those for water. The IL cannot form aggregates in ethylene glycol solvent and this result is similar to the previous observation that classical ionic and zwitterionic surfactants exhibited very weak aggregation in EG [79]. They suggest that aggregation can be controlled by selecting appropriate solvent increasing the potential uses of IL in reaction and separation media.

Yan et al. [80] studied the aggregation behavior of [HexaDecTMA]Cl in EG and water mixtures at different temperatures. They observed an increase in cac and a variation tendency for the thermodynamic parameters, upon adding EG. The thermodynamic parameters of the cationic surfactant [HexaDecTMA]Cl in binary EG/H_2O solvent mixtures showed that the cac of [HexaDecTMA]Cl increases from 2 mM to 7 mM, corresponding to the amount of EG added; however, the β value varied little and remained at about 0.5. Moreover, $\Delta G°_{agg}$ increase with addition of EG highlighting that aggregation process is more difficult to achieve in binary solvent mixtures than in water. Two main factors were considered: firstly, the presence of EG decreases the cohesive energy of the solution, thus increasing the solubility of [HexaDecT-MA]Cl in its monomeric form and leading to an increase in the cac value; and secondly, the

dielectric constant of the medium is reduced by the addition of EG, which causes the repulsion effect among the ion head groups to increase.

The aggregation of [EMIM]Cl and [EMIM][TFSA] in water, methanol, acetonitrile, and benzene, was studied by Takamuku et al. [81] using SANS. The SANS results show that the heterogeneity of [EMIM]Cl in acetonitrile mixtures is significant when the acetonitrile content is high; thus, [EMIM]Cl forms clusters in acetonitrile solutions. On the other hand, it has been revealed that [EMIM]Cl is homogeneously dissolved in water and methanol. Remarkably, [EMIM][TFSA] aggregates in methanol solutions, whereas the mixtures of [EMIM][TFSA] with acetonitrile and benzene are homogeneous. They proposed that these homogeneous mixtures are the result of the interactions between benzene molecules and imidazolium rings via π-π interactions; and the hydrogen bonds between the oxygen atoms of TFSA and the hydrogens of benzene.

Furthermore, aggregation of [EMIM]Cl and [EMIM][TFSA] in acetonitrile and methanol, respectively, was examined by using ^{1}H NMR spectroscopy. The data confirmed the results observed using SANS.

Remsing et al. [82] investigated the solvation and aggregation of [BMIM]Cl in water and dimethylsulfoxide (DMSO) by ^{1}H and $^{35/37}$Cl chemical shift perturbations. Evidence of aggregation of the IL n-butyl chains in aqueous environments at IL concentrations of 75–80 wt% was observed in the NMR experiments. A comparison of the data obtained for the imidazolium hydrogens and those in the n-butyl group also reflects that the positively charged ring is solvated prior to the alkyl chain. Indeed, the $\Delta\delta$ for the H2 at H_2O concentrations as low as 5 wt%, is larger than 0.3 ppm, but is only 0.03 ppm for H4′. The H2 is the most acidic hydrogen in the imidazolium ring. It forms the strongest hydrogen bonds with the Cl$^-$ ion and its chemical shift is the most affected by variations in the water content of the binary mixture. The authors observed that [BMIM]Cl behaves as a typical electrolyte in water, with both ions completely solvated at low concentrations.

This experimental result can explain how ILs could be employed, for instance, in the dissolution of polysaccharide, which would demonstrate the potential industrial use of ILs.

However, the data reveal that the interactions between the [BMIM] and Cl$^-$ ions strengthen as the DMSO content of the solutions increases. Thus, solvent is unable to effectively disrupt the interactions between ions and IL-rich clusters persist in this solvent even at concentrations below 10 wt%.

