

Nanoscale Control Over Interfacial Properties in Mixed Reverse Micelles Formulated by Using Sodium 1,4-bis-2-ethylhexylsulfosuccinate and Tri-*n*-octyl Phosphine Oxide Surfactants

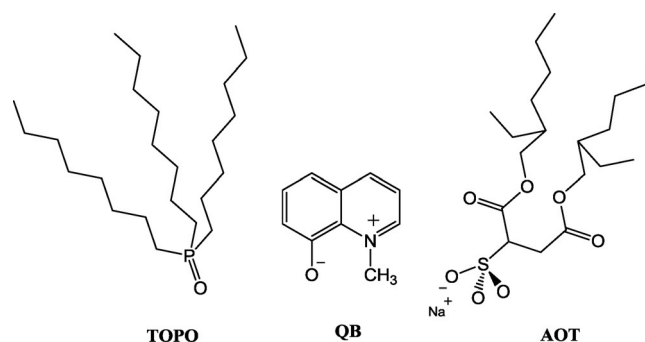
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The interfacial properties of pure reverse micelles (RMs) are a consequence of the magnitude and nature of noncovalent interactions between confined water and the surfactant polar head. Addition of a second surfactant to form mixed RMs is expected to influence these interactions and thus affect these properties at the nanoscale level. Herein, pure and mixed RMs stabilized by sodium 1,4-bis-2-ethylhexylsulfosuccinate and tri-*n*-octyl phosphine oxide (TOPO) surfactants in *n*-heptane were formulated and studied by varying both the water content and the TOPO mole fraction. The microenvironment generated was

sensed by following the solvatochromic behavior of the 1-methyl-8-oxyquinolinium betaine probe and ³¹P NMR spectroscopy. The results reveal unique properties of mixed RMs and we give experimental evidence that free water can be detected in the polar core of the mixed RMs at very low water content. We anticipate that these findings will have an impact on the use of such media as nanoreactors for many types of chemical reactions, such as enzymatic reactions and nanoparticle synthesis.

1. Introduction

Reverse micelles (RMs) are generally described as nanometer-sized water droplets dispersed in a nonpolar solvent with the aid of a surfactant (or blend of surfactants and/or a cosurfactant) monolayer, to form a thermodynamically stable and optically transparent solution. Additionally, they possess highly dynamic structures with components that are organized through different interactions or collisions, coalescence, or redispersions.^[1] They are capable of solubilizing both polar and nonpolar substances and have found applications in various fields, such as chemical and enzymatic reactions,^[2–4] nanomaterial synthesis,^[5] and drug-delivery systems.^[6] Different anionic, cationic, and nonionic surfactants have been employed to prepare RMs in nonpolar solvents. Of the anionic surfactants that form RMs in different solvents, the best known is sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT, Scheme 1).^[7] It is known that AOT forms spherical RMs in aromatic and aliphatic solvents without the addition of a cosurfactant, and a variable amount of water can be solubilized depending on the external solvent and temperature, among other factors.^[7] In terms of nonionic surfactants, a nonconventional example is tri-*n*-octyl phosphine oxide (TOPO, Scheme 1). TOPO is a molecule with a very small polar head (the P=O group) and three hydrocar-



Scheme 1. Molecular structure of QB and the surfactants TOPO and AOT.

bon tails, which distinguishes it from conventional nonionic surfactants with only a single tail.^[8] For example, the Brij surfactants are characterized by long polar heads that even manage to have the same or greater length than the hydrophobic region.^[9] The great versatility of TOPO in different scientific and technological fields lies in the unique properties of the P=O group, which has free electrons pairs with a strong ability to complex numerous species.^[10] Some studies have reported the use of this compound as an alternative for nanoparticle synthesis, for controlling and inhibiting the growth morphology.^[11,12]

However, many biophysical applications depend on the magnitude of noncovalent interactions of the micellar interface with specific solutes solubilized inside the RMs.^[13–15] Therefore, it would be of great interest if the effective control of these interactions can be regulated by changes at the interface

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through the addition of a second surfactant. It is known that certain mixtures of surfactants can provide better performance than pure surfactants with respect to, for example, the stability and activity of enzymes,^[16,17] the recovery and purification of antibiotics,^[18] and the synthesis of nanoparticles.^[19] There are studies on RMs systems with more than one surfactant that use techniques such as solubilization,^[20] viscosity,^[21] conductivity,^[22] small angle neutron scattering (SANS),^[23] FT-IR spectroscopy, and NMR spectroscopy,^[24,25] with special emphasis on understanding the mixed interface and the structure of the confined water. The findings show that the influence of surfactant mixing on overall formation and stability of microemulsions are a direct consequence of molecular interactions of the constituents at the oil/water interface.

