

Characterization of Anionic Reverse Micelles Formulated on Biobased Solvents as Replacing Conventional Nonpolar Organic Solvents

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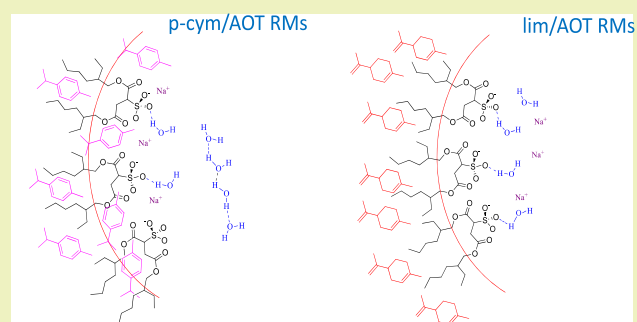
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Supporting Information

ABSTRACT: Two reverse micelles (RMs) employing 1,4-bis-2-ethylhexylsulfosuccinate (AOT) and two biobased solvents, *p*-cymene (*p*-cym) or limonene (lim), have been formulated with the aim to obtain systems more environmentally friendly. Both RMs were studied by using different techniques such as dynamic light scattering (DLS) and ^1H NMR. Additionally, spectroscopy techniques were used to obtain information such as critical micellar concentration and aggregation number of the system investigated. Our results show that both biobased solvents can be used to generate AOT RMs. Interestingly, even the maximum amount of water dispersed are similar for both RMs, and the sizes of the systems are not identical, being that the RMs are formulated in lim larger than in *p*-cym. Both the biobased solvent and RMs show interaction of the entrapped water and the interface; however, this interaction is different depending on the solvent employed to prepare the RMs. Thus, the interaction water–surfactant at the interface is weaker in *p*-cym/AOT than in lim/AOT RMs. We think that the different penetration of the external solvent to the interfacial region is the main reason for the facts observed. In this sense, the polarity of these biobased solvents could explain why the penetration of both biobased solvents is different, making the *p*-cym/AOT RMs less interactive and, therefore, with smaller droplets sizes values. In summary, the different capacities of these biobased solvents to penetrate into the AOT interface allow us to obtain a new interface with peculiar characteristics and therefore with diverse applications.

KEYWORDS: Reverse micelles, AOT, Biobased solvents, *p*-cymene, limonene



INTRODUCTION

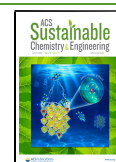
Reversed micelles (RMs) are organized systems of nanometric size formed by three components, i.e., a polar solvent (generally water), a surfactant, and some nonpolar solvent which form a thermodynamically stable and optically transparent solution.¹ Due to the diverse applications of RMs,^{1,2} in the past decade there has been much interest in assessing the nature of the surfactants and of nonpolar solvents that can be part of these organized systems.^{3–5} One of the surfactants more often used to form RMs is the anionic sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT, Scheme 1).¹ Diverse RMs using AOT and different organic nonpolar solvents, aromatic and aliphatic, have been reported.⁶ The results show that the quantity of water solubilized in these systems can be up to $W_0 = [\text{H}_2\text{O}]/[\text{surfactant}] \sim 60$, depending on the nonpolar solvent and temperature.⁶ Nevertheless, replacing these toxic and volatile petroleum-based solvents (used as nonpolar solvents in RMs) by more environmentally friendly alternatives is a challenge to generate RMs more biocompatible and with less impact on the environment.^{7,8} Given the above, recently two nontoxic lipophilic oils such as methyl laurate (ML) and isopropyl myristate (IPM) have been used to formulate

different environmentally friendly RMs. The formation of the corresponding AOT RMs and some properties of these system such as W_0 , droplets size values, CMC, and N_{agg} , among others, depending strongly on the chemical structure of the external solvent.^{3,4,7} However, the search for new nonpolar and nontoxic solvents for the elaboration of more RMs still remains of interest. In this context, solvents derived from biomass, named as biobased solvents, could be a good alternative for this purpose. These new solvents are obtained from natural resources (such as corn, beans, citrus fruit peels, among others).⁹ Some examples include, glycerol, ethyl lactate, *p*-cymene (*p*-cym), and limonene (lim), among others.¹⁰ Due to its peculiar characteristics, these biobased solvents have shown to be much safer solvents for both human beings and