Li et al. [76] used the dipolarity/polarizability parameter (π^*) to study the physicochemical and structural properties of the binary or ternary mixtures, [BMIM][PF$_6$] or [BMIM][BF$_4$], in organic solvent (acetonitrile, water, ethanol, ethyl acetate, and tetrahydrofuran). The binary systems are miscible at the molecular level; that is, there is no obvious aggregation in the solution. However, for the following systems, non-linear behavior is observed: [BMIM][PF$_6$] in ethanol/water mixture; [BMIM][PF$_6$] in ethyl acetate; [BMIM][PF$_6$] in tetrahydrofuran; [BMIM][BF$_4$] in ethanol; and [BMIM][BF$_4$] in an ethanol/water mixture. The reasonable explanation is that aggregation of the systems occurred. From the conductivity study, the

authors deduced that the higher the dielectric constant of the organic solvent, the higher the cac of the IL.

Singh et al. [83] investigated the effect of EG and its derivatives — ethylene glycol monomethyl ether (EGMME) or ethylene glycol dimethyl ether (EGDME) — on the aggregation behavior of [BMIM] in an aqueous medium. The effect of a structural variation in EG by replacing the hydroxyl protons with an ethylene group has been studied and compared. The cac increased least in the case of EG as compared to EGMME or EGDME for the same amount of organic solvent added. They explained this result considering that EG resemble with water in some properties such as high cohesive energy density and capability of hydrogen bonding. For the same amount of EG or EG derivatives added, the aggregation is found to diminish in the order EG < EGMME < EGDME. This may be due to the increased solvophobic effect of the solvents as a consequence of replacing the EG's hydroxyl proton with a methylene group. The temperature dependence of conductivity enabled us to explore the thermodynamics of aggregation, and it was concluded that at low organic solvent concentrations, $\Delta H°_{agg}$ governs the change in $\Delta G°_{agg}$, while $-T\Delta S°_{agg}$ dictates the change at higher organic solvent concentrations.

The increase in EG concentration makes it a better solvent for the IL molecules than pure water and it subsequently forms loose aggregates. Dynamic light scattering (DLS) measurements showed that the hydrodynamic radii (R_h) of the aggregates formed in mixed solvents was higher than that in water, which, however, decreased with an increase in content of EG/its derivatives. The N_{agg} results obtained by ^{1}H NMR measurements follow the same pattern. The ^{1}H NMR measurements were used to probe the aggregated structures at a molecular level. It was observed that with an increase in the content of EG/EG derivatives, the magnitude of $\Delta\delta_{obs}$ decreases, except for EGDME, in which it increases. For the same amount of EG/EG derivatives, $\Delta\delta_{obs}$ varies in the order EG < EGMME < EGDME, which indicates the increasing solvating ability of the ILs that hinders the aggregation process.

Pino et. al. [84] used surface tensiometry to investigate the influence of organic solvents (methanol, 1-propanol, 1-butanol, 1-pentanol, and acetonitrile) on surface adsorption and aggregation of [HexaDecBuIM]Br and [DiDoDecIM]Br. The cac values of the two ILs in different organic solvent/water systems tend to increase when increasing the content of the organic additive in solution, with few exceptions. For the [HexaDecBuIM]Br IL, the extent of the increase in the cac values (evaluated by comparing slopes) follows the trend: acetonitrile < methanol < 1-propanol ≈ 1-butanol < 1-pentanol. In the case of the [DiDoDecIM]Br IL, a fairly similar trend is obtained: acetonitrile ≈ methanol < 1-propanol < 1-butanol < 1-pentanol. The authors observed that for the case of the [DiDoDecIM]Br, a fixed amount of organic solvent, the cac value increases with an increase in the length of the alkyl chain of the alcohol additive. In the presence of organic solvents, the interfacial characteristics of the [DiDoDecIM]Br IL are more influenced than those of the [HexaDecBuIM]Br IL. For both ILs, when the organic solvent content in solution was increased, the following resulted: decreases in the maximum surface excess concentration (Γ_{max}), increases in the minimum surface area per surfactant molecule (A_{min}), decreases in the adsorption efficiency (pC_{20}), and decreases in the effectiveness of surface tension reduction (Π_{cac}).

