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Inhibited Phenol Ionization in Reverse Micelles: Confinement Effect at the Nanometer Scale

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We found that the absorption spectra of 2-acetylphenol (2-HAP), 4-acetylphenol (4-HAP), and *p*-nitrophenol (*p*-NPh) in water/sodium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT)/*n*-heptane reverse micelles (RMs) at various W_0 ($W_0 = [H_2O]/[surfactant]$) values studied changed with time if $^-$OH ions were present in the RM water pool. There is an evolution of ionized phenol (phenolate) bands to nonionized phenol absorption bands with time and this process is faster at low W_0 values and with phenols with higher bulk water pK_a values. That is, in bulk water and at the hydroxide anion concentration used, only phenolate species are observed, whereas in AOT RMs at this fixed hydroxide anion concentration, ionized phenols convert into nonionized phenol species over time. Furthermore, we demonstrate that, independent of the $^-$OH concentration used to prepare the AOT RMs, the nonionized phenols are the more stable species in the RM media. We explain our results by considering that strong hydrogen-bonding interactions between phenols and the AOT polar head groups result in the existence of only nonionized phenols at the AOT RM interface. The situation is quite different when the phenols are dissolved in cationic benzyl-*n*-hexadecyldimethylammonium chloride RMs. Therein, only phenolates species are present at the $^-$OH concentrations used. The results clearly demonstrate that the classical definition of pH does not apply in a confined environment, such as in the interior of RMs and challenge the general idea that pH can be determined inside RMs.

1. Introduction

Reverse micelles (RMs) and water-in-oil (W/O) microemulsions have attracted considerable attention due to their ability to host hydrophilic components in organic solvents[1,2] and broad applications in chemical reactions (e.g., nanoparticle preparation, organic synthesis, and bioorganic synthesis), separation science, material science, and in the pharmaceutical industry, among others.[1,2] Anionic, cationic, and nonionic surfactants have been employed to prepare RMs and W/O microemulsions in nonpolar solvents.[1–29] Among the anionic surfactants that form RMs, the best known are systems derived from sodium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT) in different nonpolar media. AOT has a well-known V-shaped molecular geometry, giving rise to stable RMs without the need for cosurfactants. In addition, AOT RMs have the remarkable ability to solubilize a large amount of water with W_0 ($W_0 = [H_2O]/[surfactant]$) values as large as 40 to 60, depending on the surrounding nonpolar medium, the solute, and the temperature. The cationic surfactant benzyl-*n*-hexadecyldimethylammonium chloride (BHDC) also forms spherical RMs in benzene without the addition of a cosurfactant and water can be solubilized up to $W_0 \approx 25$.[15–20,22–25] BHDC RMs seem to have properties that are characteristic of other RM systems. This occurs as a result of the nature of the water pool, which shows properties similar to that of bulk water only when the amount of water is higher than that the necessary to achieve surfactant polar head group and counterion solvation, in the BHDC RMs.[15,19,25]

Small solute particles can be located in three different compartments in RMs: 1) in the external organic solvent, 2) in the micellar interface formed by a surfactant monolayer, and 3) in the internal water pool. Subsequently, these systems contain aqueous microdroplets entrapped in a film of surfactant and dispersed in a low-polarity bulk solvent.[1,2,7,21]

Despite their simplicity, they provide an excellent method to study fundamental effects of confinement. The nature of pH and ionic concentration in the aqueous core of the micelle assumes particular significance for chemical reactions, such as acid-catalyzed reactions,[30,31] electron-transfer reactions,[22,32,33] and biochemical reactions.[34–36] Thus, studies probing the nature of the water pool in RMs attract the attention of both chemists and life scientists. Previous studies performed by some of us[37] have shown very peculiar and interesting water properties inside RMs that exist only because of the confinement effect and the interaction with the surfactant at the interface: 1) in AOT RMs, a proton gradient toward the interface exists inside the RMs, which leaves the interior neutral[37] and 2) the water properties are different for water molecules sequestered inside anionic and cationic RM systems. This is evi-

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denced by water molecules entrapped inside the AOT RM systems having enhanced electron donor ability in comparison with the water bulk structure. On the other hand, the water entrapped inside the BHDC RM media does not appear to be electron donating due to its interaction with the cationic surfactant polar head group. In particular, the water at the cationic RMs interfaces seems to have enhanced hydrogen-bond-donor capability.[27,28,38]

