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To cite this article: Cristian C Villa *et al* 2017 *Methods Appl. Fluoresc.* **5** 044001

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Methods and Applications in Fluorescence



PAPER

Subtleties of catanionic surfactant reverse micelle assemblies revealed by a fluorescent molecular probe

RECEIVED
31 May 2017

ACCEPTED FOR PUBLICATION
23 June 2017

PUBLISHED
10 October 2017

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Keywords: reverse micelles, catanionic surfactant, HC, water entrapped

Supplementary material for this article is available [online](#)

Abstract

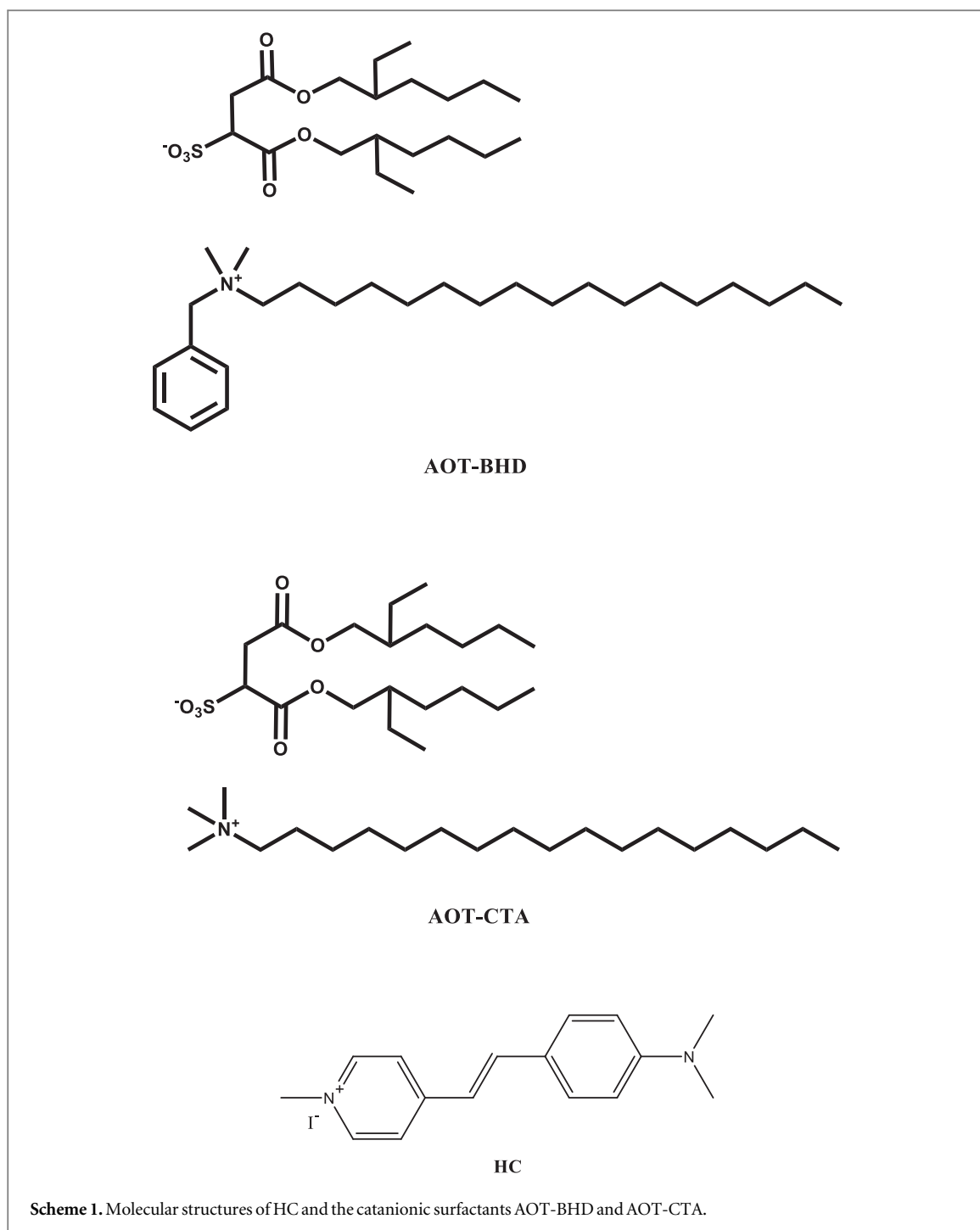
In this work, the absorption and emission behavior of the cationic hemicyanine *trans*-4-[4-(dimethylamino)styryl]-N-methylpyridinium iodide (HC) in reverse micelles (RMs) formed by the catanionic surfactants benzyl-*n*-hexadecyldimethylammonium-1,4-bis-2-ethylhexylsulfosuccinate (AOT-BHD) and cetyltrimethylammonium-1,4-bis-2-ethylhexylsulfosuccinate (AOT-CTA) have been investigated. Our results show that the spectroscopic behavior of HC changes when the dye is dissolved in AOT-BHD or in AOT-CTA RMs. While HC undergoes an intramolecular charge-transfer process upon excitation in AOT-CTA RMs, in AOT-BHD RMs this process is inhibited due to a specific interaction between HC and the polar head group of the BHD⁺ cation. This implies that the chemical structure of CTA⁺ and BHD⁺ cations has a large impact on the excited state from which HC emission occurs. Additionally, the structural difference between the two cations impacts on the water–RM interface interaction, which provides a way of controlling the solvation process in these RMs. Furthermore, differences in the interfacial fluidity between the two catanionic RMs is observed, a result that is particularly interesting with regard to these systems being used as nanoreactors.