In our previous work,^[26] we investigated RMs formed by TOPO and mixed RMs obtained from a mixture of TOPO and AOT surfactant by using dynamic light scattering (DLS) and FT-IR spectroscopy at fixed temperature. These techniques also allowed us to confirm that the surfactants mix with each other instead of creating independent RM media. DLS experiments showed the existence of discrete droplets at any W_0 ($W_0 = [\text{Water}]/([\text{AOT}] + [\text{TOPO}])$) values investigated and, in contrast to results obtained when other nonionic surfactants were mixed with AOT, the droplet sizes diminished with increased TOPO content and the changes in droplet size depend on the water content. At $W_0 = 0.5$ the droplet sizes diminished as the TOPO content was increased, whereas at $W_0 = 2$ the changes were almost negligible and the sizes of the mixed RMs at different X_{TOPO} ($X_{\text{TOPO}} = [\text{TOPO}]/([\text{AOT}] + [\text{TOPO}])$) values did not differ substantially compared with the size of AOT RMs. Furthermore, the FT-IR spectra revealed that the nature of confined water is dramatically altered by the presence of TOPO and it is possible to find "bulk-like" water, even at very low water content. We have discussed the results by taking into consideration the changes in the mixed interfacial composition and the different interactions between water and the two surfactants.^[26] However, the microscopic nature of this peculiar and unique interface could not be investigated with these techniques. Thus, it is necessary to investigate the system by using molecular probes and spectroscopic techniques to assess such issues as the micropolarity and hydrogen-bonding ability of the interface to understand the novel system fully.

As shown, the interfacial composition changes directly affect the water structure and consequently may impact on the mixed RMs micropolarity and capacity for hydrogen-bond interactions. Even though many structural properties of RMs, such as the size, shape, and interfacial rigidity, have been carefully explored,^[22,27,28] only a few studies focus attention on the mixed-interface micropolarity and its ability to make specific interactions that are key for molecular recognition. Thus, the goal herein is to obtain information about this particular property and how it can be altered by the incorporation of TOPO. Previously, we studied the micropolarity of aqueous and nonaqueous single (or pure) AOT RMs^[29–31] by following the solvatochromic behavior of molecular probe 1-methyl-8-oxyquinolinium betaine (QB; Scheme 1) because its absorption spectrum is highly sensitive to the local environment.^[29,30] The aims of the

present contribution are 1) to evaluate whether the QB probe can be used to investigate water/AOT:TOPO/*n*-heptane RM interfacial properties, and 2) to use the spectroscopic behavior of QB dissolved in mixed RMs to gain more insights about micropolarity, the water–mixed-interface interactions, and the gradual change in the interfacial composition observed when the water content is increased. To complement these studies, we used noninvasive techniques, such as ³¹P NMR spectroscopy, to determine directly and unequivocally the behavior of the nonionic surfactant at the mixed interface. Together with our earlier work,^[26] we can achieve a full characterization of these systems.

The results show that by varying both the W_0 and X_{TOPO} parameters, the existence of a specific interaction between water and QB in the generated mixed environment was detected, an interaction that was not observed when a single surfactant was used. Additionally, when the water content is low ($W_0 \leq 1$), addition of TOPO causes both the formation of a bulk-like structure and a decrease in the hydrogen-bond-donor capability of the water. In contrast, when the water content is higher ($W_0 > 1$), changes in the interfacial composition occur and the probe detects the same properties as found in AOT RMs, independent of the TOPO content. Therefore, by using a molecular probe (QB) that is anchored to the interface,^[29,30] we demonstrate features that have been suggested by using techniques such as FT-IR and DLS that do not directly monitor the interface.

The present findings may influence in the creation of a tunable and customizable interface, where different microenvironments can be generated with the AOT:TOPO mixtures. It may subsequently be extended the studies to various tests molecules to evaluate how adaptable is the mixed interface in molecular recognition.

2. Results and Discussion

2.1. Solvatochromic Studies in RMs Formed with a Single Surfactant: Water/AOT/*n*-Heptane and Water/TOPO/*n*-Heptane RMs

Figure 1 shows the typical absorption spectra of QB at varying W_0 values in RMs formed with a single surfactant: water/AOT/*n*-heptane (Figure 1 A) and water/TOPO/*n*-heptane (Figure 1 B). As shown, the probe presents two electronic absorption bands. The band in the visible region (B_1) is due to a transition from a predominantly dipolar ground state to an excited state with a considerably reduced polarity. It was found that the B_1 solvatochromism is mainly due to the polarity/polarizability ability of the medium. However, this band also correlates to the hydrogen-bond-donor ability of the medium.^[29,30] As the polarity and/or the hydrogen-bond-donor ability of the solvent is increased, the ground state becomes more stable, which leads to an increase in the transition energy, that is, negative solvatochromism.

