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## The use of two non-toxic lipophilic oils to generate environmentally friendly anionic reverse micelles without cosurfactant. Comparison with the behavior found for traditional organic non-polar solvents



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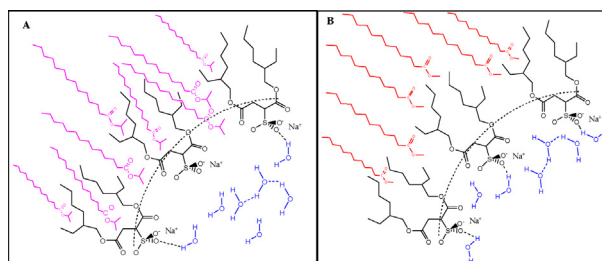
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### HIGHLIGHTS

- ML and IPM were used as external non-polar solvents to formulate aqueous AOT RMs.
- Size,  $N_{agg}$  and amount of water solubilized in both AOT RMs are different.
- Higher viscosity and polarity of IPM than ML promotes more interface penetration.
- Comparable behaviors between ML-*n*-heptane RMs and IPM-benzene RMs are observed.

### GRAPHICAL ABSTRACT

Effect of the use of non-toxic lipophilic oils (IPM, A and ML, B) to generate environmentally friendly anionic reverse micelles.



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### ABSTRACT

In this work two different non-toxic solvents/sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT)/water reverse micelles (RMs) have been investigated by dynamic (DLS) and static (SLS) light scattering techniques. Methyl laurate (ML) and isopropyl myristate (IPM) were used as external non-polar solvents to formulate the AOT RMs without cosurfactant. DLS results reveal the formation of IPM and ML AOT RMs containing water as a polar component since the droplet sizes values increase as the  $W_0$  values increase. To the best of our knowledge this is the first report where ML is used to formulate AOT RMs. The droplets size values, the maximum amount of water solubilized and the aggregation numbers ( $N_{agg}$ , determined by SLS) of both AOT RMs are dissimilar considering the chemical structure of the external solvents and they can be explained taking into account the different non-polar solvent penetration to the interface. The results suggest that IPM penetrate more the interface than ML in AOT RMs, diminishing the inter-droplets interactions and producing RMs with smaller sizes and  $N_{agg}$  than ML/AOT. The higher viscosity and polarity of IPM in comparison with ML promotes the interface penetration. Thus, the penetration of IPM into the interface is higher than ML, making the interface of IPM/AOT RMs more rigid and, in consequence with smaller droplets sizes values. Finally, a peculiar comparable behavior (droplets size, maximum amount of water solubilized and  $N_{agg}$ ) between *n*-heptane and ML AOT RMs and benzene and IPM AOT RMs was observed. These results present a very promissory field since that the unique properties of the alkanes/AOT/water RMs can be obtained using non-toxic lipophilic oils and, in the same way the opportunity to formulate environmentally friendly AOT RMs.

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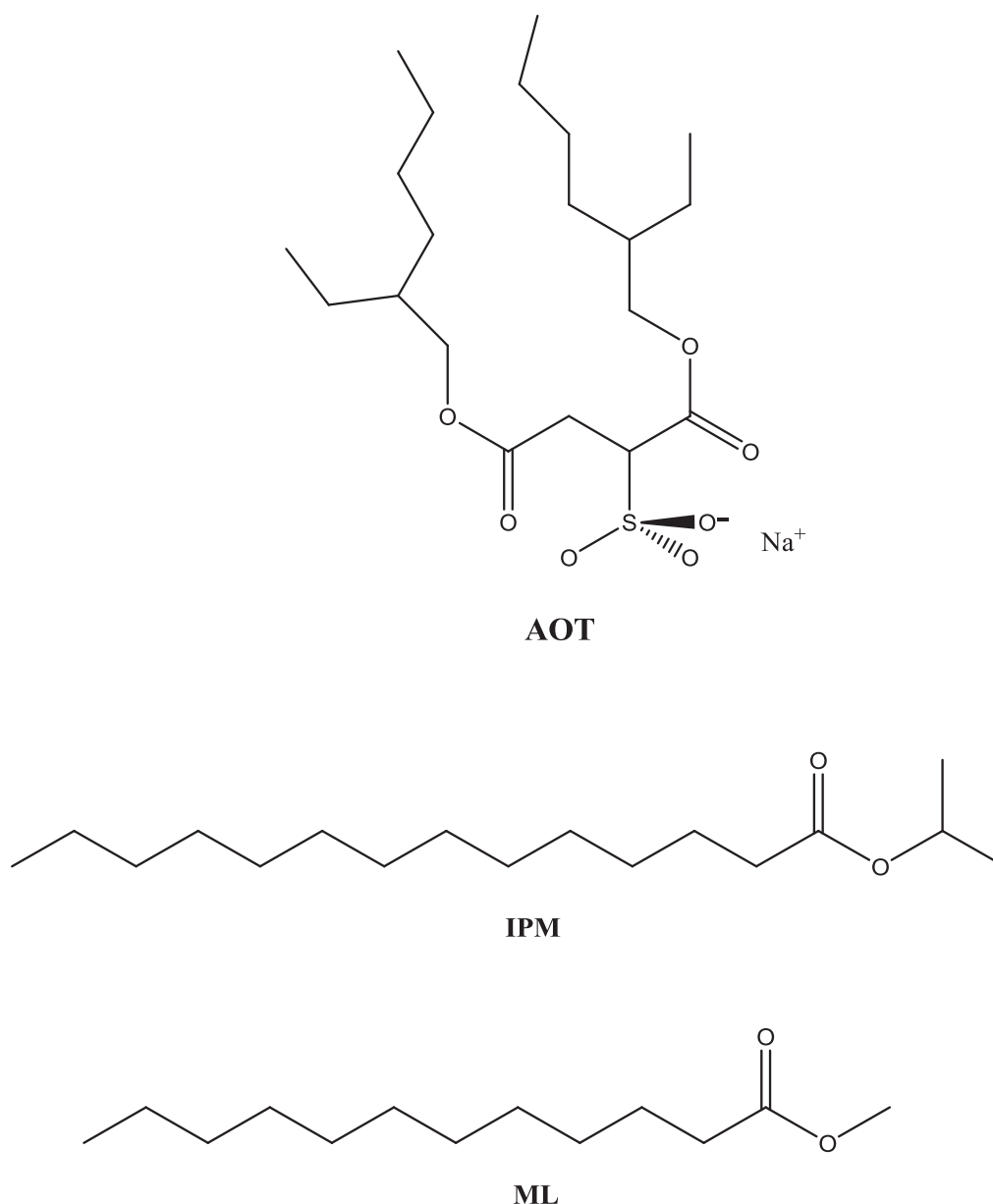
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## 1. Introduction