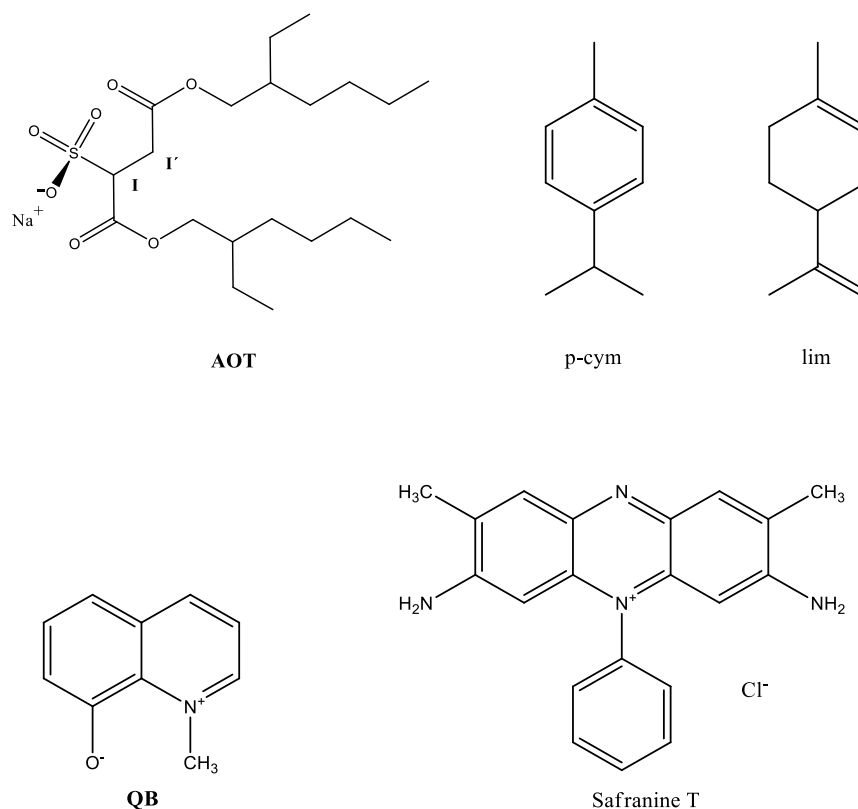
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Scheme 1. Structures of the Surfactant AOT, the Biobased Solvents (p-cym and lim), and the Molecular Probes (QB and Safranin T)



the environment, in comparison with those petroleum-based solvents.¹¹ In particular, p-cym and lim come from citrus fruit peels, and they are considered as low polar solvents with weak hydrogen bond basicity. Both of them have optimal characteristics as solvents capable of successfully replacing nonpolar petroleum-based solvents.¹² To date, there are several reports indicating the benefits of using biobased solvents.^{13,14} Nevertheless, the use of this kind of solvent in a compartmentalized system (such as reverse micelles) has not been explored.

Therefore, considering that the change in the nature of the external solvent can affect the properties in the RMs interface, we wanted to evaluate the use of two biobased solvents derived from citrus fruit (p-cym and lim) as an external solvent in AOT RMs. In this sense, four objectives are raised: (i) study the use of p-cym and lim to formulate AOT RMs; (ii) obtain the critical micellar concentration (CMC) for p-cym and lim/AOT/water RMs by UV-vis and emission spectroscopy; (iii) evaluate the water encapsulation and the water-interface interaction by dynamic light scattering (DLS) and ¹H NMR in both AOT RMs; (iv) obtain the N_{agg} for both RMs by emission spectroscopy; and (iv) compare our results with AOT RMs prepared in benzene and *n*-heptane, among others.

