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Influence of the AOT counterion chemical structure in the generation of organized systems

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ABSTRACT

The impact of the imidazolium counterions structure on the organized systems formed by the surfactant 1,4-bis-2-ethylhexylsulfosuccinate, AOT, both in aqueous solutions and in non-polar solvents is investigated. With this in mind, we investigated if the ionic liquid-like (IL-like) surfactant 1-ethyl-3-methylimidazolium 1,4-bis-2-ethylhexylsulfosuccinate, emim-AOT, forms direct micelles or vesicles in water. Dynamic Light Scattering (DLS), zeta potential, conductivity, fluorescence and UV-Visible spectroscopy measurements were performed to characterize the organized systems in aqueous solution. We also studied the self-aggregation of emim-AOT, 1-butyl-3-methylimidazolium 1,4-bis-2-ethylhexylsulfosuccinate, bmim-AOT, and of 1-hexyl-3-methylimidazolium 1,4-bis-2-ethylhexylsulfosuccinate, hmim-AOT, in non-polar solvents.

The results obtained showed that the IL-like surfactant emim-AOT forms direct micelles in water, as Na-AOT does. However, emim-AOT aggregates are larger, have a lower surface charge, are more stable, and have a more polar and less fluid micellar interface than Na-AOT micelles. It was also observed that emim-AOT and hmim-AOT form reverse micelles in non-polar solvents. The size of the imidazolium cations dramatically influences on the size of the reverse micelles as well as on their ability to solubilize water.

KEYWORDS: ionic liquid-like surfactant, organized systems, Na-AOT, emim-AOT.

INTRODUCTION

Organized systems are important and promising in the progress of various branches of modern science and technology.^{1,2} For example, they are used as detergent, in the industries of dyes, cosmetic and pharmaceutical.³ The existence of different microenvironments in these systems is one of the reasons for their applications in different areas, such as chemical catalysis,⁴⁻⁸ enzymatic hydrolysis,⁹⁻¹² and nanoparticle synthesis,¹³⁻¹⁶ among others.¹⁷ In this context, nanomedicine has become in recent years one of the most promising fields concerning the diverse applications of organized systems. For example, they are frequently used as drug delivery systems.^{7,18-21} Also, the biomimetic characteristics presented by these systems can be highlighted, since they can be considered "simplified models" that simulate the behavior of highly complex structures, such as biological membranes.^{22,23}

The surfactant sodium 1,4-bis-2-ethylhexylsulfosuccinate (Na-AOT, Scheme 1) can form direct micelles in aqueous solution,²⁴⁻²⁶ with a critical micellar concentration value $\sim 10^{-3}$ M.²⁷⁻³⁰ These aggregates have been used as a dispersing medium for hydrophobic dyes in an aqueous medium,³¹ for the synthesis of nanoparticles,^{16,32} among others.³³ Furthermore, reverse micelles formulated in non-polar organic solvents can be created using also Na-AOT as surfactant. Depending mostly on the non-polar organic medium and temperature, these systems have the ability to disperse large amounts of water. For example, it is possible to achieve a $W_0^{\max} = 12$ using benzene,³⁴ while in *n*-heptane is possible to reach a value close to $W_0^{\max} = 60$ ^{35,36} ($W_0 = [\text{Water}]/[\text{Surfactant}]$). These properties are responsible for their numerous applications, as was mentioned above.^{4-6,9,11,13-15,17}

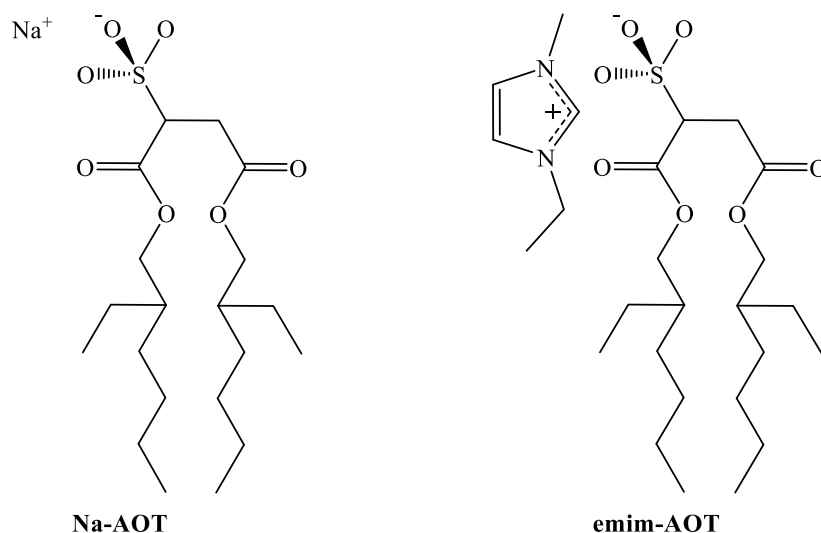
Ionic Liquids (ILs) are synthetic compounds with interesting properties such as low toxicity, friendly to the environment and very versatile.³⁷⁻³⁹ Chemically, the ILs are