Reversed micelles (RMs) are spatially ordered macromolecular assembly of surfactants formed in a non-polar solvent, in which the polar head groups of the surfactants point inward and the hydrocarbon chains point toward the non-polar medium [1–3]. RMs have been an interesting subject for decades due to their broad applications in chemical reactions, separation science, material science, and in the pharmaceutical industry, among others [1–4]. These nanoscale aggregates are suitable media for processes that involve hydrophobic and hydrophilic reactants in a variety of chemical and biological reactions [1,2,5,6]. There are a wide range of surfactants that form RMs [1–22] and probably, the most frequently surfactant used is the anionic sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT, Scheme 1) [4,7–9,15,17,18,20,21,23,24]. AOT has the ability to form RMs in aromatic (benzene, toluene, chlorobenzene, xylene) and aliphatic (*n*-heptane, *n*-hexane, isooctane, decane) solvents without addition of a cosurfactant and, water can be solubilized up to  $W_0 = [\text{H}_2\text{O}]/[\text{Surfactant}] \sim 60$  depending on the external solvent and temperature [1–3].

The potential application of highly biocompatible aqueous RMs to the food, cosmetic, and pharmaceutical industry as solubilization media of hydrophilic, hydrophobic, and amphiphilic functional materials has been of growing interest during the past decade [25–28]. These applications are mainly linked to their unique properties such as thermodynamic stability, optical clarity, and high solubilization capacity [2,29]. However, the most critical problem regarding the use of RMs in the food, cosmetic, and pharmaceutical fields is the toxicity of their partial components. Formulation and characterization of non-toxic RMs formulations based on biological amphiphiles and different oils have been studied for over a decade [28]. These bio-compatible systems are discussed as potential substitutes for chlorinated solvents in dry-cleaning applications and as solvent delivery systems for pharmaceutical applications [28]. Studies in oil like isopropyl myristate (IPM), which possesses different physical properties and structure as compared to the traditional hydrocarbon oils, have been performed before [30–38]. Compared to alkane, IPM is a kind of non-toxic lipophilic oil, which has been widely used in biological resembling systems, and pharmaceutical and drug delivery systems [30,39–43]. On the



**Scheme 1.** Molecular structure of AOT, IPM and ML.

other hand, Paul et al. [31–33,44–48] and Zhang et al. [36] have investigated in detail the behavior of different mixed surfactant reverse micellar systems stabilized by anionic (AOT)–non-ionic(s) (Brijis, Spans, Tweens, Igepal), cationic (DDAB) – non-ionic(s) (Brijis, Spans), and non-ionic (Igepal) – non-ionic(s) (Brijis, Spans) surfactants in IPM both in absence and presence of electrolytes and cosurfactants [31–33,36,44–48]. In all cases, the systems formed showed the ability of IPM to be used as external solvent in this kind of organized system. On the other hand, the data about AOT RMs prepared in other biocompatible solvents [27,49] or in IPM but in absence of cosurfactant (where the organized system is “cleaner”) is scarce. Moreover, nothing is known about interfacial properties and droplet–droplet interactions which are crucial to understand the system in order to use them as nanoreactors.

Previous, investigations about the external solvent composition of RMs have been performed [50–52], and they have shown that the droplet size and the interdroplet interaction can vary changing the composition of the AOT RMs [50–52]. For example, in *n*-heptane:toluene mixtures as the *n*-heptane molar fraction increases the AOT RMs droplet sizes are larger and, the toluene molecules are expelled from the interface. Recently, we have studied the external solvent composition (benzene:*n*-heptane mixtures) in the cationic benzyl-*n*-hexadecyl-dimethylammonium chloride (BHDC) RMs and how modifications on the non-polar component affect different RMs properties such as: micropolarity, microviscosity, water–surfactant interactions and droplets sizes among other [19,53]. The results showed that not only the BHDC RMs sizes change upon the *n*-heptane addition (as it was previously shown for AOT RMs [50]) but also the RMs interfacial composition varies with the non-polar phase blend. As the *n*-heptane molar fraction increases the RMs droplet sizes are larger and, the benzene molecules are expelled from the interface and, this phenomenon has remarkable effect on the water–surfactant interactions. Particularly, the interfacial micropolarity increase and the interfacial water molecules are located more in the oil side of the BHDC RMs interface, diminishing the interfacial water–polar head surfactant interaction [19,53]. Thus, it was demonstrated that a simple change in the composition of the external phase, promotes remarkable changes in the RMs interface.