Phenols have been used as molecular probes to determine binding constants at the AOT RMs interface[39,40] or to measure pK_a values upon confinement.[41–43] The behavior of different phenols in RMs were investigated by Magid et al.[40] They calculated the binding constants for a series of phenols to AOT RMs and found that the binding process depended mainly on the hydrogen-bonding ability of the phenols to form hydrogen bonds with the AOT polar head groups. Also, we have previously shown that hydrogen-bonding interactions are a powerful driving force for different solutes to reside at the AOT RM interface.[44–47] In studies performed by Magid et al.,[40] pure water was used to prepare the RMs, thus there was no doubt that phenols were in their acidic form, as confirmed from their absorption spectra.[40,41] Interestingly, Menger and Saito have shown that, at pH 8.5, judging from the lack of the band of the ionized species, no *p*-nitrophenolate was present in the pool of AOT RMs[41] despite the fact that the pK_a of *p*-nitrophenol (*p*-NPh) in water is 7.14.[42] Moreover, they have shown that the *p*-nitrophenolate ion is not produced until the pH (adjusted with NaOH) exceeds a value of 11.5. This was attributed to adsorption at the AOT RM interface, where phenolic hydroxyls were held in close proximity to the anionic surfactant groups through hydrogen-bonding interaction. An unfavorable desorption equilibrium precedes ionization. Menger and Saito concluded that there were two *p*-NPh species inside AOT RMs: one at the interface with a very high pK_a value relative to the species in bulk water and the other at the water pool of the RMs, with a lower pK_a value that was closer to that in bulk water.[41]

Although there are reports on the effect of pH on the spectroscopic behavior of *p*-NPh inside AOT RMs,[41,42] to the best of our knowledge, there have not been any attempts to investigate the phenol structure and/or the absorption changes with time in solutions of phenols in RMs. We believe that such a study would allow very interesting reversed micellar properties to be deduced.

Herein, we used different phenols to obtain information on the unique properties of the RM water pool. We found that the absorption spectra of different phenols, 2-acetylphenol (2-HAP), 4-acetylphenol (4-HAP) and *p*-NPh (see Figure 1), in AOT RMs at any W_0 value investigated changed with time if $^-$OH ions were present in the RM water pool. There is an evolution of the ionized phenol (phenolate ions) absorption band to the nonionized phenol absorption band with time, and this process is favored at low W_0 values and for phenols with high pK_a values. That is, in bulk water and at the hydroxide anion concentration used, only phenolate species were observed, whereas in AOT RMs at this fixed hydroxide anion concentration, ionized phenols converted into nonionized phenol species over time. Furthermore, we demonstrate that, independent of the $^-$OH concentration used to prepare the AOT RMs, the nonionized phenols are the more stable species in micelles. We explain our results by considering that strong hydrogen-bonding interactions between phenols and the AOT polar head group mean that nonionized phenols exist exclusively at the AOT RM interface. The situation is quite different when different phenols are dissolved in cationic BHDC RMs, where no hydrogen-bonding interactions are possible and only phenolate species are present at the $^-$OH concentration used.

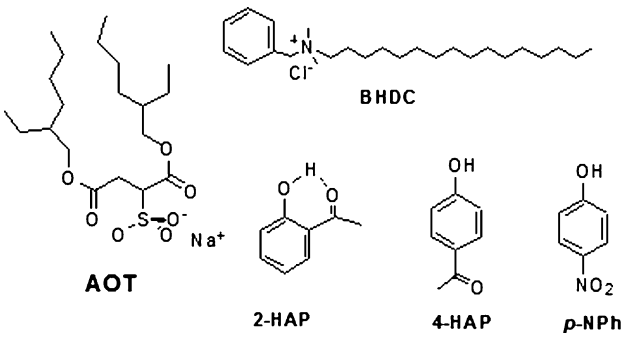


Figure 1. Structures of the molecular probes and surfactants used herein.

2. Results and Discussion

The spectroscopic behavior of different phenols, 2-HAP, 4-HAP, and *p*-NPh, in water/AOT/*n*-heptane and water/BHDC/benzene RMs at different W_0 values was investigated. In our experiments, we used pure water or a solution of 0.1 M NaOH to prepare the RMs.