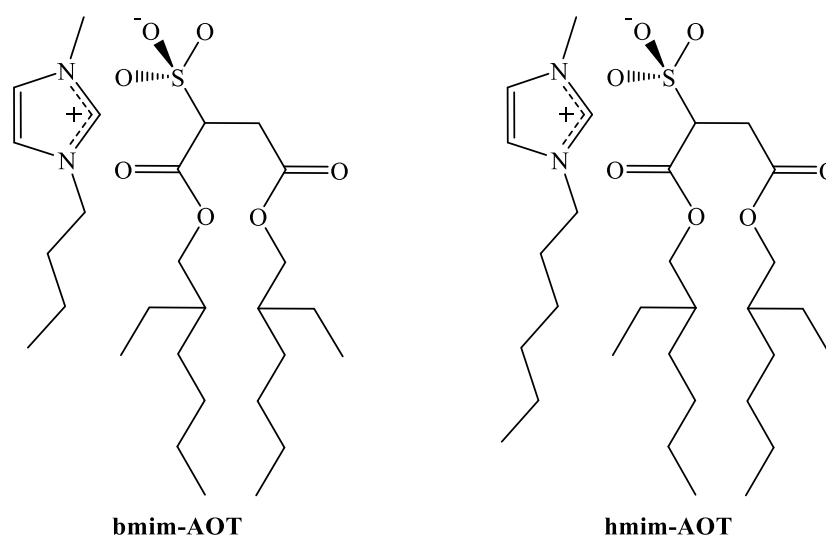
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3 salts with a low melting point (< 100 °C), composed only of ions. They also present
4 very low vapor pressure, excellent thermal and chemical stability, easy recycling, and
5 wide possibility to vary their properties such as polarity and hydrophobicity, through
6 suitable cation and anion modification.⁴⁰ In this sense, the possibility to create ILs with
7 amphiphilic properties have been increased in the last years.⁴¹⁻⁴³ These novels
8 compounds, named *IL-like surfactants*, were able to formulate direct micelles, reverse
9 micelles and vesicles as examples of organized systems.^{39,41-47} Furthermore, the *IL-like*
10 *surfactants* derived from the imidazolium group are very interesting due to the unique
11 properties of such cation: i) delocalization of the positive charge on the heterocyclic
12 ring, which produce great stability. ii) The possibility of substituting the hydrogen
13 attached to the carbon atom located between the two nitrogen atoms, for a substituent
14 that allows the rest of the imidazolium ring to act as a ligand catalyst for metals. iii)
15 Change the lipophilic character of the cation by substitution with alkyl groups at the
16 ring nitrogen's. Besides, thinking in future applications such as the design of catalysts,
17 the flat geometry of the imidazolium ring can also be a significant aspect to consider.⁴⁸⁻
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Recently^{46,51} we reported the synthesis of two IL-like surfactants 1-butyl-3-methylimidazolium 1,4-bis-2-ethylhexylsulfosuccinate and 1-hexyl-3-methylimidazolium 1,4-bis-2-ethylhexylsulfosuccinate (bmim-AOT and hmim-AOT respectively, Scheme 1). In comparison with Na-AOT, these IL-like surfactants showed very different properties.^{46,51} Particularly, we studied the physicochemical properties of the aggregates formed by bmim-AOT and hmim-AOT in different solvents.^{46,47}

Taking into account, the effect of the AOT counterion structure on the self-assembly process is investigated. With this goal, the IL-like surfactant 1-ethyl-3-methylimidazolium 1,4-bis-2-ethylhexylsulfosuccinate (emim-AOT, Scheme 1) was

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3 synthesized. Later, the emim-AOT aqueous solutions were investigated performing
4 several experiments in order to acquire information about size, surface charge, degree of
5 dissociation, critical micellar concentration (cmc), aggregation number (N_{agg}),
6 micropolarity and microviscosity. Thus, emim-AOT aggregates were investigated using
7 Dynamic Light Scattering (DLS), zeta potential and conductivity techniques.
8 Additionally, by using three molecular probes such as pyrene (Scheme S1,
9 Supplementary Material), 2,2'-[[4-[(4-nitrophenyl)azo]phenyl]imino]bisethanol⁵²⁻⁵⁴
10 (DR9, Scheme S1) and 1,3-dipyrenylpropane^{55,56} (P3P, Scheme S1), valuable
11 information about the cmc, N_{agg} ,^{57,58} polarity and viscosity of their microenvironment
12 can be obtained.^{58,59} The self-association of emim-AOT and hmim-AOT in the non-
13 polar solvents *n*-heptane and benzene was examined and the results compared with
14 those already reported on reverse micelles of bmim-AOT and Na-AOT.^{46,47,60}
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Scheme 1. Molecular structures of the surfactants Na-AOT, emim-AOT, bmim-AOT and hmim-AOT.

EXPERIMENTAL SECTION

Materials

1-Ethyl-3-methylimidazolium chloride (emim-Cl), bmim-Cl, hmim-Cl, Na-AOT, dichloromethane (DCM), benzene, *n*-heptane, *N*-hexadecylpyridinium bromide (CPyBr) and DR19 were from Sigma-Aldrich (> 99% purity) and kept under vacuum prior to use. P3P and pyrene were purchased from Molecular Probes, Inc. and used as received.

The IL-like surfactants used, bmim-AOT and hmim-AOT, were obtained following the experimental procedures previously described.^{46,51} Emim-AOT was prepared following the same methodology (fully described in Supplementary Material section),^{46,51} using as reactants emim-Cl and Na-AOT.