Hence, with the aim to continue the investigations changing the external solvents and to produce bio-compatible and environmentally friendly RMs that could be used in a range of applications (e.g. for use in food and drug delivery systems and, for use in cosmetic formulations) [39,54], this work was performed with the following goals: (i) Explore the use of non-toxic lipophilic solvents such as methyl laurate (ML) and IPM in order to formulate AOT RMs; (ii) evaluate the water encapsulation by dynamic light scattering (DLS) in both AOT RMs, (iii) obtain the  $N_{agg}$  for ML and IPM/AOT/water RMs by static light scattering (SLS) and, (iv) compare our results with AOT RMs prepared in traditional non-polar solvents such as benzene and *n*-heptane.

## 2. Experimental

### 2.1. Materials

Sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT) from Sigma (>99% purity), was dried under vacuum prior use. Isopropyl miristate (IPM) and methyl laureate (ML) both from Sigma (>98% purity), were stored over molecular sieves before use. Ultrapure water was obtained from Labonco equipment model 90901-01. 1-Methyl-8-oxyquinolinium betaine (QB) was used to evaluate the polarity of both non-toxic solvents and also to determine the absence of acidic impurities in the AOT RMs. The UV–vis spectrum of QB is very sensitive to acidity and the presence of

those impurities would have greatly reduced the intensity of the solvatochromic  $B_1$  band at 502 nm [7].

### 2.2. Methods

The stock solutions of AOT in the non-toxic solvents (IPM and ML) were prepared by mass and volumetric dilution. Aliquots of these stock solutions were used to make individual reverse micelle solutions with different amount of water, defined as  $W_0 = [\text{water}]/[\text{AOT}]$ . The incorporation of water into each micellar solutions was performed using calibrated microsyringes. To obtain optically clear solutions they were shaken in a sonicating bath. The resulting solutions were clear with a single phase and they were used in dynamic (DLS) and static (SLS) light scattering experiments. The  $W_0$  was varied between 0 and 23 for IPM/AOT/water and, between 0 and 46 for ML/AOT/water RMs. It was not possible to obtain higher values of  $W_0$  due to turbidity problems. The lowest value for  $W_0$  ( $W_0 = 0$ ), corresponds to a system without the water addition. In all cases, the surfactant concentration was kept constant and equal to 0.1 M. It is important to note that water, is not soluble in neat IPM or ML at room temperature.

### 2.3. General

The apparent diameters ( $d_{app}$ ) of the different AOT RMs were determined by DLS, in a Malvern 4700 with goniometer with an argon-ion laser operating at 488 nm. The cleanliness of the cuvettes used for the measurements was of crucial importance for obtaining reliable and reproducible data [9]. The cuvettes were washed with ethanol, and then with doubly distilled water and dried with acetone. Prior to use the samples were filtered three times using an Acrodisc with 0.2  $\mu\text{m}$  PTFE membrane (Sigma) to avoid dust or particles presents in the original solution. Before introducing each sample to the cuvette, it was rinsed twice with pure non-toxic solvent, then with the 0.1 M AOT stock solution, and finally with the sample to be analyzed. Prior making measurements on a given day, the background signals from air and non-toxic solvent were collected to confirm the cleanliness of the cuvettes. Prior to data acquisition, samples were equilibrated in the DLS instrument for 10 min at 25 °C. To obtain valid results from DLS measurements requires knowledge of the system's refractive index and viscosity in addition to well-defined conditions. Since we worked with dilute solutions, the refractive indices and viscosities for the RM solutions were assumed [55] to be the same as neat external solvents. Multiple samples at each size were made, and thirty independent size measurements were made for each individual sample at the scattering angle of 90°. The instrument was calibrated before and during the course of experiments using several different size standards. Thus, we are confident that the magnitudes obtained by DLS measurements can be taken as statistically meaningful for all the systems investigated. The algorithm used was CONTIN and the DLS experiments show that the polydispersity of the AOT RMs size is less than 5%. The droplets of IPM/AOT/water and ML/AOT/water systems do scatter very weakly at  $W_0 < 10$ , and the  $d_{app}$  is under 2 nm, which is below the particle size magnitude detectable with reliability by DLS. Consequently,  $W_0 = 10$  was selected as a measuring start point in the experiments.

The aggregation numbers ( $N_{agg}$ ) of the IPM/AOT/water and ML/AOT/water RMs were determined by SLS in the same equipment that the one used in DLS. All the measurements were made at an angle of 90° and Debye plots were created using solutions with different AOT concentration at fixed  $W_0$  for all the RMs studied. From the SLS experiments, the weight-averaged molar masses were determined and the  $N_{agg}$  values for all the systems investigated were calculated according the procedure detailed in literature [56,57]. In order to obtain the refractive index increment

**Table 1**

Comparison of the maximum amount of water solubilized ( $W_0^{\max}$ ) in different AOT RMs. [AOT] = 0.1 M.  $T = 25^\circ\text{C}$ .