RESULTS AND DISCUSSION

In the present work we evaluate two different biobased nonpolar solvents (p-cym and lim) to generate biocompatible RMs, using the well-known anionic surfactant AOT. In this sense, the mixture of the anionic surfactant and the biobased solvents were explored, first in the absence of water and later with addition of water. In absence of polar solvent, AOT showed large solubility in both biobased solvents, at least until

0.2 M. Next, we explored if the presence of water on the mixture allowed us to generate stable homogeneous solutions. As it can be observed in Figure S1, transparent and homogeneous solutions were obtained in both biobased systems when the surfactant was present, but turbid and opalescent solutions formed when AOT was absent and the biobased solvents were only mixed with water. Table 1

Table 1. Comparison of W_0^{max} Values Reached by AOT RMs ($[AOT] = 0.2$ M; $T = 25$ °C)

nonpolar solvent	W_0^{max}
<i>n</i> -heptane	50 ^a
cyclohexane	21 ^a
lim	17
p-cym	17
toluene	12 ^a
benzene	12 ^a

^aData obtained from ref 15.

summarizes the W_0^{max} (the maximal $[H_2O]$ dissolved) values obtained in both biobased systems. Larger values of W_0 were not possible to obtain due to when more water is added a turbid solution is detected (Figure S2). Additionally, traditional nonpolar solvents used to form AOT RMs are included in Table 1. Thus, a W_0^{max} value of 17 was obtained in both biobased/AOT/water solutions, and interestingly, they were able to dissolve more water than RMs formulated in benzene and toluene.¹⁵

It is interesting to investigate if some property of the nonpolar solvent has influence on the amount of water content. In this sense, Abuin et al. considered the polarity/

polarizability parameter (π^*)¹⁶ of the external solvent to explain the W_0^{\max} values reached in different aqueous AOT RMs. In Figure 1, we plot several W_0^{\max} values for AOT RMs included our data.

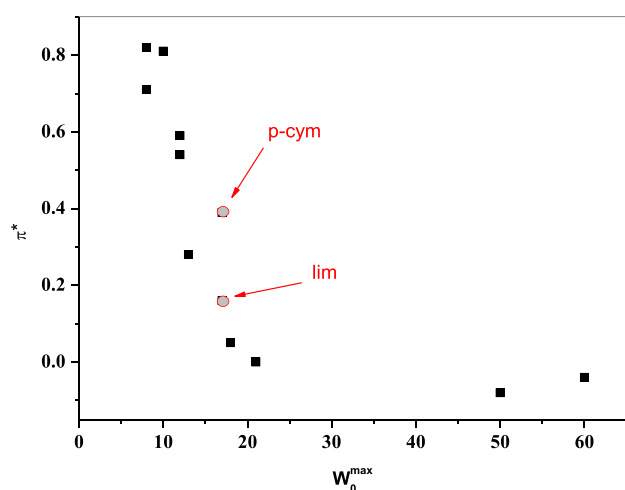


Figure 1. Profile obtained between the W_0^{\max} values corresponding to AOT RMs and the polarity/polarizability parameter (π^*) of nonpolar solvent used. Data obtained from ref 15.

As it was observed, when the nonpolar solvent has a very low π^* value, the AOT RMs can disperse a large amount of $[H_2O]$. In our cases, p-cym and lim have intermediate values between the classical aliphatic solvent *n*-heptane and the aromatic benzene or toluene.

In order to characterize these novels RMs, we used two molecular probes to obtain valuable information. Thus, the absorption probe QB and the fluorescent probe Safranin T were selected.

QB. The microenvironment of these novel RMs was explored using the very sensitive molecular probe QB.¹⁷ QB is an absorption probe that monitors simultaneously the polarity and the hydrogen bond donor ability through the exploration of their two bands, B_1 and B_2 , respectively. Similar methodology was used to investigate different AOT RMs.^{18–20}

Figure 2 shows the plot of the QB behavior as a function of [AOT] in p-cym/AOT RMs solution evaluated at $W_0 = 0$. We performed the absorption experiments varying the [AOT] in the range of 0–0.2 M due to the fact that QB is perfectly soluble in neat p-cym. A similar procedure was performed for the lim/AOT system (results not shown). Figure 2 shows that both B_1 and B_2 bands shift to lower wavelengths when the amount of AOT increases. This fact denotes a rise in the polarity around the QB. Moreover, taking into account that an isosbestic point in the absorption profiles is not detected, QB is located exclusively in the interface of the RMs when the system is formed.^{18–20} Similar results were obtained for lim/AOT RMs.