Methods

Detailed experimental procedure for all the samples preparations; DLS, zeta potential, conductivity and emission experiments are shown in the Supplementary Material

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8 **RESULTS AND DISCUSSION**

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10 As a first experiment, the solubility of emim-AOT in water was investigated.
11 This IL-like surfactant was soluble in water until 2×10^{-2} M, forming transparent
12 solutions which remain stable over time. Similar behavior was reported by the Na-AOT
13 surfactant and can suggest the formation of small size aggregates with low capacity to
14 scatter the light.⁶¹
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21 We previously observed by DLS that the surfactants bmim-AOT and hmim-
22 AOT form vesicles in water.⁵¹ In this work aqueous solutions of emim-AOT in water
23 were prepared, in a concentration range from 1×10^{-4} M to 2×10^{-2} M, and the samples
24 were analyzed by DLS. Table 1 shows the apparent hydrodynamic diameter, d_{app} , values
25 obtained for emim-AOT in water at 298 K. In Figure S3 (Supplementary Material), the
26 DLS intensity plot for emim-AOT in water at [surfactant] = 1×10^{-2} M is depicted. The
27 DLS data show the formation of aggregates with diameters ranging from 1.2 - 1.4 nm,
28 with low polydispersity indexes (within the range 0.1 - 0.2). Moreover, within the range
29 of 6×10^{-3} M – 2×10^{-2} M the sizes were independent of the surfactant concentration.
30 The sizes found for the emim-AOT aggregates and the detection of these aggregates
31 from [emim-AOT] = 6×10^{-3} M, are good evidences that the surfactant self-aggregates
32 forming direct micelles,²³ as makes the surfactant Na-AOT.^{25,26,28} The DLS results seem
33 to indicate that the critical micellar concentration is close to 6×10^{-3} M.²³
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Table 1. d_{app} and polydispersity indexes (PDI) values of emim-AOT micelles in water at different surfactant concentrations. T = 298 K.

[Surfactant] (10^{-2} M)	d_{app} (nm)	PDI
0.6	1.4 ± 0.1	0.2
0.8	1.3 ± 0.1	0.2
1.0	1.3 ± 0.1	0.2
1.2	1.2 ± 0.1	0.1
1.6	1.3 ± 0.1	0.1
2.0	1.3 ± 0.1	0.1

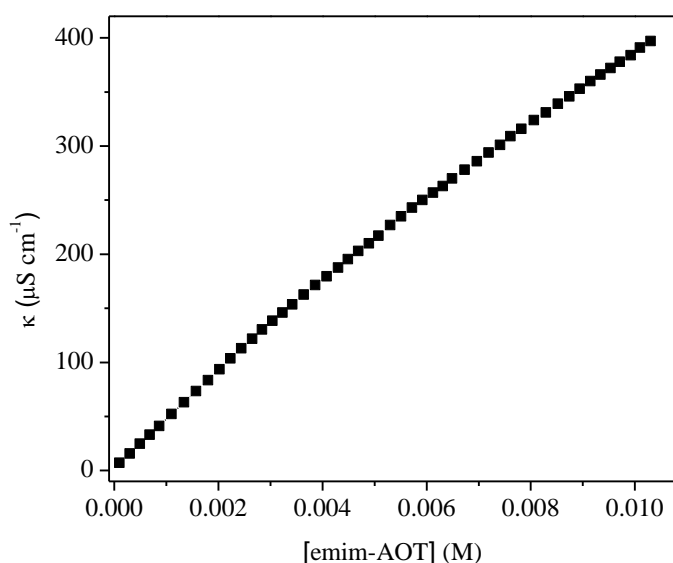
Zeta potential measurements were carried out to determine the surface charge of these aggregates and the corresponding values are listed in Table 2.

Table 2. Zeta potential values (mV) of Na-AOT and emim-AOT micelles in water at different surfactant concentrations. T = 298 K.

[Surfactant] (10^{-2} M)	Na-AOT	emim-AOT
0.6	-51 ± 2	-37 ± 2
0.8	-52 ± 2	-36 ± 2
1.0	-49 ± 2	-38 ± 2
1.2	-51 ± 2	-37 ± 2
1.6	-52 ± 2	-40 ± 2
2.0	-50 ± 2	-39 ± 2

Data in Table 2 show zeta potential values of -51 mV and -38 mV for micelles of Na-AOT and emim-AOT, respectively. Thus, the anionic part of the polar head of

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3 both surfactants appears to be exposed to the outer region of the micelle in both cases.
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5 However, the larger zeta potential value found for Na-AOT micelles compared to
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7 emim-AOT micelles could indicate the presence of a smaller concentration of positive
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9 counterions in the micellar interface of the water/Na-AOT systems than in the emim-
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11 AOT aggregates. This may due to the emim⁺ cation which is more hydrophobic than the
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13 Na⁺ cation, and therefore it prefers to be part of the micellar aggregate than to be
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15 solvated in the aqueous phase. To check this effect, the degree of counterion
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17 dissociation of micelles, α ,⁶² of emim-AOT and Na-AOT was determined by measuring
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19 the conductivity of the medium at different concentrations of surfactant, as shown in
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21 Figure 1 and Figure S3 (Supplementary Material), respectively.
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47 **Figure 1.** Variation of the conductivity with [surfactant] in the micellar system
48 water/emim-AOT. T = 298 K.
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53 The α values were determined using the method described by Carpena et al.⁶²
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55 Thus, we found for emim-AOT direct micelles a value of $\alpha = 0.73$, while for the Na-
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57 AOT micellar system is $\alpha = 0.92$. These results show that the emim⁺ counterion, in the
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emim-AOT direct micelles, is bound to the AOT⁻ head groups more extensively than the Na⁺ counterion in the Na-AOT micelles. In the latter, the Na⁺ ions can be considered practically dissociated from the micelles in aqueous solution. These results agree with the data obtained by zeta potential.