The results depended on the type of surfactant and the W_0 value used to prepare the RMs. Figure 2 shows the absorption spectra of 2-HAP, 4-HAP, and *p*-NPh as a function of time at [AOT] = 0.3 M and $W_0 = 3$ ([NaOH] = 0.1 M]). Oldfield et al. observed a slow decrease in absorbance with time for *p*-NPh in AOT RMs at $W_0 < 20$ and $[^-OH] \approx 10^{-2}$ M.[43] They attributed these results to the $^-$OH-catalyzed hydrolysis of AOT, which in turn provoked a progressive decrease in the pH of the system. This explanation is not applicable under our experimental conditions (see below).

From Figure 2 we can see that, as the time increases, the bands with maxima at 375 (2-HAP), 321 (4-HAP), and 390 nm (*p*-NPh) decrease. Moreover, a band develops at $\lambda_{max} = 272$ and 306 nm for 4-HAP and *p*-NPh, respectively, while there is an increase of the band at $\lambda_{max} = 325$ nm of 2-HAP with a clear isosbestic point in each case. That is, with time there is a conversion of one species into another.

Figure 3 shows a typical absorption spectra for 2-HAP as a function of time in the same RMs, but at $W_0 = 16$. The results show that the changes observed at low W_0 occur more slowly at higher water contents. From studies performed in aqueous solution at different pH values (data not shown) for all the molecular probes investigated, the band at higher energy matches that of nonionized species, whereas the other bands at lower energy match those corresponding to the phenolate

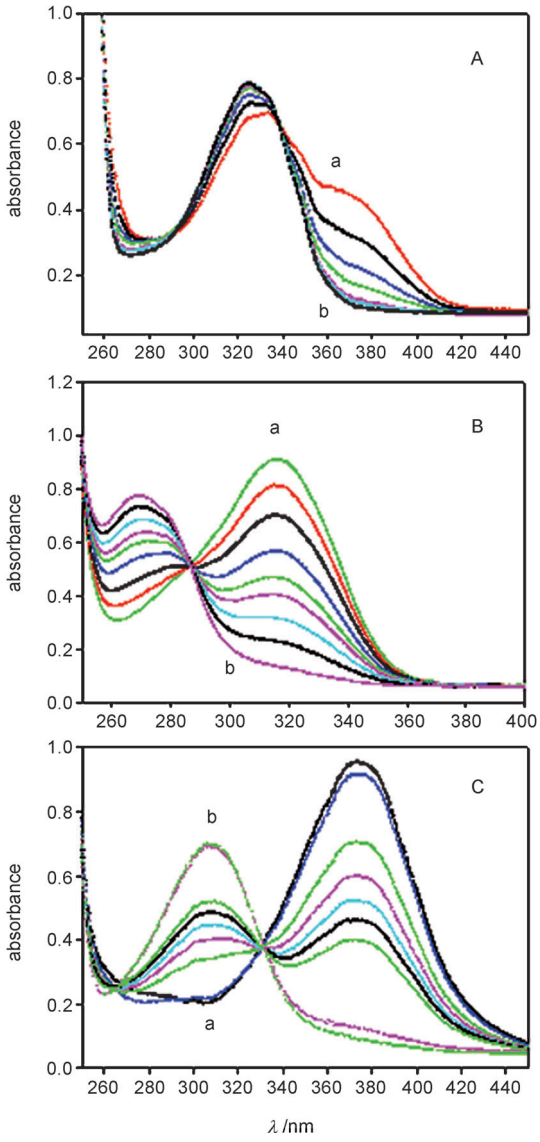


Figure 2. Changes in the absorbance spectra with time in water/NaOH/AOT/*n*-heptane RMs: [AOT] = 0.3 M, [NaOH] = 0.1 M, $T = 25\,^{\circ}C$. A) 2-HAP (1×10^{-4} M), $W_0 = 3$, $t = 0$ (a), 2, 5, 7, 11, 14 and 18 min (b). B) 4-HAP (4×10^{-5} M), $W_0 = 3$, $t = 0$ min (a), 7 min, 10 min, 15 min, 19 min, 23 min, 32 min, 56 min, and 6 h (b). C) *p*-NPh (6×10^{-5} M), $W_0 = 2.9$, $t = 0$ (a), 13 min, 37 min, 62 min, 94 min, 130 min, 185 min, 48 h, and 72 h (b).

ions. Thus, the results in Figures 2 and 3 are the same as the effect observed when lowering the pH in the aqueous solutions of the different phenols. Surprisingly, in the AOT RMs the interconversion between species takes place over time at a fixed $^{-}$OH concentration. Note that if we load the RMs with water without $^{-}$OH there are no changes in the spectra over time and only the band that corresponds to the nonionized phenols is present at any W_0 value.