The band in the UV region (B_2), which was assigned to a charge transfer from the phenoxide ion to the aromatic ring (see Scheme 1), also shifts hypsochromically with increased sol-

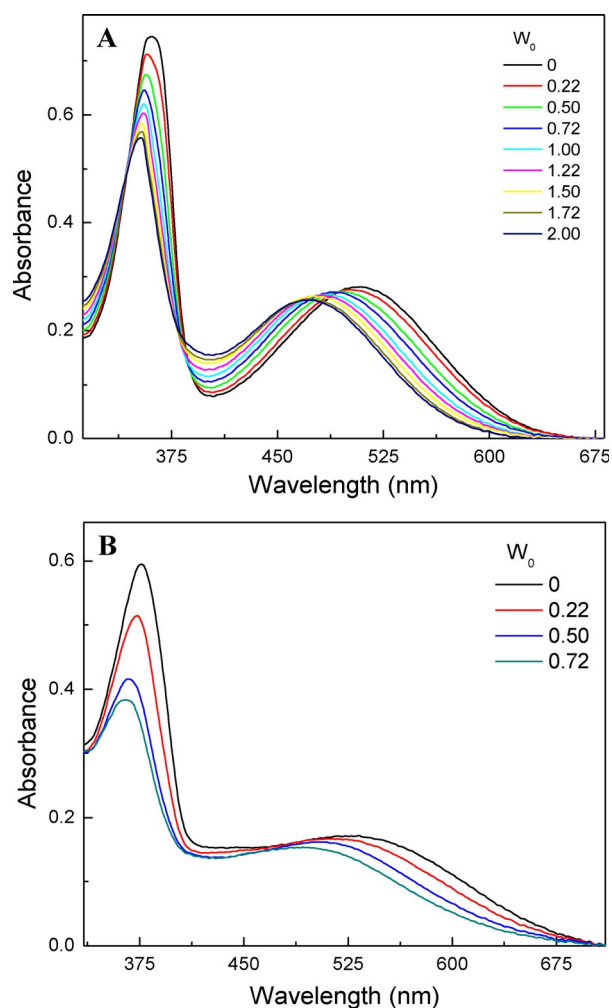


Figure 1. QB absorption spectra in RMs formed with a single surfactant: A) water/AOT/*n*-heptane and B) water/TOPO/*n*-heptane RMs at different W_0 values. [AOT] = 0.2 M, [TOPO] = 0.2 M, [QB] = 3×10^{-4} M.

vent polarity, although in lesser magnitude than the visible band.^[29,30] However, it was demonstrated that the B_2 band frequency is even more sensitive to hydrogen-bond interactions. Interestingly, it was shown that the absorbance ratio of both bands ($AbsB_2/AbsB_1$) is only sensitive to the hydrogen-bond ability of the medium. The $AbsB_2/AbsB_1$ value is large for solvents with low hydrogen-bonding ability and decreases as the solvent hydrogen-bond capability increases. Consequently, the $AbsB_2/AbsB_1$ ratio is used in combination with the absorption bands shifts to determine the properties of the microenvironment surrounding the probe.^[29,30]

The B_2 band absorption maximum ($\lambda_{max}B_2$) and the B_1 band absorption maximum ($\lambda_{max}B_1$) of QB in AOT RMs at $W_0=0$ are $\lambda=361$ and 509 nm, respectively, whereas for TOPO RMs the values are $\lambda=376$ and 530 nm, respectively. The results show that the TOPO RM interface presents a less polar environment than the AOT RMs one because the B_1 band maximum is red-shifted by 15 nm. For both systems, significant changes are observed in the QB spectra when W_0 is increased. Both $\lambda_{max}B_2$ and $\lambda_{max}B_1$ shift hypsochromically, but $\lambda_{max}B_1$ is shifted more than $\lambda_{max}B_2$. Furthermore, a significant decrease in the B_2 band in-

tensity can be noted, compared with a slight decrease in the B_1 band intensity when the water content increases. No isosbestic point is observed in either system. The hypsochromic shift is as expected, if it is considered that when W_0 is increased, the micropolarity of the RMs interface increases.^[29]

Figure 2 summarizes the $\lambda_{max}B_1$ (Figure 2A) and $AbsB_2/AbsB_1$ (Figure 2B) values for QB in RMs formed with single surfactant (water/AOT/*n*-heptane RMs or water/TOPO/*n*-heptane) by varying W_0 . The $\lambda_{max}B_1$ value for neat water is included for comparison.^[29] It is important to note, particularly for $W_0 \leq 0.72$, that the interfacial micropolarity of TOPO RMs is always lower and seems to increase faster than the AOT RMs interface upon water addition.

A possible explanation for this behavior lies in the different interaction between water and the polar heads of two surfactants. For such low W_0 values, the structure of the encapsulated water in AOT RMs has its hydrogen-bond network broken because of the strongest interaction with the polar heads and