The method described by Carpena et al.⁶² also permits the estimation of cmc values. The cmc values obtained were 2.5×10^{-3} M and 3.3×10^{-3} M for emim-AOT and Na-AOT, respectively. The Na-AOT cmc value has already been reported³⁰ and our determination agrees with this value. Nonetheless, to further investigate this point, the cmc's of both systems were estimated through fluorescence spectroscopy using pyrene as probe. Pyrene was used at a fixed concentration, varying the surfactant concentration from 5×10^{-4} M to 1×10^{-2} M. The ratio of the intensity of peaks 3 (I₃) and 1 (I₁) in the fluorescence spectrum of the pyrene was plotted, as a function of log[surfactant] for emim-AOT and Na-AOT micellar systems, as shown in Figures 2 and S4 (Supplementary Material), respectively.

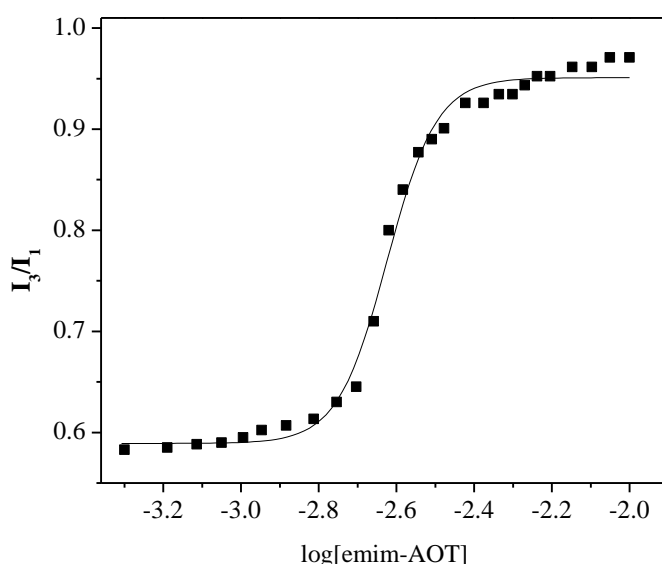


Figure 2. Dependence of the I₃/I₁ ratio on log [surfactant] in emim-AOT aqueous solutions. [Pyrene] = 1×10^{-6} M. T = 298 K.

By this methodology, the cmc value for emim-AOT micelles is 2.3×10^{-3} M, while for Na-AOT micellar system it is 3.0×10^{-3} M. Both values are in agreement with those obtained by conductivity measurements. From the α and cmc values, the Gibbs energy of micellization, ΔG_{mic} , can be calculated by using Equation 1:⁶³

$$\Delta G^{\circ}_{\text{M}} = RT (2 - \alpha) \ln(\text{cmc}) \quad (1)$$

where R and T have their usual meaning. $\Delta G^{\circ}_{\text{M}}$ values are summarized in Table 3.

Table 3. Critical micelle concentration (cmc), micellar ionization degree (α) and Gibbs energy of micellization ($\Delta G^{\circ}_{\text{M}}$) for the emim-AOT and Na-AOT surfactants in water. T = 298 K.

Surfactant	α	cmc (mM)	$\Delta G^{\circ}_{\text{M}}$ (kJ mol ⁻¹)
emim-AOT	0.73 ± 0.02	2.3 ± 0.2	-19.2
Na-AOT	0.92 ± 0.02	3.0 ± 0.2	-15.5

Analyzing the data in Table 3, it can be seen that the micellization process of emim-AOT micelles is more favored than that of Na-AOT micelles. This could be explained by considering the more hydrophobic character of the emim⁺ cation as compared to Na⁺.

The N_{agg} of emim-AOT micelles was determined, using pyrene and CPyBr, as a quencher. In the experiments the quencher concentration was changed while the surfactant and pyrene concentrations were kept constant at 1×10^{-2} M and 1×10^{-6} M, respectively. The N_{agg} value was obtained from the slope of the plot of $\ln(I_0/I_q)$ vs. [CPyBr], as shown in Figure 4, where I_0 and I_q are the intensity of the pyrene peak 1 in the absence and in the presence of the quencher, respectively, as was previously

described.³⁰

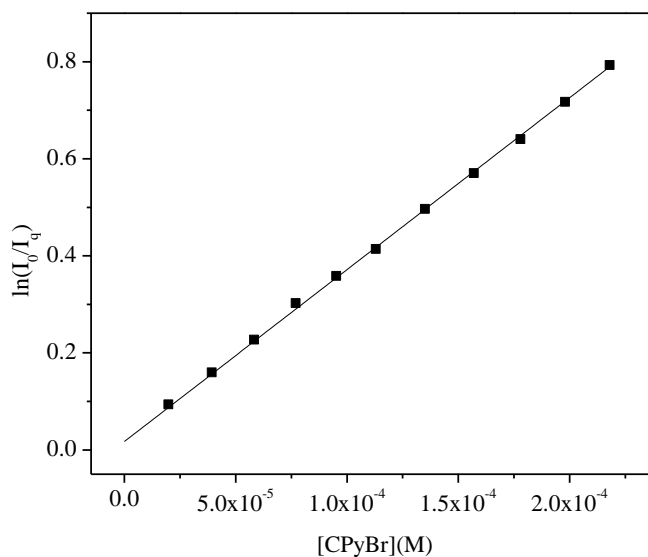
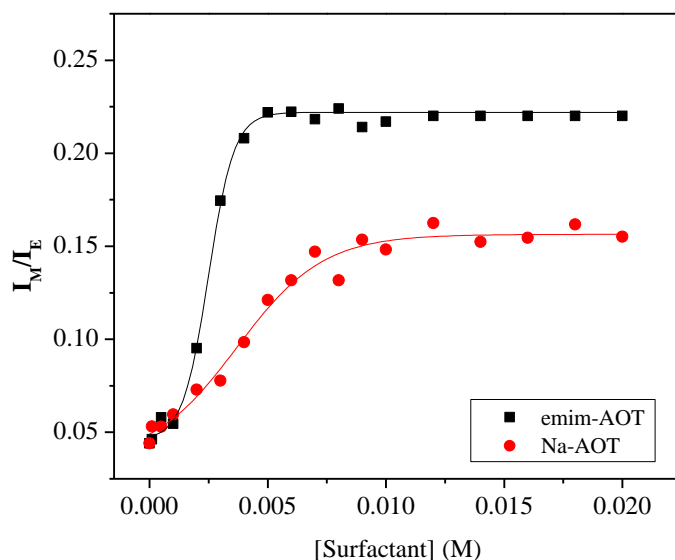