From Figure 2 it can be observed that at $t = 0$ for 4-HAP and *p*-NPh, the spectra correspond to the phenolate species residing in the water pool probably due to electrostatic repulsion with the anionic interface. However, in the case, of 2-HAP the bands for both ionized (in the water pool) and nonionized species are initially observed. It seems that the intramolecular hydrogen bond in 2-HAP (see Figure 1) plays an important role in the ionization of this molecule within the RMs. It is likely that the nonionized phenol species is located more on the oil side of the AOT RM. Similar results were found for other molecular probes in which the intramolecular hydrogen bond prevents ionization of the probes inside RMs.[48,49]

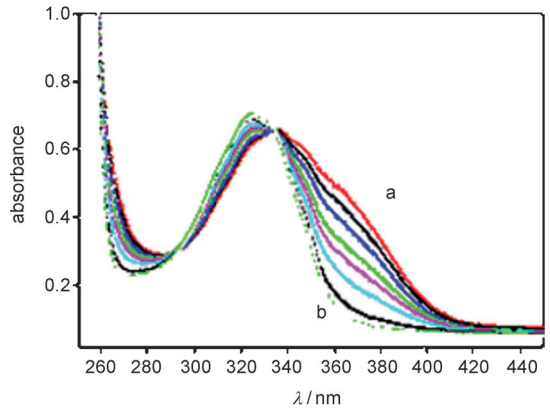


Figure 3. Changes in the 2-HAP (1×10^{-4} M) absorbance spectra with time in water/NaOH/AOT/*n*-heptane RMs: [AOT] = 0.3 M; [NaOH] = 0.1 M; $T = 25\,^{\circ}C$; $W_0 = 16$; $t = 0$ (a), 21, 29, 45, 58, 78, 128, and 212 min (b).

The change in absorption with time for solutions of all phenols can be fitted with a typical exponential equation for pseudo-first-order kinetics [Eq. (1)]:[50]

$$(A_t - A_\infty) = (A_o - A_\infty)\exp(-k_{obs}t) \quad (1)$$

The k_{obs} values obtained are shown in Table 1. Figure 4 depicts a representative plot of k_{obs} as a function of W_0 values for 2-HAP. The same experiments were conducted at [AOT] = 0.1 M (data not shown) and the same values of k_{obs} at each W_0 were found, so the rate of interconversion of the species inside AOT RMs is independent of the AOT concentration; this demonstrates that there is no partition between the organic and micellar interface.[2,19]

An interesting result can be extracted from Figure 4: k_{obs} values diminish significantly when the water content increases. The same trends are observed for the other phenols and the results are summarized in Table 1. Figure 5 shows the dependence of k_{obs} values at $W_0 = 3$ with the pK_a values (Table 1) of

Table 1. Observed rate constants for the processes occurring in AOT RMs.[a]

Substrate (pK_a)	W_0	k_{obs} [10^{-2} min^{-1}]
p-NPh (7.14)[b]	3	1.00 ± 0.04
	16	0.053 ± 0.008
4-HAP (7.87)[c]	3	3.0 ± 0.1
	16	0.080 ± 0.008
2-HAP (10.07)[c]	3	21.7 ± 0.6
	16	1.7 ± 0.2

[a] Water/NaOH/AOT/*n*-heptane RMs, [AOT] = 0.3 M, [NaOH] = 0.1 M. [b] Value taken from reference [42]. [c] Values taken from reference [61].

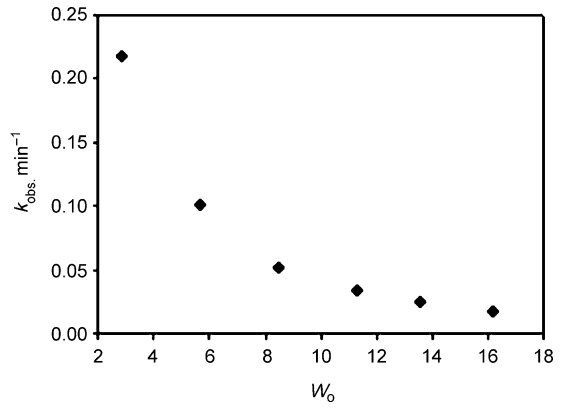


Figure 4. Dependence of k_{obs} on the content of water in AOT/*n*-heptane/NaOH RMs for 2-HAP. [AOT] = 0.3 M, [NaOH] = 0.1 M, $T = 25\,^{\circ}C$, [2-HAP] = 10^{-4} M.