The profile of the λB_1 maximum band (as polarity sensor) obtained at different [AOT] for both biobased solvent/AOT systems is plotted in Figure S3. Additionally, the corresponding CMC values for both AOT systems were determined from these data. Table 2 summarizes the data collected using QB as the molecular probe. As it was observed, CMC values of 10^{-3} M were obtained in both RMs, which are similar to those reported for AOT RMs formulated in solvents such as benzene or *n*-heptane.²¹

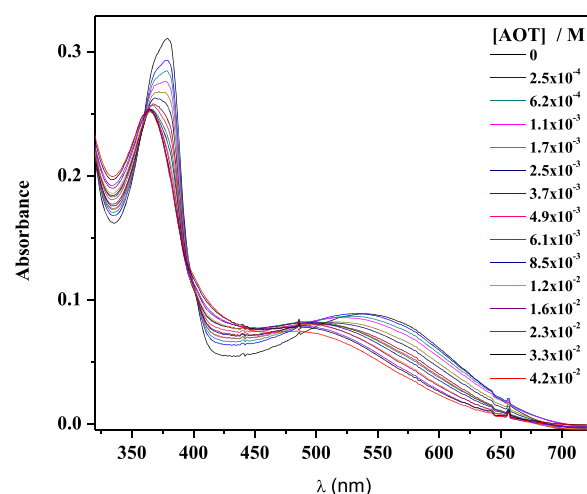


Figure 2. Absorption spectra of QB varying the [AOT] in p-cym/AOT RMs in the absence of water ($W_0 = 0$). $[QB] = 3 \times 10^{-4}$ M.

Table 2. CMC Values of p-cym/AOT and lim/AOT RMs Obtained from QB and ST Spectroscopic Behavior at $W_0 = 0$

RMs	QB ^a	ST ^b
p-cym/AOT	$2.4 \pm 0.5 \times 10^{-3}$ M	$3.2 \pm 0.7 \times 10^{-3}$ M
lim/AOT	$2.2 \pm 0.4 \times 10^{-3}$ M	$2.5 \pm 0.8 \times 10^{-3}$ M

^aMean value obtained from spectral changes of B_1 band (Figure S3).

^bMean value obtained from stock shift (Figure S5).

Safranin T. We also explored the behavior of the fluorescence probe Safranin T (ST) in both RMs. As a sensor of the formation of the organized media, the stock shift of ST was evaluated varying the [AOT].^{22–25} Figure 3 shows the

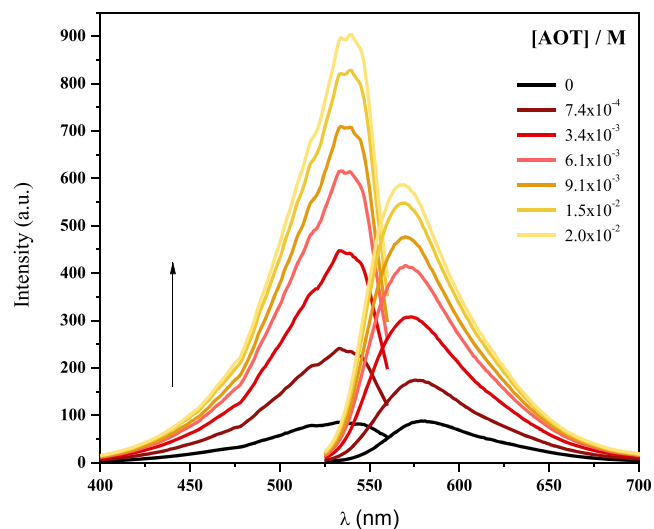


Figure 3. ST emission and excitation spectra varying the [AOT] in p-cym/AOT RMs. $W_0 = 0$. $[ST] = 2 \times 10^{-6}$ M. $T = 25$ °C.

emission and excitation bands of ST in p-cym/AOT RMs varying [AOT] at $W_0 = 0$. A similar plot for lim/AOT RMs is included in the Supporting Information section (see Figure S4). The values of the stock shift of ST (defined as $\Delta\lambda$) in both systems is plotted in Figure S5A and B. From this figure, it can also be seen that the CMC values can be obtained (see

values in Table 2). Similar CMC values between ST and QB were obtained.