Figure 3. Variation of the $\ln(I_0/I_q)$ with $[CPyBr]$ in the micellar system water/emim-AOT. $[emim-AOT] = 1 \times 10^{-2}$ M. $[Pyrene] = 1 \times 10^{-6}$ M. $T = 298$ K.

The N_{agg} value calculated from Figure 3 for emim-AOT direct micelles is 28. This value seems reasonable since the N_{agg} reported in the bibliography for Na-AOT is 22.³⁰ Since the α value of emim-AOT is lower than that of Na-AOT, this could indicate that there is a greater presence of the emim⁺ counterions in the micellar interface, thus decreasing the electrostatic repulsions between the AOT⁻ negatively charged heads.

The interfacial microviscosity of these organized systems is also interesting information to explore. To do that, the probe P3P was employed ($[P3P] = 2 \times 10^{-6}$ M) and the [surfactant] was varied. The dependence of the ratio I_M/I_E on [Surfactant], I_M and I_E being the intensities of the emission bands of the monomer and of the excimer of the probe, respectively, can provide this information.⁵⁶ As it is presented in Figure 4, an increase in the microviscosity of the environment (where the molecular probe is located) can be invoked if an increment in the I_M/I_E ratio is observed.^{55,58,64} In both systems, a

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3 sigmoidal tendency in the I_M/I_E ratio is observed. Moreover, for all the surfactant
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5 concentrations investigated a higher ratio for emim-AOT in comparison with Na-AOT
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7 was found. This fact would suggest a larger rigidity of the micellar interface of emim-
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9 AOT micelles than that of the Na-AOT aggregates.



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34 **Figure 4.** Values of I_M/I_E ratio as a function of [surfactant] in the micellar systems
35 water/Na-AOT and water/emim-AOT. $[P3P] = 2 \times 10^{-6}$ M. $T = 298$ K.

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41 Results in Figure 4 indicate a higher viscosity for the emim-AOT micellar
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43 interface than that for Na-AOT. This agrees with the results obtained so far, since the
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45 emim-AOT micelles have a higher N_{agg} and a lower α than Na-AOT aggregates. A
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47 higher concentration of $emim^+$ in the micellar interface results in a lower solvent
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49 penetration in this region, thus generating a more compact micelle with a higher
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51 viscosity.

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55 Direct micelles have the potential to solubilize hydrophobic compounds in
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57 water.⁶⁵⁻⁶⁹ For this reason, the ability of both micelles to incorporate a water-insoluble
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59 molecule such as the DR19 dye⁵²⁻⁵⁴ was tested. Thus, the amount of DR19 dissolved in
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both micellar solutions by varying the [surfactant] is plotted in Figure 5.