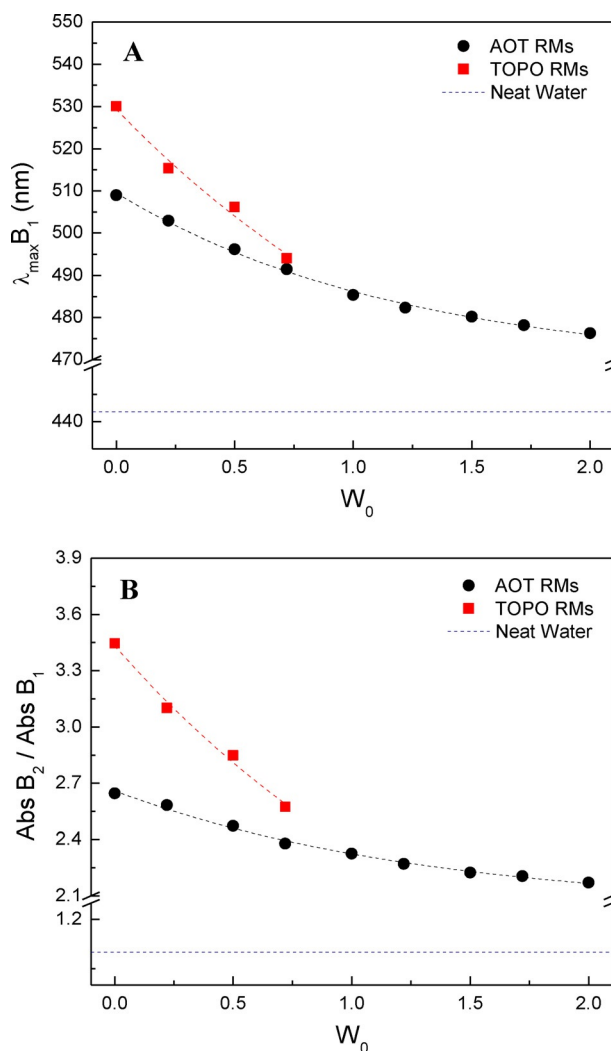


Figure 2. Variation in A) the B_1 band maximum ($\lambda_{max}B_1$) and B) the absorbance ratio between the B_2 and B_1 bands ($AbsB_2/AbsB_1$) of QB as a function of W_0 in single-surfactant RMs; ●: water/AOT/*n*-heptane and ■: water/TOPO/*n*-heptane RMs. The neat water value (—) is included for comparison.^[29] [AOT] = 0.2 M, [TOPO] = 0.2 M, [QB] = 3×10^{-4} M.

the counterions of AOT, as already known.^[32–34] Above $W_0 \approx 10$, it is considered that the water molecules interact with each other to form a water pool with similar properties to neat water.^[35–38] It is for this reason that QB, anchored at the interface, only recognizes changes at the interfacial level and is extremely sensitive to the bound water in AOT RMs.^[29,30] In contrast, and as demonstrated in our previous studies,^[26] for water/TOPO/*n*-heptane RMs there are two different types of water that coexist in the RMs media, one bound to the polar heads of TOPO and the other strongly associated with other water molecules, that is, a bulk-like structure. Furthermore, the water–TOPO interaction is weaker than the water–AOT interaction.^[26] In this way, the progressive separation of water molecules from the interface to establish stronger interactions with each other in TOPO RMs could explain the decrease in interfacial micropolarity sensed by the optical probe.

As shown in Figure 2B, the $\text{AbsB}_2/\text{AbsB}_1$ ratio at $W_0 = 0$ is 2.6 for the AOT/*n*-heptane system and 3.4 for the TOPO/*n*-heptane system. Given the structure of the surfactants and the fact that no water is present, there is no possibility of hydrogen-bonding interactions between QB and its microenvironment. Thus, the difference in absorbance ratio between the two systems shows that QB could be sensing other types of interaction and this is different depending on the surfactant used. We have observed^[39] certain facts that lead us to think that other factors that have not hitherto been considered should also be responsible for the changes in the QB $\text{AbsB}_2/\text{AbsB}_1$ value, in addition to the hydrogen-bond-donor ability of the microenvironment. For example, we have noted^[39] that the $\text{AbsB}_2/\text{AbsB}_1$ values found in neat ionic liquids (ILs) are surprisingly high, and we have suggested an extra (electrostatic) interaction between QB and the IL ions, other than the expected hydrogen-bonding interaction, to explain the anomalous results. Although TOPO has no charge on the polar head, the nonbonding electron pairs on the oxygen of the P=O group may be interacting with the positively charged nitrogen of the pyridinium ring of QB. Thus, the charge-transfer transition is affected and the $\text{AbsB}_2/\text{AbsB}_1$ ratio increases accordingly.

When water is incorporated, we can observe a decrease in the $\text{AbsB}_2/\text{AbsB}_1$ ratio for both systems, which shows that the water actually interacts with the surfactant polar heads in each interface. However, as shown in Figure 2B for $W_0 \leq 0.72$ values, the $\text{AbsB}_2/\text{AbsB}_1$ ratios are always higher in TOPO RMs than in AOT RMs, which implies that QB senses a lower hydrogen-bonding interaction in the first system. Similarly, the $\text{AbsB}_2/\text{AbsB}_1$ value for TOPO RMs at the maximum evaluated W_0 value ($W_0 = 0.72$) is 2.57, which is different to the corresponding value when QB is dissolved in neat water.^[29,30] This indicates that, similar to the micropolarity, the hydrogen-bond-donor capability of water is modified within TOPO RMs.