DLS. Considering the CMC values obtained from the molecular probes QB and ST, the droplet sizes of both biobased solvents/AOT solutions at $[AOT] > 10^{-3}$ M by DLS technique were evaluated. Figure 4 shows the diameter (D_{app})

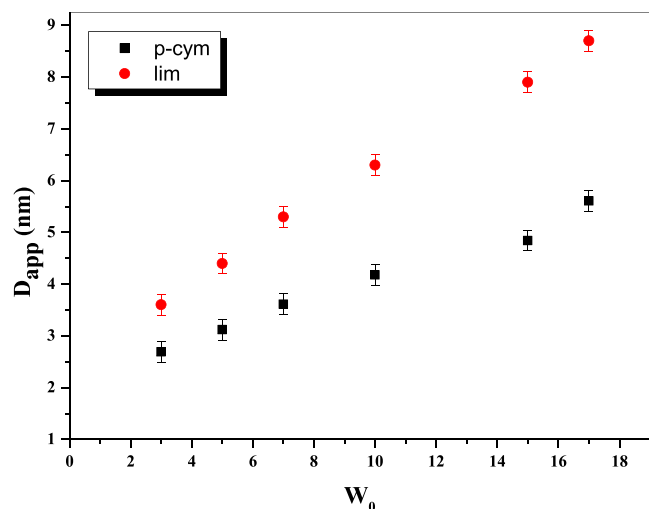


Figure 4. Effect of the water content (W_0) on the D_{app} values in p-cym/AOT/water RMs (■) and lim/AOT/water RMs (●). $T = 25$ °C. $[AOT] = 0.2$ M.

values of the droplets acquired in the biobased solvents/AOT solutions at $[AOT] = 0.2$ M varying the water content. Additionally, the polydispersity index (PDI) values obtained for these measurements are included in Table S1. As it can be observed, only one population in all cases was detected. Additionally, small PDI values (Table S1) were obtained, confirming the uniformity of the organized media formed.

As it is observed from Figure 4, an increase in the droplets sizes and linear tendency in both RMs is detected. Interestingly, the sizes are not identical for both RMs, being that the RMs formulated in lim larger than in p-cym. Additionally, the differences in size appear more important when the water content increases. Thus, when $W_0 = 3$, the droplets size for p-cym/AOT RMs is 2.7 nm and for lim/AOT RMs is 3.6 nm. At a large W_0 , e.g., at $W_0 = 17$, the sizes are 5.6 and 8.7 nm, respectively.

The DLS data exposed the sizes of the biobased AOT RMs, which were interpreted taking into account the magnitude of the external solvent penetration toward the interfacial zone. It is known that if the solvent can penetrate the interface, it alters the interfacial organization and, in consequence, the size. Thus, we think that p-cym can penetrate more than lim, altering the volume of the hydrocarbon region (v), changing the effective packing parameter (p) of the surfactant. This parameter is determined by the chemical structure of the amphiphile as $p = v/al_c$, where l_c is the length of the hydrocarbon chain and a is the area of polar headgroup of the surfactant.²⁶ Consequently, if some factor on p is altered, the droplet size changes. For example, a reduction on p is suggested when the RM sizes increase.^{27,28} Thus, in our RMs an increase in the biobased solvent penetration increase the factor v (decreasing p) and produce smaller droplets. In this sense, AOT RMs formulated in traditional solvents (aromatic and aliphatic) or in biocompatible solvents (IPM and ML)³ showed similar

behavior to the present work. Moreover, as it will be demonstrated in the next sections, this phenomenon also alters the interfacial properties of the RMs.

We believe that the penetration of the external solvent is a crucial factor to alter the micellar interface. To reinforce this idea, we determined the aggregation numbers (N_{agg}) of both biobased solvent/AOT RMs at equal W_0 (Table 3) using the well-known methodology²⁹ by emission spectroscopy using the couple $Ru(bpy)_3Cl$ and $K_3Fe(CN)_6$. For a detailed procedure see Figures S6 and S7.