3. Conclusion

In this chapter we examined the literature, considering the main effects involved in the aggregation behavior of ILs. The results demonstrate the potential applications of these designer ILs in the field of colloid and interface science, as well as in several analytical applications. Aggregate features, such as length and composition of the hydrophobic portion, nature of the head group, and anion characteristics, significantly influence the characteristics of ILs. These studies have shown that the self-assembly and surface activity of ILs can be finely modulated by varying the alkyl length chain, introducing specific cation or polar groups in the side chain, or changing the nature of the anion [27], [34], [36], [62]. A systematic decrease in cac values was observed with an increase in methylene units in the alkyl chain of anion or cationic ions. Additionally, ILs with two long alkyl chains had lower cac values than ILs with one long chain. However, when polar groups (like ester) were added to side chains, aggregation behavior was not different to that of apolar alkyl chains.

The surveys of cationic heads revealed that, in general, the aggregation is favorable in the following order: ammonium > imidazolium ~ pyridinium > pyrrolidinium. However, it is important to note that there were no substantial differences among values obtained for different cationic heads. This fact was attributed to the similar hydrophobic characteristics of the cations investigated. The authors observed that the van der Waals volumes of cationic rings can assume an important role in the aggregation process, and smaller values are related to a more favorable aggregation.

In relation to the counter-ion effect, the aggregation of ILs with different anions followed the Hofmeister series. The increase in the hydrophobicity and decrease in hydration radius caused a decrease in the cac and $\Delta G°_{agg}$ values. When anion bears the alkyl chain, it has the same effect when alkyl chain is bear for the cation. Thus, it was found that the presence of hydrophobic chains in both cationic and anionic moieties of ILs work synergistically and favor the aggregation and improvement of tensoative properties.

The dicationic IL (gemini) aggregation process was the same for analogous monocationic ILs; however, generally the cac values for dicationic ILs were lower than their monocationic analogues.

The temperature of the system is found by influencing the self-assembly of ILs in solutions. An increase in the temperature strongly affects the cation/anion, cation/solvent, and anion/solvent interactions. In general, cac values increased with an increase in temperature, independent of the IL structure. This occurs because the energy supply to the system can lead to the break in intermolecular interactions and avoid aggregation. The most aggregation process described here for ILs were enthalpy-driven at lower temperature, while entropy-driven at higher temperature. This thermodynamic behavior is similar to conventional surfactants. However, it was found some cases, where aggregation process of ILs on water was only enthalpy-driven or only entropy-driven. The thermodynamic parameters revealed no following of a pattern for cationic or anionic structure.

Finally, the addition of organic solvents was found to have a vital effect on the cac value, the standard Gibbs energy of aggregation, the aggregation number, and aggregate size. Generally, the cac values of the ILs in different organic-solvent systems tend to increase when increasing the content of the organic additive in solution, with few exceptions.

The review addressed in this chapter demonstrates that the interactions present in the IL-solution system are variable, showing that it is essential to have a better understanding of the interactions of ILs with various classes of organic molecules. This particular aspect allows us to actually consider ILs (when dispersed in aqueous and/or organic solutions) to be a new class of surfactants with unique abilities.

Abbreviations and symbols

$Å^3$	cubic angstroms
AAILs	amino acid ionic liquid
A_{min}	area per molecule at the interface
C_{20}	concentration of IL to reduce the surface tension of pure solvent by 20 mN/m
cac	critical aggregation concentration
cac_1	first critical aggregation concentration
cac_2	second critical aggregation concentration
DLS	dynamic light scattering
DMSO	dimethylsulfoxide
EG	ethylene glycol
EGDME	ethylene glycol dimethyl ether
EGMME	ethylene glycol monomethyl ether
G	gordon parameter
I_I	first emission band of pyrene
I_{III}	third emission band of pyrene
ILs	ionic liquids
ITC	isothermal titration calorimetry
K_a	equilibrium constant of aggregation
mM	millimolar
mN/m	millinewtons per mole
N_{agg}	aggregation number
nm	nanometers