2.2. Solvatochromic Studies in Water/AOT:TOPO/*n*-Heptane Mixed RMs

Figure 3 shows the absorption spectra of QB at various W_0 in Water/AOT:TOPO/*n*-Heptane mixed RMs at a X_{TOPO} value of 0.5. Figure S1 in the Supporting Information shows the absorption

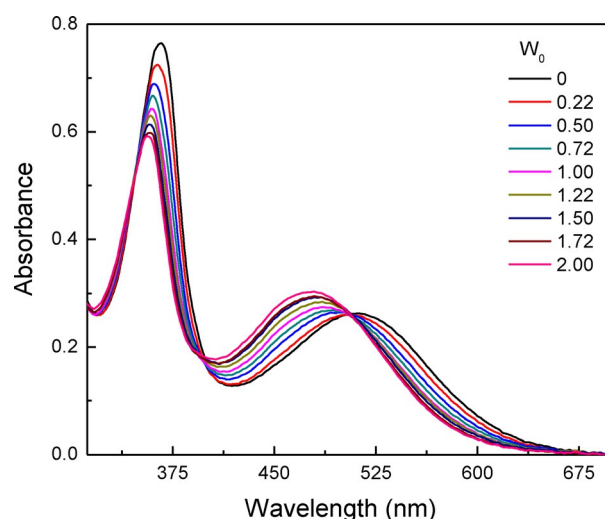


Figure 3. QB absorption spectra upon increasing the W_0 value in water/AOT:TOPO/*n*-heptane mixed RMs at $X_{\text{TOPO}} = 0.5$. [Surfactant]_T = 0.2 M, [QB] = 3×10^{-4} M.

spectra of QB in the mixed RMs at X_{TOPO} values of 0.1, 0.3, and 0.7.

It is interesting to note that all the systems (except for the mixture with $X_{\text{TOPO}} = 0.1$, see Figure S1 A) display an isosbestic point at around $\lambda = 505$ nm in their absorption spectra, which is indicative of a simple equilibrium of two spectrophotometrically distinguishable species in different microenvironments. The general discussion and quantification of the equilibrium will be discussed later.

Figure 4 summarizes the λ_{maxB_1} (Figure 4A) and the $\text{AbsB}_2/\text{AbsB}_1$ (Figure 4B) values for QB varying W_0 at different X_{TOPO} values in mixed RMs. As can be seen in Figure 4A, at $W_0 \leq 1$ the increment in X_{TOPO} has an effect on the λ_{maxB_1} band position. Specifically, a bathochromic shift was observed when X_{TOPO} was increased at fixed W_0 . In contrast, it may be noted that for $W_0 > 1$ there is no effect on λ_{maxB_1} with a change in X_{TOPO} , and the λ_{maxB_1} values are the same as in AOT RMs ($X_{\text{TOPO}} = 0$).

When the water content is small ($W_0 \leq 1$), the bathochromic shift observed with increased X_{TOPO} at fixed W_0 suggests a decrease in the interfacial micropolarity. This decrease could be due to two factors that act simultaneously: 1) a mixed interface composed mostly of nonionic surfactant molecules and/or 2) a progressive decrease in the interfacial water that interacts with the polar heads of the surfactants. These results seem to verify the hypotheses proposed in our previous studies^[26] with regard to the interfacial composition and the nature of encapsulated water at very low water contents. These two complementary effects result in the lower micropolarity sensed by QB and this decrease is proportional to the increase in the TOPO content.

In contrast, when the water content was increased ($W_0 > 1$), the interfacial micropolarity sensed by the probe in all systems is the same as that observed in AOT RMs. These results are related to the gradual change in the interfacial composition of mixed RMs, in which it was assumed that if the water content