1. Introduction

Reverse micelles (RMs) are self-assembly systems where a layer of surfactant molecules confines a water nano-droplet, with hydrophilic head groups pointing inward to the center containing the polar solvent, and the hydrophobic tails extending outward into the organic non-polar continuous phase [1, 2]. These systems are appropriate media for processes that involve hydrophobic and hydrophilic reactants providing ‘nanoreactors’ for a variety of chemical and biological reactions [3–5]. The study of RMs has grown considerably due to their applications in mimetic agent and cell biomembrane modeling, drug delivery, oil recovery, and enzymology [6, 7]. The properties of RMs are affected by several parameters such as non-polar solvent composition, temperature, type of surfactant, and water content, usually defined as $W_0 = [\text{Water}]/[\text{Surfactant}]$ [1, 8–13]. The most commonly used surfactants to form RMs are anionic sodium 1,4-bis (2-ethylhexyl) sulfosuccinate (Na-

AOT) [1, 2] and cationic benzyl-*n*-hexadecyldimethylammonium chloride (BHDC) [13–16] or hexadecyltrimethylammonium bromide (CTAB) [17–19]. Na-AOT and BHDC form RMs without the addition of cosurfactants [1, 2, 13–16], however, CTAB needs the presence of an *n*-alcohol to generate RMs [17–19].

In recent years, research into RMs has moved towards the development of new surfactants with a wide array of physicochemical properties [20–22]. These new kinds of surfactants include *catanionic surfactants*, which are the result of mixtures of oppositely charged surfactants. In the literature, it is easy to find two categories of *catanionic surfactants*: one, known as *catanionic mixtures*, are simple mixtures of anionic and cationic surfactants without the removal of their respective counterions. The other category corresponds to catanionic systems where surfactants are mixed and the counterions are removed [23–25]. The usual way to obtain this kind of catanionic surfactant is by combining two ionic surfactants in a 1:1 molar ratio and the inorganic salt formed by their counterions



being totally removed using an appropriate method [26]. Cationic surfactants thus obtained have shown the ability to form different organized systems, such as direct and RMs [25–29], vesicles [25, 29, 30] and liquid crystals [29, 31]. Related to this topic is a very attractive field where ionic liquids [32, 33] (ILs) with amphiphilic properties (IL-like surfactants) are used to form organized systems [34–36]. Thus, imidazolium ILs, including a charged hydrophilic head group and one or more hydrophobic tail, have been used as surfactants [34–36]. Previously we have reported [25, 37, 38] the synthesis of two new cationic IL-like surfactants, AOT-BHD and AOT-CTA (scheme 1), resulting from the mixture of BHDC and CTAB with Na-AOT,