NMR	nuclear magnetic resonance
pC_{20}	adsorption efficiency
R_h	hydrodynamic radius
SAILs	imidazole-based surface active ionic liquids
SANS	small angle neutron scattering
SAXS	small angle X-ray scattering
Sp	solvophobic parameter
$-T\Delta S^{\circ}_{agg}$	entropic term of Gibbs Free Energy equation
wt%	molar fraction
α	degree of counter-ion dissociation
β	degree of counter-ion binding
γ	surface tension
Γ_{cac}	Surface tension at cac
δ_{obs}	chemical shift observed
$\Delta\delta$	chemical shift variation
π^*	polarity/polarizability parameter
Π_{cac}	effectiveness of the IL in decreasing the surface tension of the solvent
$\Gamma_{máx}$	excess surface concentration
ΔG°	Gibbs free energy
ΔG°_{ads}	Gibbs free energy of adsorption
ΔG°_{agg}	Gibbs free energy of aggregation
ΔH°_{agg}	enthalpy of aggregation
ΔS°_{agg}	entropy of aggregation

Representation of IL cations in this chapter

Representation	Structure	Name
[EMIM]	$H_3C-N\overset{\oplus}{\underset{}{N}}-(CH_2)_2H$	1-Ethyl-3-methylimidazolium
[BMIM]	$H_3C-N\overset{\oplus}{\underset{}{N}}-(CH_2)_4H$	1-Butyl-3-methylimidazolium

Representation	Structure	Name
[HexMIM]	$H_3C-N{\oplus}N-(CH_2)_6H$	1-Hexyl-3-methylimidazolium
[OctMIM]	$H_3C-N{\oplus}N-(CH_2)_8H$	1-Octyl-3-methylimidazolium
[DecMIM]	$H_3C-N{\oplus}N-(CH_2)_{10}H$	1-Decyl-3-methylimidazolium
[DoDecMIM]	$H_3C-N{\oplus}N-(CH)_{12}H$	1-Dodecyl-3-methylimidazolium
[TetDecMIM]	$H_3C-N{\oplus}N-(CH)_{14}H$	1-Tetradecyl-3-methylimidazolium
[HexaDecMIM]	$H_3C-N{\oplus}N-(CH_2)_{16}H$	1-Hexadecyl-3-methylimidazolium
[HexaDecBuIM]	$H(H_2C)_4-N{\oplus}N-(CH_2)_{16}H$	1-Hexadecyl-3-butylimidazolium
[DoDecEtIM]	$H(H_2C)_2-N{\oplus}N-(CH_2)_{12}H$	1-Ethyl-3-dodecylimidazolium
[DoDecPrIM]	$H(H_2C)_3-N{\oplus}N-(CH_2)_{12}H$	1-Propyl-3-dodecylimidazolium
[DoDecBuIM]	$H(H_2C)_4-N{\oplus}N-(CH_2)_{12}H$	1-Dodecyl-3-butylimidazolium
[DiDoDecIM]	$H(H_2C)_{12}-N{\oplus}N-(CH_2)_{12}H$	1,3-Didodecylimidazolium
[N-BPy]	$\oplus N-(CH_2)_4H$	1-Butylpyridinium
[N-HexPy]	$\oplus N-(CH_2)_6H$	1-Hexylpyridinium
[N-OctPy]	$\oplus N-(CH_2)_8H$	1-Octylpyridinium
[N-HexaDecPy]	$\oplus N-(CH_2)_{16}H$	1-Hexadecylpyridinium

Representation	Structure	Name
[N-Oct-2-MePy]		1-Octyl-2-methylpyridinium
[N-Oct-3-MePy]		1-Octyl-3-methylpyridinium
[N-Oct-4-MePy]		1-Octyl-4-methylpyridinium
[N-Bu-3-MePy]		1-Butyl-3-methylpyridinium
[BMPyrr]		N-Butyl-N-methylpyrrolidinium
[OctMPyrr]		N-Octyl-N-methylpyrrolidinium
[DoDecMPyrr]		N-Dodecyl-N-methylpirrolidinium
[TetDecMPyrr]		N-Tetradecyl-N-methylpirrolidinium
[HexaDecMPyrr]		N-Hexadecyl-N-methylpirrolidinium
[OctBuPyrr]		N-Butyl-N-octylpyrrolidinium
[DoDecBuPyrr]		N-butyl-N dodecylpyrrolodinium