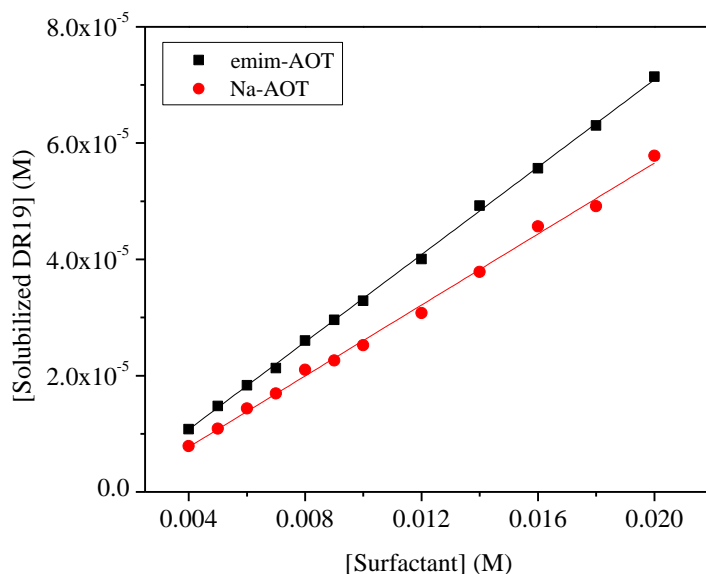
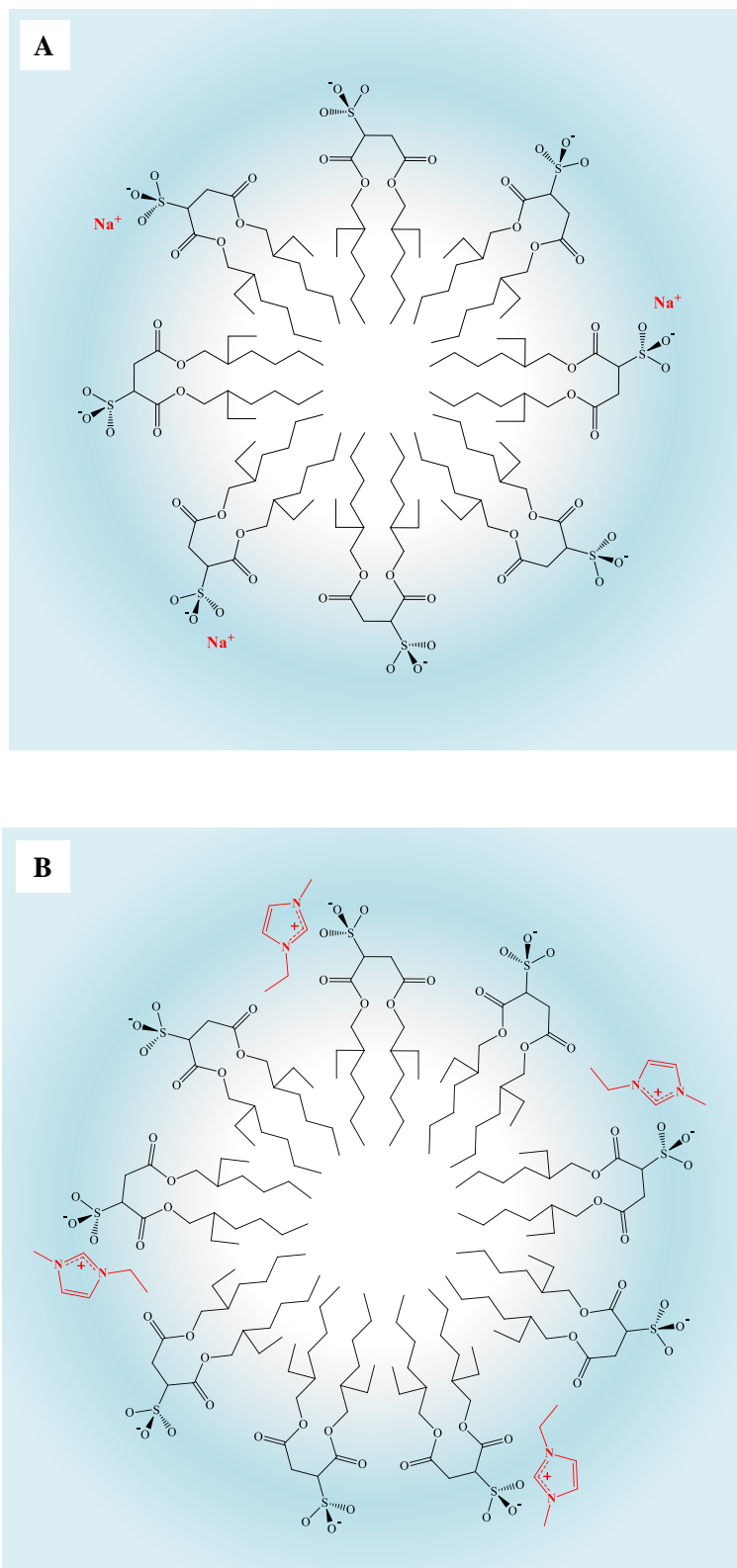


Figure 5. Amount of DR19 solubilized by the micellar systems water/Na-AOT and water/emim-AOT as a function of the [surfactant]. T = 298 K.

As can be seen in Figure 5, the emim-AOT micelles solubilize a higher concentration of DR19 than the Na-AOT ones. This points out that the emim-AOT micelles might be less polar than the Na-AOT micelles, which could be because emim⁺ has a lower charge/volume ratio than the cation Na⁺. Besides, emim⁺ has a methyl and an ethyl group as substituent of the ring nitrogen's, creating a more hydrophobic environment in the interface.

The compactness of the interface and consequently the size of the micelles can be interpreted invoking the effective packaging parameter of the surfactant p , which is defined as $p = v/al_c$, where v and l_c are the volume and the length of the hydrocarbon chain, respectively, and a is the area of the surfactant head group.⁷⁰ In general, for direct micelles is $p < 1/3$, vesicles present $1/2 < p < 1$, and bilayers $p \approx 1$.⁷¹ The size of the micelles is larger when the p value is closer to $1/3$. Therefore, all factors that increase

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3 the ν value and/or decrease the a value, increase the packaging parameter that affects
4 the size of the micelles.⁷¹ Based on the results obtained in this work and considering
5 those obtained previously from the IL-like surfactants bmim-AOT and hmim-AOT in
6 water,⁵¹ a similar reasoning can be applied. The IL-like surfactant emim-AOT forms
7 direct micelles, like the Na-AOT surfactant, but larger because of the substitution of the
8 Na⁺ counterion by emim⁺. The emim⁺ counterion has alkyl groups that could be located
9 near to the hydrocarbon tails of AOT, which favors hydrophobic interactions. In this
10 way, the p value would increase, but not exceeding 1/3, since the hydrocarbon tail that
11 has the emim⁺ counterion is shorter than those of bmim⁺ and hmim⁺ counterions in the
12 analogous bmim-AOT and hmim-AOT surfactants. The latter have a p value between
13 1/2 and 1, so they form vesicles in water.⁵¹ In Scheme 2 is postulated the ions
14 distribution around the interface in both micelles.
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Scheme 2. Schematic representation of the direct micelles of Na-AOT surfactant (A) and IL-like surfactant emim-AOT (B).