System	$W_0^{\max}$
Benzene/AOT	12 <sup>a</sup>
<i>n</i> -Heptane/AOT	50 <sup>b</sup>
IPM/AOT	23
ML/AOT	46

<sup>a</sup> Value obtained from Ref. [2].

<sup>b</sup> Value obtained from Ref. [15].

( $dn/dc$ ) values (data required for the SLS measurements) a differential refractometer was used (Brookhaven Instruments Corporation, BI-DNDCW model) with a tungsten lamp operating at 470 nm.

All the experiments were carried out at  $25 \pm 0.5^\circ\text{C}$ .

### 3. Results and discussion

#### 3.1. Solubilization of AOT in the non-toxic lipophilic solvents

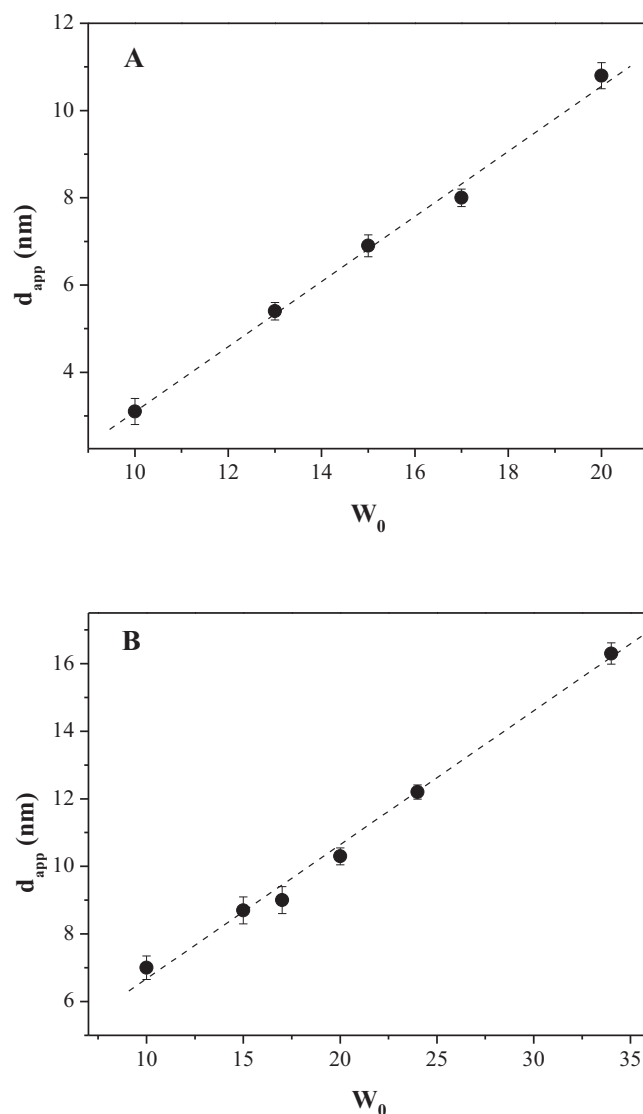
In order to evaluate if the non-toxic lipophilic solvent ML can be used as the external non-polar solvent to generate RMs, the first experiment performed was to investigate the phase diagram of the ternary system. First, the AOT solubility in neat ML was tested. As it was described above, there are only few reports [31–33,36] about the use of IPM and AOT in absence of other surfactant or cosurfactant. Moreover, at the moment no information about the employment of ML to prepare AOT RMs is available. Therefore, the AOT solubility in ML was tested and, additionally it was repeated the experiments performed by Zhang et al. [36] using IPM as solvent, in order to make the comparison with the system herein studied. It was observed that AOT is completely soluble in both solvents in absence of water ( $W_0 = 0$ ) even at [AOT] = 0.2 M.

#### 3.2. Solubilization of water in non-toxic solvents/AOT systems

In view of the facts observed in the previous section, the next step was to evaluate the amount of water that both RMs can be solubilized forming clear and stable ternary mixtures. In Table 1 are summarized the maximum amount of water solubilized ( $W_0^{\max}$ ) in different AOT RMs at [AOT] = 0.1 M. The results obtained in IPM/AOT are similar to those reported by Mitra et al. [31–33] and Zhang et al. [36] For comparison, also are included AOT RMs prepared in benzene and *n*-heptane, two very common non-polar solvents used to formulate RMs that gives RMs with very different properties [2,4,8,19]. As it can be observed, the  $W_0^{\max}$  values reached for IPM/AOT and ML/AOT are different being, the later RMs able to dissolve approximately the double amount of water than IPM/AOT. Additionally, the  $W_0^{\max}$  values observed in ML/AOT and *n*-heptane/AOT are quite similar and, for IPM/AOT and benzene/AOT slightly different but both are able to dissolve less water than ML/AOT or *n*-heptane/AOT RMs. These results show that not only is possible dissolve AOT in both non-toxic solvents but the systems have the ability to dissolve considerable amount of water. Moreover, different amounts of water can be encapsulated as the traditional oils do [2,4]. The results also suggest that both non-toxic solvents present an unexpected different behavior as non-polar solvents for RMs preparation, and may be due to difference in their chemical structures (see Scheme 1) and physicochemical properties, which can include viscosity, polarity, among others.