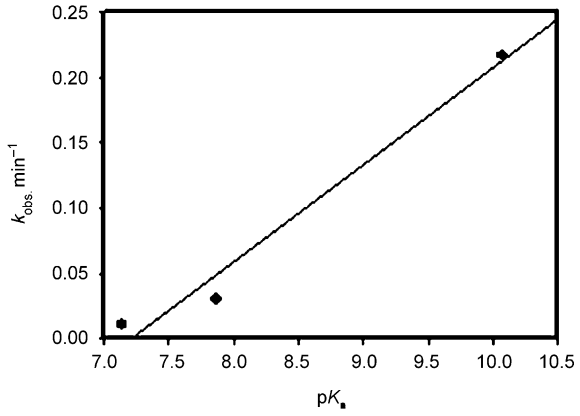


Figure 5. Dependence of k_{obs} on bulk water pK_a values of *p*-NPh, 2-HAP, and 4-HAP in water/NaOH/AOT/*n*-heptane RMs. [AOT] = 0.3 M, [NaOH] = 0.1 M, $W_0 = 3$. The straight line is for visual purposes only.

the different phenols in bulk water. The process is faster at low W_0 values and with phenols with higher pK_a values.

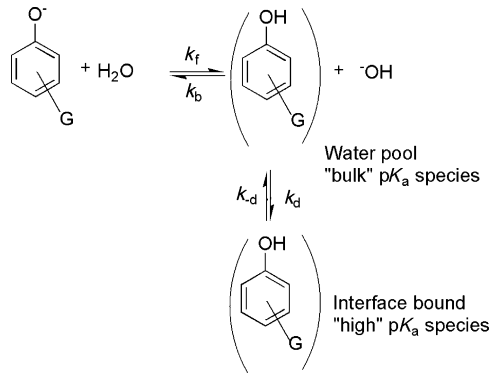
To explain what happens with the different molecular probes inside the AOT RMs, it is worth mentioning here the work performed by Menger and Saito.[41] They demonstrated that *p*-NPh experiences an increase of 4.5 pK_a units when is solubilized inside AOT RMs due to interaction with surfactant polar head groups. They explained their results by considering that there were two different phenol species inside the RM media: 1) phenol in the water pool with a pK_a closer to that in bulk water and 2) phenol at the interface, bound phenol species, that had a higher pK_a value because unfavorable desorption equilibria preceded ionization.[41] Also, they saw that the amount of species with low pK_a values increased when imidazole was added to the water pool of the RMs because it competed with *p*-NPh at the interface for the AOT polar head group, and therefore, the amount of *p*-NPh in the water pool (low pK_a value) increased. In other words, a surprising series of absorbance–pH profiles was observed when imidazole was added. They concluded that there were two *p*-NPh species, the relative abundance of which depended on imidazole concentration. When there was no imidazole present, *p*-NPh existed solely in the nonionized form. It must be taken into account that they did not observe changes in the absorption spectra in the AOT RMs at $W_0 = 25$ within 3 h. Herein, we show that the two *p*-NPh species can experience an interconvertion process without the addition of any other molecules and at a fixed $^{-}$OH concentration, but this process is slow and can only be observed after 4 h at $W_0 = 25$.[51]

What is the nature of the phenomenon that is experienced by the phenols inside AOT RMs? When no $^{-}$OH is present, the phenols exist solely in the form of nonionized species. As we have previously demonstrated,[44–47] the AOT SO_3^- head is a very good hydrogen-bond acceptor, thus the different phenols should be located at the AOT RM interface and interact through hydrogen bonding with the surfactant. This interaction prevails over that of water molecules for the AOT polar head group at any water content. This is not surprising because phenols are better hydrogen-bond donors than water as measured by α, which is the hydrogen-bond-donor ability parameter.[52] In this way, nonionized phenols are bound at the interface to the AOT polar head group through hydrogen-bonding interactions for any W_0 value.