respectively. Interestingly, these ILs have amphiphilic properties in which the cationic components are ammonium salts rather than the imidazolium salts more commonly found for ILs. We demonstrated using dynamic light scattering, that these new surfactants form spherical RMs in different non-polar solvents and can disperse water [37]. Remarkably, the apparent diameter (d_{app}) values of these two cationic RMs at fixed W_0 were quite different. For example, at $W_0 = 1.5$ the d_{app} value for benzene/AOT-BHD RMs was around 10.5 nm and for benzene/AOT-CTA RMs it was around 4.9 nm. These differences in droplet size suggest a different water–surfactant interaction in the cationic systems. A weak

interaction with the catanionic interface in benzene/AOT-CTA/water RMs causes modification of the effective packing parameter of the surfactant p , defined as $p = v/al_c$, in which v and l_c are the volume and the length of the hydrocarbon chain, respectively, and a is the surfactant head group area [13, 36, 51]. Thus, in AOT-CTA RMs it seems that the water–surfactant interaction is quite weak, hence the area a and the droplet sizes increase only slightly with W_0 . In contrast, when AOT-BHD is used as the surfactant, water interacts strongly with the surfactant, increasing the effective area a (consequently, the p parameter decreases) and the d_{app} values increase. This difference in the magnitude of the water–catanionic surfactant interaction at the interface was also corroborated by FT-IR and ^1H NMR data [37]. We hypothesized that the benzyl group present in the BHD⁺ moiety in AOT-BHD surfactant has a notable impact on the behavior of the catanionic interface in comparison with the interface created with AOT-CTA. These results are interesting since a simple change in the cationic component of the catanionic surfactant promotes changes in the RM interface, particularly in the water–surfactant interaction.

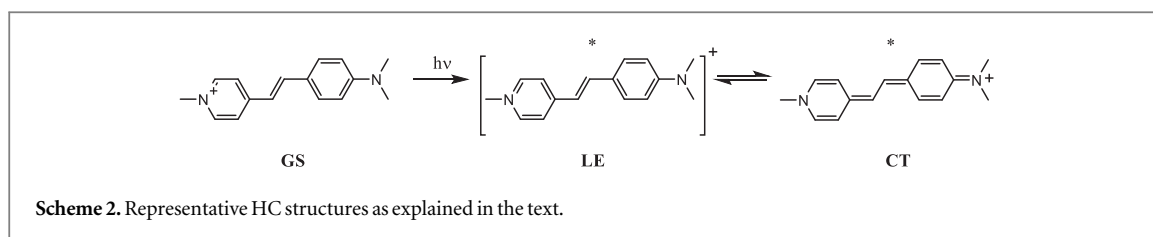
Understanding the structure of the water entrapped in RMs is of great importance in many contexts, including, for example, dehydration of biological molecules [39, 40], enzyme activity [4, 6], water trapped in nanoporous materials [41], and nanoparticle synthesis [3, 42, 43], among others. In this sense, the water–interface interaction has a significant effect on different physicochemical characteristics of the RMs [1]. For example, in benzene/BHDC the water of the RMs interacts with the cationic surfactant polar head group through ion–dipole interaction [16]. This produces a polar but non-electron donating interface [16, 44]. On the other hand, in benzene/Na-AOT RMs the entrapped water interacts by hydrogen bonding with the sulfonate group of the anionic surfactant polar head [1, 16]. This interaction allows the non-bonding electron pairs of water to be available, producing a polar and electron donor interface [16].

Taking into account the peculiar and unique interfaces created by these catanionic surfactants, and in order to complement the information obtained by DLS, FT-IR and NMR techniques, we decided to investigate both systems using molecular probes. Thus, to fully understand the novel systems with regard to properties such as the micropolarity, microviscosity and electron donor ability of the interface and how the interfacial water is altered by the type of surfactant used in catanionic RMs, a fluorescent molecular probe and absorption and emission spectroscopies have been used. The molecular probe chosen was the hemicyanine *trans*-4-[4-(dimethylamino)-styryl]-*N*-methylpyridinium iodide (HC, scheme 1), which has a unique photophysical behavior [45–47]. The styryl dyes emission has been related to different states, a planar locally excited state (LE in scheme 2),