#### 3.3. DLS experiments

To evaluate the formation of RMs and to discard the presence of bicontinuous microemulsions, the systems formed by



**Fig. 1.** Apparent diameter ( $d_{app}$ ) values for IPM/AOT (A) and ML/AOT (B) RMs obtained at  $25^\circ\text{C}$  varying  $W_0$ . [AOT] = 0.1 M. The straight lines were plotted to guide the eye.

IPM/AOT/water and ML/AOT/water were studied using DLS technique. When new reversed micellar systems are explored, a crucial question has to be answered: is water effectively entrapped by the surfactant creating a true RMs in the organic solvent or is water dissolved only in the organic solvent/AOT mixture without any molecular organization (bicontinuous microemulsion)? [4,58]. Thus, DLS can be used to assess this matter because if water is really encapsulated to form RMs interacting with the interface, the droplets size must increase as the  $W_0$  value increases with a linear tendency (swelling law of RMs) as it is well established for other RMs [2,4,9]. This feature would also show that non-toxic lipophilic solvents/AOT/water system consists of discrete spherical and non-interacting droplets of water stabilized by the surfactant layer.

In this work, all the DLS experiments were carried out at finite surfactant concentrations (0.1 M) when interdroplet interactions have been neglected [56]. Hence, it is appropriate to introduce an apparent hydrodynamic diameter ( $d_{app}$ ) in order to make the comparison with the system herein studied as it was used before [19,50]. Fig. 1A and B, report the  $d_{app}$  values obtained for water solubilized in the IPM/AOT and ML/AOT RMs at different  $W_0$  values, respectively. Additionally, in Table S1 (Supplementary

Information section) are reported the polydispersity index (PDI) values obtained. As it can be seen in both Figures, there is an increase in the droplet sizes values when the water content increases, showing that the water molecules are effectively entrapped by the surfactants layer yielding RMs. For example, the  $d_{app}$  value for the IPM/AOT RMs at  $W_0 = 10$  is 3.1 nm and this value increases up to 10.8 nm at  $W_0 = 20$ . These results are within the range the data reported by Zhang et al. [36], although most of their work concentrated the efforts in mixed solvents (IPM + alcohols). In the case of ML/AOT RMs, the  $d_{app}$  value is 7 nm at  $W_0 = 10$  and increase up to 16.3 nm at  $W_0 = 34$ . To the best of our knowledge this is the first report where it is shown that ML can be used as non-polar component in AOT RMs and that water is entrapped in ML/AOT RMs.

Supplementary Table S1 related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2014.05.077>.

The linear tendency observed in Fig. 1 and the low PDI values reported in Table S1 in both RMs, confirm that the droplets effectively are not interacting and the shapes are probably spherical. Deviation from the linearity could be due to several factors being the most relevant: strong droplet–droplet interaction and/or other RMs shapes [59]. Thus, from the DLS data it is possible to conclude that water is in fact encapsulated by IPM/AOT and ML/AOT yielding RMs media with the water molecules interacting with the interface.

The largest droplets sizes values are observed for the ML/AOT RMs in comparison with the RMs formed by IPM/AOT (see Fig. 1). Two main effects can be invoked in order to understand how the droplets size change: (i) the characteristic of the external solvent [19,53] and (ii) the interaction between water and the RM interface [9,58].

Recently [19,50–53], it was demonstrated that the phase behavior and/or the properties of RMs can be affected by the external non-polar solvent composition. Even though it is known that the properties of RMs depend on the type of surfactant, the  $W_0$  values [1–3,17,18,21] and the external non-polar organic pseudophase, the influence of the organic media on AOT RMs has been less examined [7,8,60–65]. AOT is a kind of surfactant that can form RMs in a variety of non-polar solvents, for example in pure benzene and *n*-heptane [2]. The properties of both AOT RMs are different and, for example: the micropolarity and microviscosity of the interface, the droplets sizes and the maximum amount of water that can be dissolved, are strongly dependent on the kind of external solvent used [2,7,8]. Several authors [50,66–68] and we [19,53] have tried to explain these results trying to understand how the RMs properties are influenced by the interdroplets interactions. Larger oils molecules have difficulty to penetrate into the interface, increasing the magnitude of the droplet–droplet interactions. The larger radius of gyration of the long chains prevents them from close packing on the surfactant interface. In consequence, the surfactants are optimally packed and hence have a larger network attraction. Consequently, decreasing the oil chain length also decreases the network interdroplet attraction since the external solvent molecules can penetrate easily to the interface. In other words as the oil chain length decreases, the difference between oil and surfactant packing decreases and the neat attraction of two droplets is thus reduced [69]. In this sense it was noticed that, although the origin of attractive forces in RMs is still not clear, the oil penetration to the interface is thought to be a major factor. For example, comparing benzene/AOT with *n*-heptane/AOT RMs the rigid benzene molecule penetrates easily to the RMs interface in comparison to *n*-heptane, being benzene/AOT RMs smaller than the *n*-heptane/AOT RMs at the same  $W_0$  value [7,8,60,70].