On the other hand, the situation is quite different when $^{-}$OH is present and phenolate ions appear. The spectral changes shown in Figures 2 and 3 are consistent with very complex processes that phenols may undergo inside the RMs. It could be the result of a combination of acid–base equilibria at the interface, acid–base equilibria at the water pool, and distribution equilibria between the nonionized phenol species at the water pool and at the interface. Furthermore, the above events also depend on the water content. When the $W_0 = 3$, the amount of water is not enough to form a water pool with free water molecules,[1,2,19] so acid–base equilibria at the water pool can be discarded. Thus, the process occurs near the negative interface of the AOT RMs. It is known that, according to the Gouy–Chapman theory of the diffuse double layer, the proton concentration at the negative interface is higher than the bulk concentration, and consequently, an acid–base equilibrium located at the interface is sensitive to the interfacial potential.[53,54] Thus, phenolate ion protonation is favored in this situation. Also, the production of nonionized phenols species (neutral) has to be favored because electrostatic repulsion between phenols and the interface diminishes. On the contrary, the high ionic strength at the interface and the small amount of water make the proton-transfer process extremely slow in comparison with bulk water.[55]

On the other hand, when W_0 is larger than 8–10 and the amount of water is enough to create the water pool with relatively free water molecules,[1,2,19] the processes can be described as those shown in Scheme 1. It should be noted that in this situation and because of the electrostatic repulsion between the phenolates species and the negative AOT RM interface, it is likely that the acid–base equilibrium takes place only at the water pool of the RMs.

Thus, at $W_0 = 16$, when the phenolate ions are present in the water pool, they experience acid–base equilibria that yield the nonionized phenol. These species may migrate to the AOT in-



Scheme 1. Different possible equilibria for phenols occurring in the AOT RMs.

terface due to hydrogen-bonding interactions with the AOT polar head groups, as explained above, giving bound, nonionized phenol species at the RM interface with "higher" pK_a values, as suggested by Menger and Saito.[41]

Based on previous ideas and to explain the kinetic results, we analyzed the simplified reaction shown in Scheme 1. For these two-step reactions, the possibility that either k_d or k_f are rate determining may be considered. If k_d is rate determining then the relationship $k_d < k_b[^-OH]$ should hold. Since the proton-transfer equilibrium is thermodynamically favorable for the reaction of nonionized phenols with ^-OH in the water pool, k_b should be diffusion controlled and the value can be estimated to be around 10^8–$10^9\ M^{-1}s^{-1}$.[56] The concentration of ^-OH in the bulk solution is 0.1 M; therefore, the value of $k_b[^-OH]$ should be in the order of 10^7–$10^8\ s^{-1}$. It has been calculated that 7-hydroxiquinoline in AOT RM at $W_0 = 4$ can diffuse 0.6 nm (the radius of a water pool at $W_0 = 4$) in 7 ns.[57] By assuming a similar diffusion rate for the phenols studied herein in the water pool of the RMs, the relationship $k_d > k_b[^-OH]$ holds and the proton-transfer rate constant is rate determining. The observed pseudo-first-order rate constant for the proton-transfer process is several orders of magnitude lower than the value expected for the same reaction in bulk water. This result probably indicates the higher energy for the process due to the confinement of the water molecules, which are mainly involved in the solvation of the ions present in the interface and water pool.

The reactions shown in Scheme 1 explain two intriguing facts: 1) the whole process is favored for phenols with high pK_a values in bulk water because the acid–base equilibrium shifts to nonionized phenol species for those phenols with a stronger conjugated base and 2) the whole process is favored at low W_0 values because the acid–base reaction happens at the interface, since no water pool is present.[2]