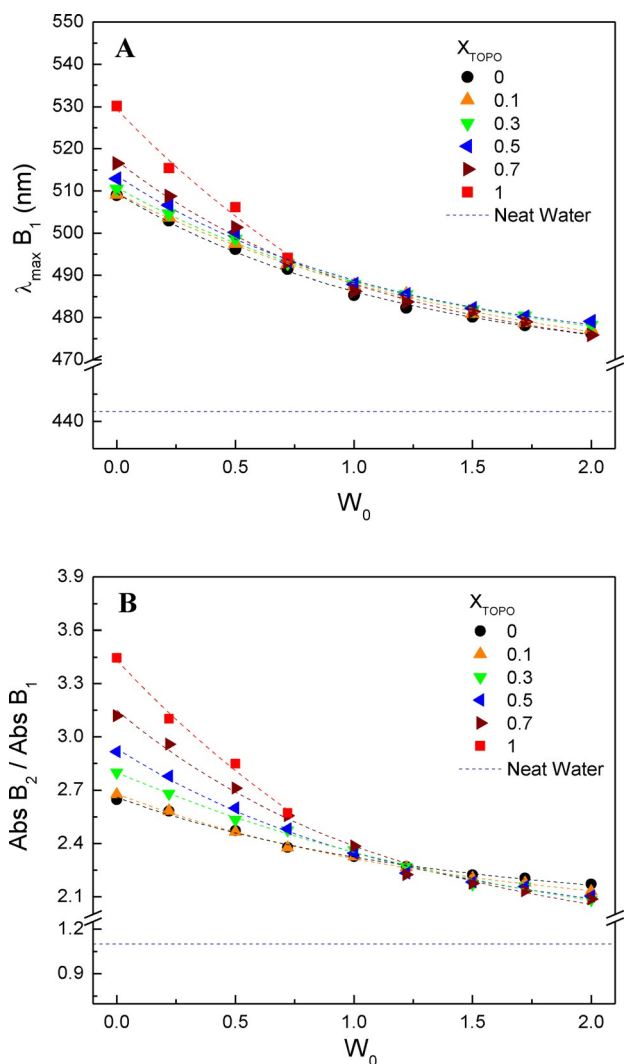


Figure 4. Variation in A) the B_1 band maximum and B) the absorbance ratio between the B_2 and B_1 bands ($Abs B_2/Abs B_1$) of QB as a function of W_0 in water/AOT:TOPO/*n*-heptane mixed RMs at different X_{TOPO} values: 0 (●), 0.1 (▲), 0.3 (▼), 0.5 (◄), 0.7 (◄), and 1 (■). The neat water value (—) is included for comparison.^[29] $[Surfactant]_T = 0.2$ M, $[QB] = 3 \times 10^{-4}$ M.

is increased, the RMs interface is formed mainly with AOT molecules.^[26] Thus, QB always monitors the same micropolarity regardless of the TOPO content in the mixture.

From Figure 4B, two regions of different behavior can be observed depending on the W_0 value. That is, for $W_0 \leq 1$, the change in X_{TOPO} at constant W_0 has an influence on the donor ability of water to form hydrogen-bonding interactions; specifically it can be noted an increase in $Abs B_2/Abs B_1$ ratio when the X_{TOPO} increases. Thus, TOPO incorporation decreases the hydrogen-bond-donor ability of water.

In contrast, for $W_0 > 1$ the addition of a nonionic surfactant in the mixture does not appreciably alter the $Abs B_2/Abs B_1$ ratio, and these values are similar to those observed in AOT RMs.

This behavior supports previous conclusions that the decrease in bound water in the interface is caused by the presence of TOPO surfactant. Note that with a progressive increase

in X_{TOPO} , the specific hydrogen-bonding interaction between the probe and the water molecules at the interface become smaller due to the progressive formation of bulk-like water. In contrast, when the water content is increased and a change in the interfacial composition takes place, QB senses the same hydrogen-bond-donor ability as found in AOT RMs. This could be because 1) there is a preferential interaction between water and AOT due to its greater abundance in the interfacial region and/or 2) the TOPO surfactant cannot effectively interact with the water molecules.

As has been mentioned above, the UV/Vis absorption spectra of QB in water/AOT:TOPO/*n*-heptane mixed RMs at various water contents and at different X_{TOPO} values have a clear isosbestic point, which indicates a simple equilibrium of the probe between two different microenvironments. Because QB is not soluble in *n*-heptane, these microenvironments could be the RM interface and the polar core of the mixed RMs. This phenomenon is very striking because it is known that for aqueous RMs formed from AOT only, there is no possibility of finding bulk-like water at such low W_0 values and the QB absorption spectra do not exhibit any isosbestic point, which indicates that the probe is anchored at the interface.^[29,32] Evidently, incorporation of the nonionic surfactant causes a significant change at interfacial level, which is recognized indirectly through the anomalous spectroscopic response of QB compared with when the probe is located in a purely anionic interface. In summary, the existence of an isosbestic point in the absorption spectra of QB in mixed RMs supports the existence of bulk-like water, even at very low water content, and shows that AOT and TOPO are mixed to form a new RM system.

The calculation of the partition constant (K_p) of QB between the RMs interface and the water pool is shown in the Supporting Information. Furthermore, Figure S2 shows representative plots of $A_T^\lambda/[QB]_0$, in which A_T^λ is the total absorbance at $\lambda = 530$ nm and $[QB]_0$ is the analytical concentration of QB as a function of water concentration in the water/AOT:TOPO/*n*-heptane mixed RMs at $X_{TOPO} = 0.3, 0.5$, and 0.7 . The data shown in Figure S2 were fitted to Equation (S6) by using a nonlinear regression method and the obtained K_p values are gathered in Table 1.

As shown in Table 1, the K_p values increase with larger X_{TOPO} values (within experimental error). These findings suggest that the probe really interacts with the bulk-like water structure, which is more likely to exist at higher TOPO content.

Table 1. Equilibrium constant (K_p) values for the interaction between QB and bulk-like water in water/AOT:TOPO/*n*-heptane mixed RMs at different X_{TOPO} values.