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3 Considering that Na-AOT and emim-AOT form direct micelles, while bmim-
4 AOT and hmim-AOT form vesicles in water, the counterion nature has a clear influence
5 on the type of aggregates formed in aqueous solution. With this in mind, information
6 on the type of aggregates formed in aqueous solution. With this in mind, information
7 about the effect of the counterion on the self-aggregation of the IL-surfactants in non-
8 polar solvents was also investigated. Na-AOT and bmim-AOT form reverse micelles in
9 these media and present several differences.^{46,47} Therefore, our interest was focused in
10 the study of the self-aggregation of emim-AOT and hmim-AOT in different non-polar
11 solvents.

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13 Firstly, non-polar solvents such as benzene and *n*-heptane were selected to
14 evaluate the solubility of emim-AOT and hmim-AOT. Emim-AOT was soluble at least
15 up to 0.1 M in benzene, but not in *n*-heptane, whereas hmim-AOT was soluble in both
16 solvents. Next, water aliquots were added to the surfactants/non-polar solutions in order
17 to investigate the maximal amount of polar solvent (W_0^{\max}) able to be dissolved. In
18 Table 4 the results obtained in all the systems evaluated that provide clear and stable
19 ternary mixtures at [surfactant] = 0.1 M is summarized. Additionally, the results found
20 in Na-AOT and bmim-AOT micellar systems are also included.

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42 **Table 4.** Values of W_0^{\max} obtained in different systems at [surfactant] = 0.1 M. T = 298
43 K.

Non-polar solvent	W_0^{\max}			
	Na-AOT ^a	emim-AOT	bmim-AOT ^b	hmim-AOT
<i>n</i> -Heptane	60	-	-	14
Benzene	12	11	5	2

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^a Value obtained from ref. 60. ^b Value obtained from ref. 46.

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3 As can be seen in Table 4, the values of W_0^{\max} depends on the surfactant used.
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5 This result indicates that the counterion nature considerably influences the amount of
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7 solubilized water. For benzene/surfactant systems it can be seen that W_0^{\max} decreases
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9 with increasing the hydrocarbon tail length of the imidazolium counterion, while in the
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11 *n*-heptane/surfactant micellar systems at a [surfactant] = 0.1 M, only the IL-like
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13 surfactant hmim-AOT can dissolve water. The hmim⁺ counterion appears to act as a
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15 kind of co-surfactant. Therefore, the impact of the different counterions (imidazolium vs
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17 Na⁺) on properties such as the size or the interactions of water molecules at the interface
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19 is interesting to explore.
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24 The solutions consisting of benzene/emim-AOT/water, benzene/hmim-
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26 AOT/water and *n*-heptane/hmim-AOT/water were studied by the DLS technique in
27
28 order to investigate the formation of reverse micelles. Table 5 shows the d_{app} and PDI
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30 values of the DLS experiments that were performed at a surfactant concentration of 0.1
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32 M for the emim-AOT and hmim-AOT solutions in non-polar solvents at $W_0 = 5$. These
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34 working conditions were chosen to compare the data obtained in this work with those
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36 corresponding to the micellar systems formed by Na-AOT and bmim-AOT in the same
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38 solvents.^{46,47} It should be noted that the d_{app} value of the benzene/hmim-AOT/water
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40 system was performed at $W_0 = 2$, since this micellar system does not allow to prepare
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42 homogenous solutions at W_0 larger than this value (Table 4).
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Table 5. Apparent hydrodynamic diameters (d_{app}) and polydispersity indexes (PDI) for the benzene/surfactant/water and *n*-heptane/surfactant/water reverse micelles at $W_0 = 5$.
 $T = 298$ K.

Surfactant	benzene		<i>n</i> -heptane	
	d_{app} (nm)	PDI	d_{app} (nm)	PDI
Na-AOT	2.9 ± 0.3^a	0.05	5.1 ± 0.1^a	0.05
emim-AOT	3.5 ± 0.2	0.04	-	-
bmim-AOT	3.9 ± 0.2^b	0.03	-	-
hmim-AOT	5.3 ± 0.1^c	0.02	14.1 ± 0.1	0.01

^a Value obtained from ref. 60. ^b Value obtained from ref. 46. ^c Value at $W_0 = 2$.

The apparent hydrodynamic diameter values listed in Table 5 make evident the existence of reverse micelles for emim-AOT and hmim-AOT surfactants in benzene.^{72,73} Furthermore, the low PDI values observed for the studied micellar systems suggest that the particles are essentially monodisperse.⁷⁴

It is interesting to note that the d_{app} values of these IL-like surfactant micelles are higher than those of Na-AOT in benzene. Besides, the d_{app} value is higher as the larger the size of the of imidazolium cation is. In this regard, it is interesting to consider that when the effective packaging parameter of the surfactant, p , diminishes, the diameter of reverse micelles increases.⁷¹ The values of v and l_c are similar for both the IL-like surfactants and Na-AOT.⁴⁶ The substitution of Na^+ by the imidazolium cations can produce an increase in the a value because the alkyl tails of the counterions would be close to the chains of AOT favoring the hydrophobic interactions and producing an increase in d_{app} .