We have considered other possible explanations for the behavior of phenols in RMs derived from the fact that AOT is a diester (Figure 1) that can be hydrolyzed in basic media, as proposed previously.[43,58] Certainly, basic hydrolysis of the surfactant could be a competitive process that would affect the ionization of phenols in AOT RMs because this process consumes ^-OH and $[^-OH]$ would decrease over time. Thus, any equilibrium where ^-OH is present should be modified.[58] We are able to assert that, under our experimental conditions, ^-OH consumption due to AOT hydrolysis is not a process that has to be taken into account based on the following evidence: 1) Phenolate ion conversion to the nonionized phenol species is a process that does not depend on AOT concentration nor depend on ^-OH concentration in the range 0.01 to 0.4 M (data not shown). The effect is negligible in comparison to "strong" hydrogen-bonding interactions between the phenols and the AOT polar head groups. 2) Under the experimental conditions used in our work, [AOT] = 0.3 M and $[^-OH] = 0.1$ M, if the hydrolysis reaction takes place, then more than 80% of the surfactant should be hydrolyzed with consequent RMs structure destruction.[59] Dynamic light scattering experiments confirmed the spherical shape of the AOT nanodroplets, which were the same sizes with and without ^-OH ions in the water pool. 3) To reinforce the concept that ^-OH consumption due to AOT hydrolysis did not take place in our systems, we performed the following experiment: a 0.3 M AOT RM solution in *n*-heptane at $W_0 = 16$ with $[^-OH] = 0.1$ M was prepared and left to stand for 24 h. Subsequently, 4-HAP was added and the UV-visible spectra were recorded. The results were the same as those obtained with fresh AOT solution. That is, at $t = 0$ the only species present was the phenolate ion, which converted to the nonionized phenol species over time. 4) It has been recently demonstrated that there is a proton gradient toward the interface within the AOT RMs that leaves the interior neutral.[37] Accordingly, at the AOT RM interface where nonionized phenols species interact with AOT, there are no ^-OH ions present because the ions are in the water pool due to the fact that they have the same negative charge. 5) The k_{obs} values shown in Table 1 are dependent on the structures of the different phenol used. If hydrolysis of AOT explained our results then the k_{obs} values would only be dependent on AOT and ^-OH concentrations.

To obtain further support for our reasoning, we performed the same experiments in other RMs: the cationic water/BHDC/benzene RMs. We specifically chose this RM because the interface was not able to accept hydrogen bonds, unlike AOT RMs, and according to the Gouy–Chapman theory the ^-OH concentration at the interface was expected to be higher than that in the water pool.[53] Figure 6 shows typical absorption spectra for 2-HAP in BHDC RMs as a function of time at $W_0 = 3$ and $[^-OH] = 0.1$ M. As observed, only the band that corresponds to the phenolate ion ($\lambda_{max} = 369$ nm) remains even after 24 h. It is important to note that if pure water is added to the BHDC RMs, only the nonionized phenol bands are observed.

The same results were observed for 4-HAP and *p*-NPh (data not shown). Therefore, the equilibria shown in Scheme 1 are not present in the BHDC RMs because there is no possibility for hydrogen bonding between the nonionized phenols species and surfactant polar head groups; in addition, the positive RM interface can stabilize the negative ionized phenol species. Also, very recently we found that 2-naphthol converted into 2-naphtholate in BHDC RMs, but not in AOT RMs.[28] We explained this fact by considering differences in the interfacial water properties. Water molecules trapped inside the AOT RMs had enhanced electron-donor abilities than those of bulk

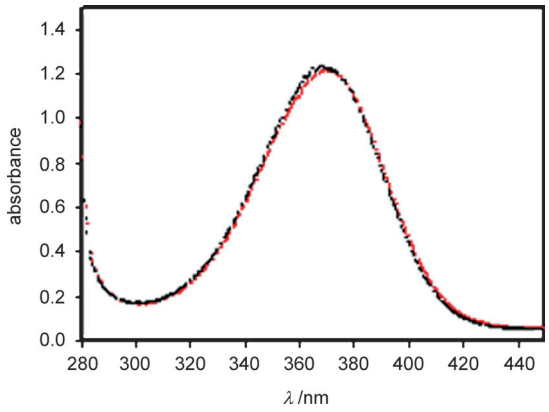


Figure 6. Changes in the absorbance spectra of 2-HAP with time in water/NaOH/BHDC/benzene RMs. [BHDC] = 0.18 M, [NaOH] = 0.1 M, $W_0 = 3$, $T = 35\,^{\circ}C$, [2-HAP] = 10^{-4} M, $t = 0$ min (a) and 24 h (b), $\lambda_{max} = 369$ nm.

water.[38] Thus, water at the AOT RM interface is not suitable for solvating anions.

3. Conclusions

We have investigated the behavior of different phenols, 2-HAP, 4-HAP, and *p*-NPh, in water/AOT/*n*-heptane and water/BHDC/benzene RMs under basic and neutral conditions as a function of time. Our results showed that, in AOT RMs, the stable phenol species was nonionized at any ^{-}OH concentration studied and the opposite was valid for the BHDC RMs investigated.

Therefore, we clearly demonstrated that hydrogen-bonding interactions between nonionized phenols and AOT polar head groups, as well as unique interfacial water properties, were a powerful driving force that made nonionized phenols the most stable species trapped in AOT RMs at any ^{-}OH concentration.