Table 3. Aggregation Number (N_{agg}) Values Obtained for the Biobased AOT RMs. $T = 25$ °C. $W_0 = 10$.

RMs	d_{app} (nm) ^a	N_{agg}
p-cym/AOT/water	4.2 ± 0.4	134 ± 3
lim/AOT/water	6.3 ± 0.4	189 ± 6

^aData obtained at $W_0 = 10$ from Figure 4.

As can be seen, at $W_0 = 10$ the RMs formulated in lim present a greater amount of AOT monomers (large N_{agg}) than p-cym/AOT RMs. Assuming that both biobased solvent/AOT RMs are practically spherical, we think that the differences of the droplet sizes suggest a dissimilar interfacial conformation. Thus, as p-cym penetrates more, the interface needed less surfactant molecules to entrap water.³

¹H NMR. Our systems present several protons sensitive to the microenvironment, as displayed in Figures S8 and S9. In this sense, we monitored them as a function of the water content. Specifically, we analyze the chemical shifting of the protons corresponding to the entrapped water and to the polar headgroup of the anionic surfactant (I and I', Scheme 1).

Protons of Entrapped Water. Figure 5 shows how the variation of W_0 affects the proton chemical shift values of entrapped water in both biobased AOT RMs. From the figure, a downfield shifting as the amount of water entrapped increases in both systems is detected; however, the value reached is not similar. For example, in p-cym/AOT RMs, changes from 4.02 ppm up to 4.81 ppm when the W_0 varied

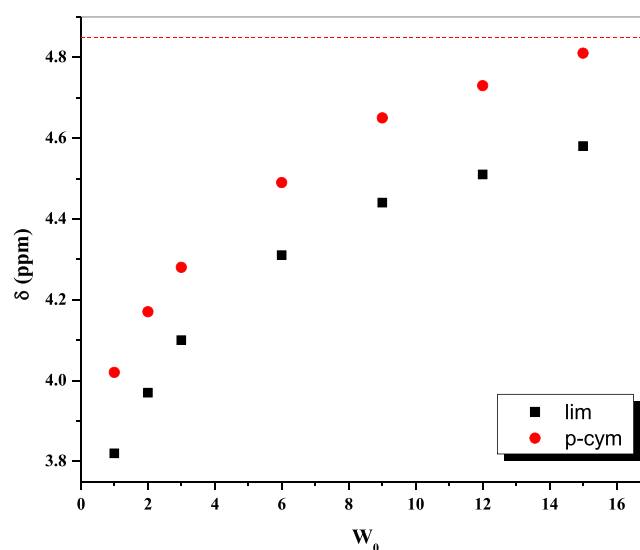


Figure 5. Effect of the water content on the chemical shifts of protons of entrapped water inside of both biobased RMs. $[AOT] = 0.2$ M. For comparison, the value of neat water (—) is also plotted.

from 1 to 15 were observed. For lim/AOT RMs in the same W_0 range, the value changes from 3.82 ppm up to 4.58 ppm. As it was noted from Figure 5, in the RMs formulated in p-cym the proton of water entrapped with the maximum W_0 evaluated appears to be quite similar to the neat water.³⁰ A different situation for the system formulated with lim is observed, where the chemical shift is 4.58 ppm at the W_0 maximum evaluated.

Compared with neat water, the position upfield of the protons of the entrapped water observed in our data was described previously for similar AOT RMs formulated in C_6D_6 ^{30,31} and in C_6D_{12} .³² Disruption of the normal hydrogen bond structure of water as a consequence of the surfactant interaction was invoked to explain the detected shifts. As consequence of that, the water molecules interact less with each other, appearing at a more upfield region. As W_0 increases, the protons of water inside the organized media begin to recover the hydrogen bond structure of neat solvent. Thus, the chemical shifts of these H tend to the neat value. In our cases, both the biobased solvent and RMs show water molecules interacting with the anionic interface, and the hydrogen bond structure is disrupted by this phenomena. However, this interaction is quite different depending on the biobased solvent employed to prepare the RMs. Thus, a weaker interaction of water–surfactant at the interface in p-cym/AOT as compared to that in lim/AOT RMs is suggested.