As it was invoked before, the interaction between water and the RMs interface also modify the droplets sizes. It is important

**Table 2**

Comparison of the droplets sizes ( $d_{app}$ ) and aggregation numbers ( $N_{agg}$ ) values obtained in different AOT RMs. [AOT] = 0.1 M.  $T = 25^\circ\text{C}$ .

System	$W_0$	$d_{app}$ (nm)	$N_{agg}$
Benzene/AOT/water	10	4.5 ± 0.2	33 ± 2 <sup>a</sup>
	12	5.1 ± 0.2	–
<i>n</i> -Heptane/AOT/water	10	7.5 ± 0.2	96 ± 5
	15	9.0 ± 0.3	180 ± 10 <sup>b</sup>
IPM/AOT/water	10	3.1 ± 0.1	31 ± 2
	15	6.9 ± 0.1	49 ± 3
ML/AOT/water	10	7.0 ± 0.2	–
	15	8.7 ± 0.2	182 ± 8

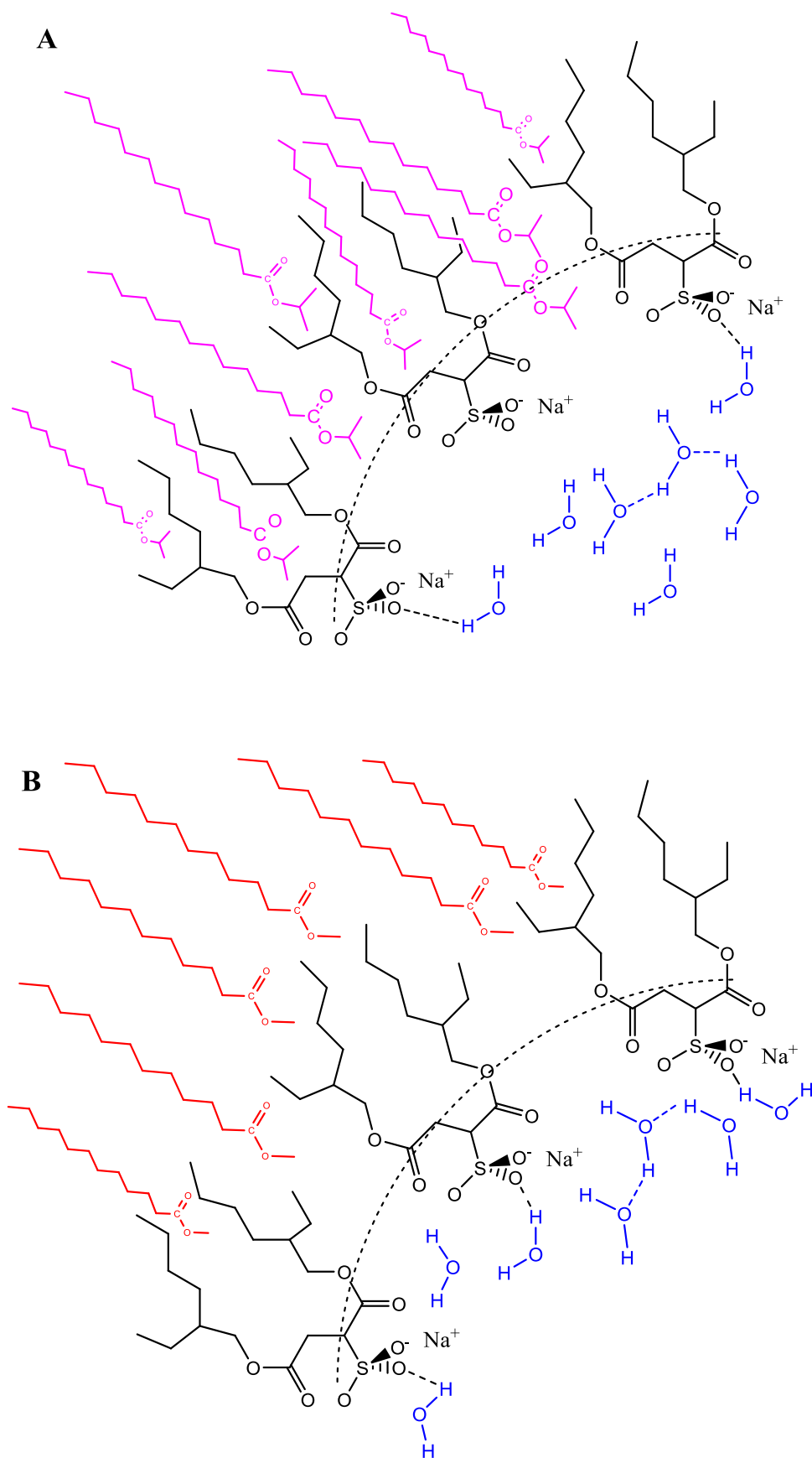
<sup>a</sup> Value obtained at  $W_0 \approx 9$  and [AOT] =  $6 \times 10^{-2}$  M from Ref. [71].