The results also corroborated that the classical definition of pH did not apply inside RMs. As the number of water molecules decreased, the classical concept of pH no longer had a meaning inside RMs because there were no more than a few thousand water molecules in a nanosized water pool interacting strongly with the surfactant polar head groups and counterions. Several approaches to this problem have been described in the literature; however, all methods involve indirect measurements on probe molecules. Our results clearly challenge the general idea that pH can be determined inside RMs and demonstrate that the concept of pH cannot be used straightforwardly in a confined environment, such as the interior of RMs. Difficulties with defining pH inside RMs have been considered by other authors.[37,60]

We feel that these results could have a tremendous impact on chemical reactions occurring in RMs, such as acid–base and/or enzyme-catalyzed reactions.

Experimental Section

Materials and Methods

AOT (Sigma > 99% purity) was used as received. BHDC from Sigma (> 99% purity) was recrystallized twice from ethyl acetate.[19] Both surfactants were kept under vacuum over P_2O_5 to minimize water absorption. The absence of acidic impurities was confirmed through the 1-methyl-8-oxyquinolinium betaine absorption bands.[20]

n-Heptane (Riedel de Haën, HPLC quality); benzene (Carlo Erba, HPLC quality); and molecular probes 2-HAP (Aldrich, > 99%), 4-HAP (Aldrich, > 99% purity), and *p*-NPh (Mallinckrodt, > 98%) were used as received. Ultrapure water was obtained from Millipore equipment.

Stock solutions of AOT/*n*-heptane and BHDC/benzene RMs were prepared by mass and volumetric dilution. To obtain optically clear solutions, they were shaken in a sonicating bath.

To introduce the probe, an appropriate amount of probe stock solution in methanol (Sintorgan HPLC grade) was transferred into a volumetric flask by using a calibrated microsyringe. The solvent was evaporated by bubbling dry N_2, and stock solutions of AOT in *n*-heptane and BHDC in benzene were added to the residue. The appropriate amount of stock surfactant solution was transferred into a cuvette and water was added by using a calibrated microsyringe. Molecular probe concentrations were around 5×10^{-5} M. The amount of water present in the system was expressed as the molar ratio between water and the surfactant ($W_0 = [H_2O]/[surfactant]$). W_0 was varied between 0 and 16 for AOT/*n*-heptane and BHDC/benzene RMs. It was not possible to obtain higher values of W_0 due to turbidity problems. The lowest value of W_0 ($W_0 = 0$) corresponded to a system with no added water and its presence corresponded to the intrinsic humidity of the system ($W_0 \approx 0.3$), as previously determined by using 1-methyl-8-oxyquinolinium betaine as a molecular probe.[20]

The absorption spectra were measured by using Shimadzu 2101 PC spectrometers at $(25.0 \pm 0.1)\,^{\circ}C$. The path length used in all spectroscopic experiments was 1 cm.

Kinetic Measurements

RMs with appropriate concentration of AOT, NaOH, and water were prepared and obtained as clear solutions. 2-HAP was dissolved in *n*-heptane, whereas for the other phenols a solution with the desired amount of phenol in methanol was placed in a flask and the solvent was evaporated and the phenol was redissolved in the RM solution. In some cases, it took some time to get clear solutions and it was observed that the time required to get clear solutions was longer for RMs with higher W_0 values. Once the solutions became clear, spectra were recorded at different times and from the absorbance reading at the wavelength of the maximum absorption of the phenol or phenolate ion the apparent observed rate constants were determined. In all cases, the changes in absorbance versus time gave an excellent fit to a monoexponential equation.

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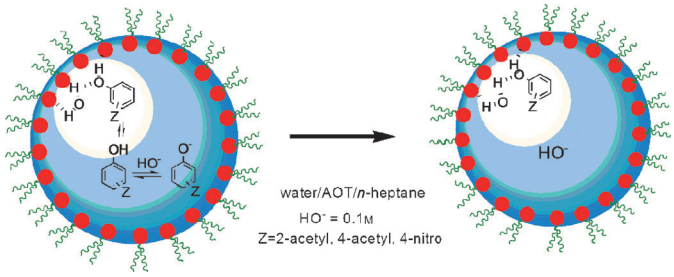
Inhibited Phenol Ionization in Reverse Micelles: Confinement Effect at the Nanometer Scale



Hidden depths: The absorption spectra of several phenols in water/sodium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT)/*n*-heptane reverse micelles (RMs) change with time if $^{-}$OH ions are present in the RM water pool. The results challenge the general idea that pH can be determined inside RMs.