Protons of AOT Polar Head. The microenvironment created in the biobased solvent/AOT RMs can be monitored by following the chemical shift corresponding to the protons of the polar headgroup of the surfactant.^{30,31} As it can be observed in Figure S9A and B, when the water content increases, an upfield shift of the signals of protons I and I' of AOT (see label in Scheme 1) is observed. Thus, in p-cym/AOT RMs the H I signal appears at 4.70 ppm at $W_0 = 1$ and shifts to 4.55 ppm at $W_0 = 15$, while the H I' signal appears at 3.52 ppm at $W_0 = 1$ and shifts to 3.46 ppm at $W_0 = 15$. For the AOT RMs formulated in lim, the signals changes in the same W_0 range from 4.41 ppm up to 4.27 ppm and from 3.25 to 3.19 ppm, respectively. Similar shifting was observed for AOT RMs generated using traditional nonpolar solvents. For example, Heatley^{30,31} reported that changing the W_0 range from 1 to 5.3 in the systems C_6D_6 /AOT/water resulted in the H I signal shifting from 4.86 ppm, while the H I' shifts from 3.64 to 3.55 ppm in the same range of W_0 . The increment of the spatial separation between anion AOT and its counterion, due to the interaction via hydrogen bond between the sulfonate group and the entrapped water, was invoked to explain these data.

Several arguments were invoked in the past to explain the different penetration of the external solvent in AOT RMs; one of these was the value of the molar volume (V_m) of the nonpolar solvents. For example, benzene has smaller V_m than *n*-heptane, and the behavior of AOT RMs generated in both nonpolar solvents was explained considering that the aromatic solvent penetrated more than the aliphatic. As it can be observed in Table 4, the V_m of p-cym is larger than lim;³³ thus, lim (minor V_m) should penetrate the AOT interface more than p-cym, producing smaller RMs. However, our DLS results show a D_{app} value two units smaller for the p-cym/AOT system in comparison to the D_{app} value found for the lim/AOT system. This fact evidences that the V_m is not the appropriated factor to explain the results and that others such as polarity, viscosity, and molecular geometry (long or branched hydrocarbon chain) should be considered.

Table 4. Different Parameters Evaluated to Explain the External Solvent Aot Rms Penetration ($T = 25^\circ C$)

solvent	V_m ($cm^3 mol^{-1}$) ^a	viscosity (mPa s)	π^* ^c
p-cym	184.8	0.82 ^a	0.39
lim	162.1	0.89 ^b	0.16

^aValues obtained from ref 33. ^bValue obtained from ref 34. ^cValues obtained from ref 15.

In this sense, the viscosity explains the nonpolar solvent interface penetration. Thus, if the solvent is more viscous, more penetration occurs into the interface.³

In our case, both biobased solvents have similar viscosity values (see Table 4). As it was mentioned above, the π^* parameter was invoked before to explain facts such as why the maximal W_0 reached its value in the organized media.¹⁵ In this sense, as it is shown in Table 4, p-cym appears as more polar than lim, and consequently, its penetration to the interfacial region is larger (see Scheme 2).

Thus, the dissimilar penetration of both biobased solvents, which also perturb the water–surfactant interaction, can be explained due to the polarity having a stronger effect than the viscosity of these nonpolar solvents. Consequently, the p-cym/AOT RMs are less interactive and smaller than those formulated in lim. Finally, new interfaces with unexplored physicochemical properties are generated due to the ability of the biobased solvent to penetrate or not into the AOT interface.

CONCLUSIONS

We demonstrated that biobased solvents such as p-cym and lim can be used to generate more sustainable AOT RMs. Interestingly, even the maximum amount of water dispersed is similar for both RMs, and the sizes of the systems are not identical, being that the RMs are formulated in lim larger than in p-cym.