Representation	Structure	Name
[EtOHDoDecIM]	$HO(H_2C)_2-N$⊕$N-(CH_2)_{12}H$	1-hydroxyethyl-3-dodecylimidazolium
[HexaDecHyPrIM]	$H(H_2C)_{16}-N$⊕$N-$ CH_2OH/H/CH_3	S-3-hexadecyl-1-(1-hydroxy-propan-2-yl) imidazolium
[DecPhMIM]	H_3C-...CH_3...N⊕$N-(CH_2)_{10}H$...CH_3	1-(2,4,6-trimethylphenyl)-3-decylimidazolium
[DoDecPhMIM]	H_3C-...CH_3...N⊕$N-(CH_2)_{12}H$...CH_3	1-(2,4,6-trimethylphenyl)-3-dodecylimidazolium
[TetDecPhMIM]	H_3C-...CH_3...N⊕$N-(CH_2)_{14}H$...CH_3	1-(2,4,6-trimethylphenyl)-3-tetradecylimidazolium
[1,3-DiDec-2-MIM]	$H(H_2C)_{10}-N$⊕$N-(CH_2)_{10}H$ CH_3	1,3-didecyl-2-methylimidazolium
[HexaDecTMA]	⊕CH_3 $H_3C-N-CH_3$ $(CH_2)_{16}H$	hexadecyltrimethylammonium
[HDaEtBzDMA]	Me/⊕N/Me - NH - $(CH_2)_{15}H$, O	Benzyl(3-hexadecanoylaminoethyl)dimethylammonium
GlyPrELS	⊕H_3N...O...CH_3/CH_3, O; ⊖$O-S-(CH_2)_{12}H$, O, O	Glycine propyl ester lauryl sulfate

Representation	Structure	Name
AlaPrELS		Alanine propyl ester lauryl sulfate
ProPrELS		Proline propyl ester lauryl sulfate
ValPrELS		Valine propyl ester lauryl sulfate
GluPrELS		Glutamine propyl ester lauryl sulfate
[DoDecIMCH₂COO]		1-carboxymethyl-3-dodecylimidazolium inner salt
[Bis-AlkylDoDecIM]Br2 (Alkyl = Et, Bu, Hex)		1,2-bis(3-dodecylimidazolium-1-yl) alcane (alcane = etane, butane, hexane)
[Bis-BuAlkylIM]Br2 (Alkyl = Dec, DoDec, TetDec)		1,2-bis(3-alkylimidazolium-1-yl) butane (alkyl = dec, dodec, tetdec)
[Bis-BuAlkylPyrr] (Alkyl = Dec, DoDec, TetDec)		1,1-(butane-1,4-diyl)bis(1-alkylpyrrolidinium) (alkyl = decyl, dodecyl, tetradecyl)

Representation	Structure	Name
[Pyr][AlkylCO₂]	(n = 5, 6, 7, 8)	pyrrolidinium alkylcarboxylates (alkyl = pen, hex, hep, oct)
[IM][AlkylCO₂]	(n = 5, 6, 7, 8)	imidazolium alkylcarboxylates (alkyl = pen, hex, hep, oct)
[AlkylCMIM]Br (Alkyl = Hex, Oct, Dec, DoDec, TetDec)	(n = 6, 8, 10, 12, 14)	3-methyl-1-alkyloxycarbonylmethylimidazolium bromide (alkyl = hexyl, octyl, decyl, dodecyl, tetradecyl)
[AlkylCMPy]Br (Alkyl = Hex, Oct, Dec, DoDec, TetDec)	(n = 6, 8, 10, 12, 14)	1-alkyloxicarbonylmethylpyridinium bromide (alkyl = hexyl, octyl, decyl, dodecyl, tetradecyl)
[CₙH₂ₙ₊₁MIM][CₘH₂ₘ₊₁SO₃] (n = 8, 10, 12; m=1 and n = 4, 8; m=4, 8)	(n = 8, 10, 12; m=1 and n = 4, 8; m= 4, 8)	1-alkyl-3-methylimidazolium alkylsulfonate (alkyl = metyl, butyl, octyl, decyl, dodecyl)
[EMIM]TFSA		1-ethyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)amide)
[BMIM][C₈OSO₃]		1-Butyl-3-methylimidazolium octyl sulfate

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