X_{TOPO}	K_p [M^{-1}]
0.3	1.77 ± 0.01
0.5	4.58 ± 0.06
0.7	5.70 ± 0.10

2.3. ^{31}P NMR Spectroscopy Studies in RMs Formed with a Single Surfactant (Water/TOPO/*n*-Heptane) and with Mixed Surfactants (Water/AOT:TOPO/*n*-Heptane)

To gain more insight into the changes in the mixed RM composition, the water–surfactant interactions, and the impact on the counterion–surfactant interactions at the interface, we investigated the RMs by using ^{31}P NMR spectroscopy. In particular, this technique has the advantage of providing a single signal for the nonionic surfactant that allows us to monitor only the TOPO behavior in the mixed systems. Figure S3 displays the ^{31}P NMR spectra for TOPO/*n*-heptane RMs (Figure S3A) and water/AOT:TOPO/*n*-heptane mixed RMs (Figure S3B) at $X_{\text{TOPO}}=0.5$ in the absence of water ($W_0=0$). The signal positions of the P=O group of TOPO in homogeneous and micellar media are given in Table 2.

	X_{TOPO}	W_0	δ [ppm]
<i>homogeneous media</i>			
TOPO/ CDCl_3	1	0	47.9
AOT:TOPO/ CDCl_3	0.5	0	47.8
<i>TOPO pure RMs</i>			
TOPO/ <i>n</i> -heptane	1	0	40.9
water/TOPO/ <i>n</i> -heptane	1	0.5	42.9
<i>AOT:TOPO mixed RMs</i>			
AOT:TOPO/ <i>n</i> -heptane	0.5	0	48.5
water/AOT:TOPO/ <i>n</i> -heptane	0.5	0.5	48.7
water/AOT:TOPO/ <i>n</i> -heptane	0.5	2	50.3

The P=O signal of TOPO/*n*-heptane RMs is found at $\delta=40.9$ ppm. It can be seen that the ^{31}P NMR signal of TOPO shows a large downfield shift from $\delta=40.9$ to 48.5 ppm with the incorporation of AOT (see Table 2). This behavior can be explained by the large affinity of TOPO for Na^+ counterions at the interface once the RM is formed.^[26] The oxygen in the P=O group can donate free electron pairs and so complex the cation, which causes a pronounced decrease in electron density in the valence orbitals of phosphorus. The situation is very different when the surfactants are dissolved in polar solvents, such as chloroform (see Figure S4), in which only they form a solution without surfactant organization. Accordingly, the change in δ is negligible (see Table 2).

Figure S5 shows the ^{31}P NMR spectra for TOPO RMs at $W_0=0$ (Figure S5A) and 0.5 (Figure S5B). When water is encapsulated in TOPO RMs, the P=O signal appears at $\delta=42.9$ ppm, which is 2 ppm downfield compared with the value observed in the absence of water (see Table 2). This corroborates the interaction between water and the TOPO polar head in the confined environment.

Conversely, Figure S6 shows the ^{31}P NMR spectra upon increasing the W_0 for the mixed RMs at $X_{\text{TOPO}}=0.5$. It can be seen that there is a slight downfield shift in the P=O signal. At $W_0=0.5$, the P=O signal at $\delta=48.7$ ppm moves only 0.2 ppm downfield compared with the value of the chemical shift at

$W_0=0$ ($\delta=48.5$ ppm). It is important to note that when water is incorporated in small quantities into mixed RMs, the difference in the chemical shift is 10 times less than observed in the system made up exclusively of TOPO surfactant ($\Delta\delta=2$ ppm, see Table 2). Thus, as proposed, at low W_0 values, water has a weak interaction with the mixed interface; thus the phosphorous signal remains unchanged.

In contrast, and according to the solvatochromic behavior of QB and our previous studies,^[26] when the water content was increased progressively in the mixed RMs ($W_0=2$), the interface became richer in AOT molecules and interacted more strongly with AOT than TOPO, which left the free electron pairs of the polar head of TOPO available to complex the counterions. Therefore, a further downfield shift to $\delta=50.3$ ppm was observed.

3. Conclusions

The microenvironment of water/TOPO/*n*-heptane RMs and water/AOT:TOPO/*n*-heptane mixed RMs was investigated by using the solvatochromic behavior of QB as an absorption probe and ^{31}P NMR spectroscopy. For single-surfactant RMs, both the interfacial micropolarity and hydrogen-bond-donor ability of water in TOPO RMs are always smaller than in AOT RMs, which indicates a weak interaction between water and the interface in the former.

We also demonstrate that the molecular probe is a useful tool to investigate how addition of TOPO affects the micelle interface properties of AOT media by using a relatively mundane experiment that makes it possible to understand the complex environments present in mixed RMs. In general, when the water content is small ($W_0\leq 1$), an increase in X_{TOPO} causes a progressive decrease in both the mixed interfacial micropolarity and the hydrogen-bond-donor capability of water. This phenomenon, together with the ^{31}P NMR spectroscopy results and FT-IR and DLS techniques previously published,^[26] suggest that the mixed interface is mostly composed by nonionic surfactant molecules, which results in two complementary effects: 1) a progressive weakness of the water–surfactant interaction and 2) the formation and existence of bulk-like water even at low W_0 values, in contrast to the results for AOT RMs.^[7,32–34] The isosbestic point found in the absorption spectra is consistent with this fact.