<sup>b</sup> Value obtained from Ref. [72].

to consider that the RMs droplet sizes depend, among many other variables, on the effective packing parameter of the surfactants  $p$ , defined as  $p = v/al_c$ , in which  $v$  and  $l_c$  are the volume and the length of the hydrocarbon chain, respectively and  $a$  is the surfactant head group area [59]. The RMs sizes are larger when the surfactant packing parameter values are smaller [9]. It has been shown using DLS, that in aqueous and non-aqueous *n*-heptane/AOT RMs [4,9], the polar solvents–AOT interactions are the key for the RMs droplets sizes control. For example, when a polar solvent encapsulated interact strongly (for example by hydrogen bonding) with the AOT polar head group, increases the surfactants'  $a$  values with the consequent decrease in the surfactant packing parameter and, the increase in the RM droplet size [9].

Taking into account all these background, the small droplets sizes obtained for water entrapped in IPM/AOT in comparison with the values obtained for ML/AOT/water RMs, can be explained considering both phenomena: the penetration of the external non-polar solvent and its effect over the water–AOT interaction. Thus, in IPM/AOT/water RMs IPM probably penetrate the interface, the  $p$  parameter increase and the droplets size decrease. This also would produce that the water molecules interact weakly with the anionic interface. Contrary, when ML is used as external solvent, it cannot penetrate into the interfacial pseudophase as IPM does and water could interact strongly with the surfactant, increasing the effective area  $a$  and, consequently,  $p$  parameter decreases and  $d_{app}$  values increase. Scheme 2 shows the probably location of IPM and ML, respectively at the AOT interface. Thus, the simple change in the external solvents (IPM or ML), promotes remarkable changes in the RMs interface. For example, we expect an interface more polar in ML/AOT/water than in IPM/AOT/water due to the strong water–AOT interaction and the less external solvent penetration.

Furthermore, if the  $d_{app}$  values of the non-toxic solvents/AOT RMs are compared with the corresponding values reported in benzene or *n*-heptane (depicted in Table 2), an interesting observation emerges. For example, at the same water content value ( $W_0 = 10$ ), the droplets sizes are quite similar for IPM and benzene AOT RMs but different for the similar ML and *n*-heptane AOT RMs. This tendency is also observed for other values of  $W_0$ . For example, at  $W_0 = 12$  the droplets size obtained in benzene/AOT is 5.1 nm being around 5.4 nm for IPM/AOT. Moreover, for ML/AOT/water at  $W_0 = 15$  the value obtained is 8.7 nm and 9 nm for *n*-heptane/AOT/water. Thus, considering all these data (droplets sizes and maximum values of  $W_0$  shown in Table 1) reported in this work, we suggest a similar behavior (solvent penetration and water–AOT interactions) for AOT RMs formed in IPM and benzene. Besides, when AOT is dissolved in ML, this solvent does not penetrate into the interface, showing droplets sizes and ability to encapsulate water similar to the observed when *n*-heptane is used. Interestingly, these facts show that it is not easy to predict the external solvent effect on the



**Scheme 2.** Schematic representation of the different penetration of the IPM (A) and ML (B) in the AOT RMs interfaces.

**Table 3**  
Comparison of the molar volume ( $V_m$ ), viscosity and  $E_T(30)$  values of the different solvents used in the present work.  $T = 25^\circ\text{C}$ .

Solvent	$V_m$ ( $\text{cm}^3 \text{mol}^{-1}$ )	Viscosity (mPa s)	$E_T(30)$ ( $\text{kcal mol}^{-1}$ )
Benzene	89.8 <sup>a</sup>	0.60 <sup>a</sup>	34.3 <sup>b</sup>
<i>n</i> -Heptane	146 <sup>c</sup>	0.38 <sup>a</sup>	31.1 <sup>b</sup>
IPM	317 <sup>c</sup>	6 <sup>d</sup>	39.4
ML	246.6 <sup>e</sup>	2.82 <sup>f</sup>	36.1

<sup>a</sup> Values obtained from Ref. [73].

<sup>b</sup> Values obtained from Ref. [80].

<sup>c</sup> Values obtained from Ref. [32].

<sup>d</sup> Value obtained from Ref. [75].

<sup>e</sup> Value estimated using the density and molar mass values obtained from Ref. [74].

<sup>f</sup> Value obtained from Ref. [74].

AOT RMs, even though the similarity in the chemical structure of ML and IPM.

### 3.4. SLS experiments

In order to obtain more valuable information about the different behavior of the non-toxic solvents/AOT RMs investigated and, to support the idea about the similarity observed between benzene-IPM and *n*-heptane-ML, SLS technique was used to determine the aggregation numbers ( $N_{agg}$ ) of the systems at different  $W_0$  and, the values are listed in Table 2. It can be expected that for AOT RMs formed in non-polar solvents that penetrate to the interface, such as benzene, smaller  $N_{agg}$  should be determined [71], in comparison with solvents that cannot penetrate the interface such as *n*-heptane [72]. As it can be seen in Table 2, the  $N_{agg}$  values are very different between IPM and ML RMs, for example in IPM/AOT/water at  $W_0 = 15$   $N_{agg}$  is around 49, being around 182 for ML/AOT/water. Thus, in concordance with the values reported for AOT in benzene [71] and *n*-heptane [72], the  $N_{agg}$  value obtained for IPM/AOT is smaller than ML/AOT (See Table 2). Moreover, the similar  $N_{agg}$  values obtained for IPM/AOT/water and benzene/AOT/water, around 30, and for ML/AOT/water and *n*-heptane/AOT/water around 180 reinforces the idea that IPM and ML have similar behavior in AOT RMs that benzene and *n*-heptane [19,53], respectively. These results also suggest that the shape of the RMs can be considered as practically spherical as it was assumed by DLS experiments.