Data in Table 5 show that the droplet sizes of the hmim-AOT reverse micelles

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3 are larger in *n*-heptane than in benzene. This result could be explained by considering
4 the different penetration of the two non-polar solvents at the interface. It is well known
5 that in Na-AOT reverse micelles, the penetration of the aromatic solvents into the
6 interface is larger than aliphatic solvents.^{13,60} This phenomena can alter the *p* value and,
7 consequently, the sizes of reverse micelles. Thus, benzene penetrates deeper into the
8 interfacial zone in Na-AOT reverse micelles than those of *n*-heptane. Consequently, at
9 similar W_0 value the Na-AOT/benzene reverse micelles are smaller than Na-AOT/*n*-
10 heptane reverse micelles.⁶⁰ Furthermore, the micelle-micelle interactions and the water
11 structure inside reverse micelles can be altered by the type or composition of the non-
12 polar phase.^{13,60} Thus, it was found that when aromatic solvents are used, inter-micellar
13 interactions are weaker than in aliphatic solvents. As consequence of this fact, a notable
14 impact on the practical applications of reverse micelles as nanoreactors can be
15 produced.^{13,60} For example, in the synthesis of nanoparticles one of the key steps that
16 controls the synthetic pathway is the coalescence process. In this sense, the inter-micelle
17 interactions can be controlled by the nature of the non-polar solvent.⁷⁵
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40 CONCLUSIONS

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42 Our investigations demonstrate that the substitution of Na^+ cation by alkyl-
43 imidazolium cations on the AOT surfactant alter significantly the type and
44 characteristics of the organized systems that they form, both in water and in non-polar
45 solvents.
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51 The IL-like surfactant emim-AOT forms direct micelles, while bmim-AOT and
52 hmim-AOT can spontaneously form unilamellar vesicles in water, as previously shown.
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54 The emim-AOT micelles are larger, with less negative surface charge, a lower degree of
55 ionization, and lower critical micellar concentration than those of Na-AOT. As a
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3 consequence, they have a higher Gibbs energy of micellization. Emim-AOT direct
4 micelles also present a lower fluidity of the micellar interface and a greater capacity to
5 solubilize low polarity molecules than Na-AOT ones.
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10 In non-polar solvents emim-AOT forms reverse micelles in benzene, while
11 hmim-AOT does in both benzene and *n*-heptane. It was observed that, depending on the
12 imidazolium cation nature, the micellar systems have a different capacity to solubilize
13 water in their interior and that the aggregates have different sizes.
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19 These results show the importance of the surfactant counterion nature in the
20 behavior of surfactants, converting them into ILs and determining the aggregates
21 formed in the self-association process. Indeed, it is a very important factor to consider
22 when designing new surfactants for different applications in which aggregates play a
23 key role, such as drug nanocarriers, nanoreactors in the synthesis of nanoparticles or in
24 different chemical reactions.
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35 ASSOCIATED CONTENT

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37 **Supplementary Material.** Full experimental methodology, molecular structures of the
38 probes, NMR characterization of emim-AOT, DLS data of aqueous solution of emim-
39 AOT, conductivity measurements and determination of cmc with pyrene of Na-AOT
40 aqueous solution, are available free of charge.
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58 Notes

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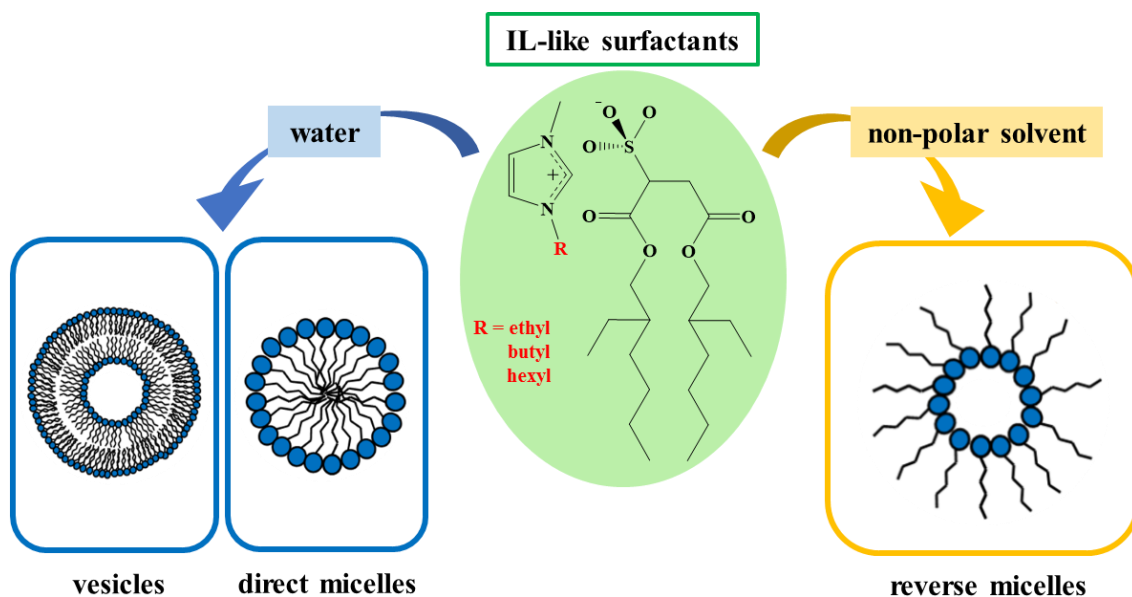
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GRAPHICAL ABSTRACT



The IL-like surfactant emimAOT forms direct micelles in water, while bmimAOT and hmimAOT form vesicles in water. The three IL-like surfactants form reverse micelles in non-polar organic solvents.