However, when the water content is higher than a W_0 of around 1, the interfacial micropolarity and the hydrogen-bond-donor ability is the same as the AOT RMs. This behavior is related to the gradual change in the interfacial composition of mixed RMs, for which it was assumed that when the water content was increased, the interface is formed from a higher percentage of AOT molecules. Thus, the molecular probe always detects the same micropolarity and hydrogen-bond-donor ability of water regardless of the TOPO content.

We demonstrate that a simple change in the TOPO content in the RM composition promotes remarkable changes at the RM interface, which makes it possible to have specific control of the micropolarity and the sequestered water structure in the mixed system. This could have an impact on using this

media as a nanoreactor for nanoparticle synthesis. Preliminary results in our lab show that the shape, concentration, and morphology of gold nanoparticles depend on the TOPO content, which is in agreement with the amount of bulk-like water structure present in the mixed RMs. We are currently investigating this avenue and we want to encourage the scientific community to explore and take advantage of the unique properties of these mixed media.

Experimental Section

Materials

Sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT) from Sigma (> 99% purity) and tri-*n*-octyl phosphine oxide (TOPO) from Sigma (> 99% purity) were used as received. Both surfactants were dried under vacuum prior use. The D₂O, CDCl₃, and *n*-heptane from Sigma (HPLC quality), were used without prior purification. 1-Methyl-8-oxyquinolinium betaine (QB) was synthesized by following a previously reported procedure.^[40] The UV/Vis spectra of QB in the presence of AOT:TOPO mixed RMs showed that the surfactants are free from acidic impurities, which would have greatly reduced the B₁ band intensity at $\lambda = 502$ nm.^[29,30] Ultrapure water was obtained from Labonco equipment model 90901-01.

Methods

AOT and TOPO (0.25 M) were dissolved in *n*-heptane or CDCl₃ to prepare two stock solutions and then mixed in the desired proportions. For RMs formed with single surfactants, the surfactant concentration employed was 0.2 M. For all experiments with the mixed systems, the mole fraction of TOPO, $X_{\text{TOPO}} = [\text{TOPO}] / ([\text{AOT}] + [\text{TOPO}])$, was varied from 0 to 0.7. In this case, the total surfactant concentration ($[\text{Surfactant}]_{\text{T}} = [\text{AOT}] + [\text{TOPO}]$) was kept constant at 0.2 M.

To introduce the molecular probe, a 0.01 M solution of QB was prepared in methanol (Sintorgan HPLC quality). An appropriate amount of this solution to obtain a given concentration (3×10^{-4} M) of the probe in the micellar medium was transferred into a volumetric flask, and the methanol was evaporated by bubbling dry N₂; then, the AOT:TOPO/*n*-heptane solution was added to the residue and agitated in a sonication bath until the system was optically clear.

The addition of water was performed by using a calibrated microsyringe. The molar ratio between water and the surfactants is defined as $W_0 = [\text{H}_2\text{O}] / ([\text{AOT}] + [\text{TOPO}])$. The W_0 value was varied between 0–2 in both the AOT/*n*-heptane system and the mixed systems. In the TOPO/*n*-heptane system, W_0 was varied between 0–0.8. For TOPO RMs and mixed RMs with high TOPO content ($X_{\text{TOPO}} > 0.7$), values of $W_0 \geq 2$ could not be reached due to turbidity problems.^[26] The lowest value for W_0 ($W_0 = 0$) corresponds to a system without addition of water.

General

UV/Vis spectra were recorded by using a Shimadzu 2401 spectrophotometer equipped with a thermostatted sample holder. The path length used in absorption experiments was 1 cm. All experimental points were measured three times with different prepared samples. The pooled standard deviation was less than 5%. The ³¹P NMR spectra were recorded at 121 MHz by using a Bruker 400

NMR spectrometer. Basic ³¹P NMR spectra were measured by using a single-pulse sequence with WALTZ decoupling during acquisition; usually 128 or 256 scans were collected. The spectrometer probe temperature was periodically monitored by measuring the chemical shift difference between the two singlets of a methanol reference sample.^[41] The probe thermal stability was assured by the observation that successive measurements of the sample chemical shift (after 10 min in the probe for thermal equilibration) were within digital resolution limit. For the study on RMs, a capillary coaxial tube that contained D₂O was introduced in the NMR tube and was used as a frequency "lock". Chemical shift values, δ [ppm], were referenced to 85% H₃PO₄ (0 ppm) as the internal standard. The NMR spectroscopy data were processed by using MesstReC 4.8.6 for Windows and plotted and fitted by using OriginPro 8 SR0 v8.0724 software. All the experiments were carried out at $(25.0 \pm 0.5)^\circ\text{C}$.

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