The question is why IPM can penetrate at the AOT interface and ML does not? Recently, it has been shown that the replacement of benzene by *n*-heptane as external solvent in BHDC RMs [19] produces changes in the magnitude of the interdroplets interactions and it was attributed to the differences in the solvent penetration to the RMs mainly due to the differences in their molar volume ( $V_m$ ) values [19]. In Table 3, is summarized the  $V_m$  values of all the solvents used [73–75]. As it can be observed, the  $V_m$  of IPM is slightly larger than ML but both values are much larger than benzene or *n*-heptane. Thus, considering only the  $V_m$  of IPM and ML, it would be expected a more interfacial penetration of ML (minor  $V_m$ ) than IPM in AOT RMs, producing droplets sizes in ML/AOT RMs smaller than in IPM/AOT RMs. Moreover, considering the magnitude of the  $V_m$  values reported for benzene and *n*-heptane, no penetration to the AOT RMs interface for both non-toxic solvents would be expected. However, the results showed herein suggest that not only the  $V_m$  of the external solvent, but other factors like polarity, viscosity, molecular geometry (long or branched hydrocarbon chain), among others of oils [32,33,76,77] may play key roles in the solvent penetration to these AOT RMs interfaces. For example, Wang et al. [76] have proposed that IPM, which has a branch in the short part of the ester moiety (see Scheme 1), could penetrate and promote a more flexible interface in several RMs formulated with mixtures of non-ionic surfactants (Tween 80 and

Span 20), favoring the formation of smaller RMs than non-polar solvents without branch, as for example methyl decanoate. On the other hand, viscosity has never been suggested as a parameter for solvent penetration. In our case if the viscosity values of the oils are analyzed (see Table 3), the much higher viscosity of IPM in comparison with ML (Table 3) probably reflects its ability to penetrate to the AOT RMs interface. It seems that the more viscous is the solvent the greater is the ability to penetrate to the interface. For example, long chain alcohols (such as *n*-octanol) are used as cosurfactants and they have an appreciable viscosity [73]. Moreover, benzene is less viscous than *n*-heptane and penetrates more to the interface in AOT [78] and BHDC RMs [19,53].

To explore even more these ideas the solvatochromism of the molecular probe 1-methyl-8-oxyquinolinium betaine (QB) was used to evaluate the polarity of both non-toxic solvents. The transition energy (expressed in  $\text{kcal mol}^{-1}$ ) of QB can be used as a polarity parameter [7,19],  $E_{QB}$ , because it has been shown [7,19] that correlates in a linear relationship with the Dimroth et al.  $E_T(30)$  [79] polarity parameter. Thus, in Table 3 are summarized the  $E_T(30)$  values obtained for the non-toxic solvents investigated and the corresponding values for benzene and *n*-heptane obtained from literature [80]. As can be seen, IPM is more polar ( $E_T(30) = 39.4 \text{ kcal mol}^{-1}$ ) than ML ( $E_T(30) = 36.1 \text{ kcal mol}^{-1}$ ) and consequently can penetrate better the polar interface than ML. Thus, the viscosities and polarities of these non-toxic solvents can be invoked to explain why the penetration of IPM into the interface is larger than ML (see Scheme 2) making the IPM/AOT RMs less interactive and, in consequence with smaller droplets sizes values. It worthy to mention that benzene is also more viscous [73] and polar [80] than *n*-heptane and penetrates easily to the AOT RMs interface. Furthermore, long chain alcohols are used frequently as co-surfactants and they are solvents very viscous and with high interfacial activity. Thus the ability of the non-toxic solvent to penetrate or not into the AOT interface produces a new interface with unexplored physicochemical properties.

## 4. Conclusions

In summary, in this work the non-toxic IPM/AOT/water and ML/AOT/water RMs were investigated in absence of cosurfactant. DLS results reveal the formation of the corresponding AOT RMs and that water interacts with the RMs interface since the droplet sizes values increase as the  $W_0$  values increase. Furthermore, they show that the RMs consist of discrete spherical and non-interacting droplets of water stabilized by the anionic surfactant. To the best of our knowledge this is the first report where ML is used to formulate AOT RMs and encapsulate water. The droplets size values, the maximum amount of water solubilized and the  $N_{agg}$  of both AOT RMs are dissimilar considering the chemical structure of the external solvents and they can be explained taking into account the different non-polar solvent penetration to the interface. The results suggest that IPM penetrate more the interface than ML in AOT RMs, diminishing the interdroplets interactions and producing RMs with smaller sizes and  $N_{agg}$  than ML/AOT. The higher viscosity and polarity of IPM in comparison with ML promotes the interface penetration. Thus, the penetration of IPM into the interface is higher than ML, making the interface of IPM/AOT RMs more rigid and, in consequence with smaller droplets sizes values. Finally, a peculiar comparable behavior (droplets size, maximum amount of water solubilized and  $N_{agg}$ ) between *n*-heptane and ML AOT RMs and benzene and IPM AOT RMs was observed. These results present a very promissory field since that the unique properties of the alkanes/AOT/water RMs can be obtained using non-toxic lipophilic oils and, in the same way the opportunity to formulate environmentally friendly AOT RMs.

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