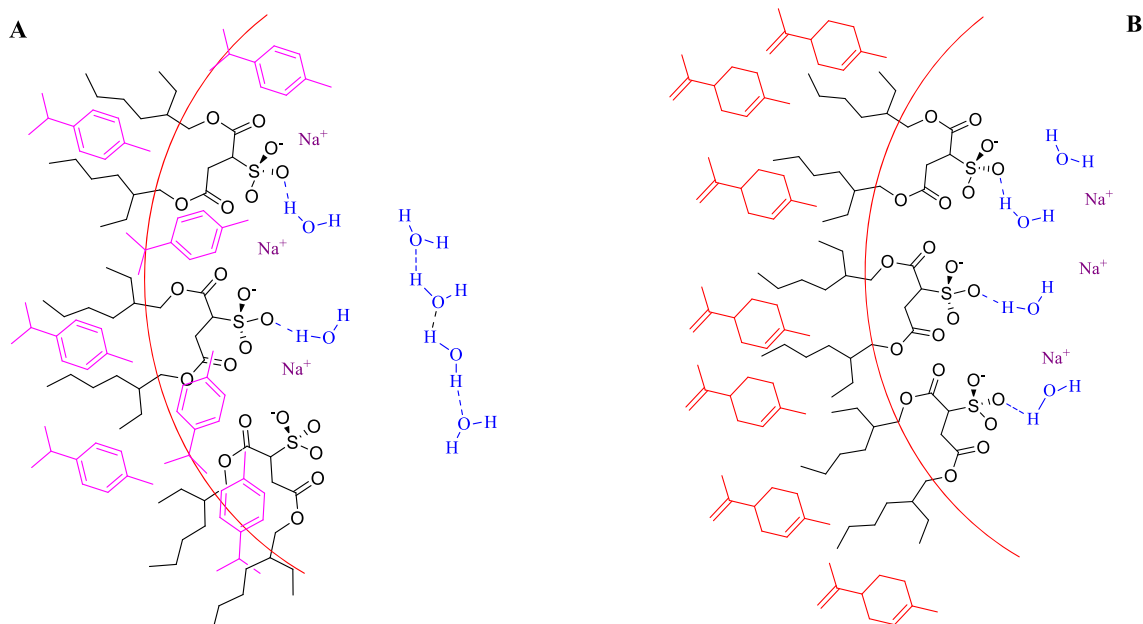
In both the biobased solvent and RMs, the confined water showed that its hydrogen-bond structure was altered by the interaction with the interface; however, this interaction is quite different depending on the biobased solvent employed to prepare the RMs. Thus, the interaction of water–surfactant at the interface is weaker in p-cym/AOT than in lim/AOT RMs. We think that the different penetration of the external solvent to the interfacial region is the main reason for the facts observed. In this sense, the polarity is more than the viscosity or molar volume of these biobased solvents, explaining the dissimilar penetration suggested in both RMs. Finally, the possibility to formulate more friendly and versatile AOT RMs extends the future applications of these organized systems.

EXPERIMENTAL SECTION

Materials. The surfactant sodium 1,4-bis (2-ethylhexyl) sulfosuccinate (AOT) was provided by Sigma-Aldrich (>99% purity), and prior to use it was dried under vacuum. *p*-cymene (99% purity) and (R)-(+)-limonene (97% purity), both provided by Sigma-Aldrich, were dried before use in a vacuum oven at 70 °C for at least 12 h and stored over molecular sieves. Labonco equipment model 90901-01 was used to generate Ultrapure water. 1-Methyl-8-oxyquinolinium betaine (QB) was synthesized according to Ueda et al.²¹ Safranin T (Merck, ≥85% purity), $K_3[Fe(CN)_6]$ (Sigma-Aldrich, 99% purity), and $Ru(bpy)_3Cl$ (Sigma-Aldrich, 97% purity) were used as received.

Methods. The preparation of the biobased solvents and AOT RMs, the absorption, the emission, and NMR experiments are fully described in the Supporting Information.

Scheme 2. Effect to the External Solvent Penetration on the Biobased (A: p-cym and B: lim) AOT RMs



■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.9b06578>.

Experimental procedure of the AOT RMs preparations; absorption, emission and NMR experiments (PDF)

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Notes

The authors declare no competing financial interest.

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