originating directly from the S_0 to S_1 transition; a second emitting state that is also planar with a significant charge-transfer character, CT state (scheme 2); and a third one, a twisted intramolecular charge-transfer excited state (TICT state) which is usually non-radiative [48, 49]. The observation of the different emission states is associated with the characteristics of the media, such as polarity and viscosity. Accordingly, the HC emission and absorption bands shift in opposite directions when the polarity of the media increases. Thus, the emission maximum shows a bathochromic shift while the absorption maximum shows a hypsochromic shift. This behavior has been attributed to both an intramolecular charge transfer (CT) process in the excited state, and to different interactions of the ground (GS) and CT states with the environment. In this sense, the asymmetrical solvatochromism can be explained considering that the positive charge moves from the pyridinium ring in the GS to the aniline ring in the excited state (CT in scheme 2), proving that the positive charge position in the GS and CT states are different [44]. Moreover, HC has been shown to undergo specific interactions with solvents with good electron donor ability (measured by the β solvent parameter). The absorption band shifts bathochromically as β increases and the emission band shifts hypsochromically [44–46]. It seems that the positive charge located at the pyridinium ring of the HC in the ground state interacts with the electrons in a different way to that of the positive charge located in the aromatic dialkylamino group in the CT excited state (scheme 2). On the other hand, in solvents where the β parameter is null or low, HC tends to aggregate or cannot be dissolved [46].

When HC was used to study different characteristics of RMs' interfaces, interesting results were observed [44–47]. For example, while in an electron rich interface like Na-AOT RMs HC emission occurs from the CT state, but in a non-electron donor interface like BHDC RMs emission occurs from the LE. This is interesting because in homogeneous media HC emission only occurs from the CT state. In contrast to the CT state, the LE state is much less sensitive to the microenvironment [44, 45]. On the other hand, with regard to the viscosity effect, it was demonstrated by Moyano *et al* [46] that there is no dependence on time or the kind of solvent on the emission maxima or lifetime of HC. These results reinforce the idea that TICT state is nonradiative. Additionally, the quantum chemical calculations performed by Strehmel *et al* [49] suggested that these molecular probes have very low *trans* to *cis* isomerization quantum yields and therefore they present a high photostability.

Taking into account this peculiar behavior, in the present work we show results obtained in RMs formed by two catanionic surfactants, AOT-BHD and AOT-CTA, dissolved in benzene and using absorption and emission spectroscopies. We chose these systems because, although they have the same electron donor



environment, the cationic component is different. Thus, we explore how the electrostatic interaction among the ions affects HC photophysics. We compare the results with previous studies for Na-AOT and BHDC RMs in order to elucidate similarities and differences between these RMs, information that could be very valuable for future applications of the new systems.

2. Experimental section

2.1. Materials

Sodium 1,4-bis (2-ethylhexyl)sulfosuccinate (Na-AOT), cetyltrimethyl ammonium bromide (CTAB) and benzyl-n-hexadecyldimethylammonium chloride (BHDC) all from Sigma (>99% purity) were used as received. All surfactants were dried under vacuum prior to use. Ultrapure water was obtained from Labonco equipment model 90901-01. Benzene, dichloromethane and chloroform from Sigma (HPLC quality), and methanol from Sintorgan (HPLC quality), were used without prior purification.

trans-4-[4-(dimethylamino)-styryl]-N-methylpyridinium iodide (HC) was synthesized through a modification of a known method [50, 51].

2.1.1. Catanionic IL-like surfactant preparation

The catanionic IL-like surfactants used, benzyl-n-hexadecyldimethylammonium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT-BHD, scheme 1) and cetyltrimethylammonium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT-CTA, scheme 1), were obtained following the methodology previously reported [25, 37, 38]. Equimolar solutions of Na-AOT and BHDC or CTAB were prepared in dichloromethane and combined by magnetic stirring over 72 h. During the stirring, a white precipitate appeared and it was attributed to salt (NaCl or NaBr, respectively) formation from the original surfactant's counterions. The salt was removed, first by centrifugation and then by liquid-liquid extraction using water until the water fractions were free of chloride or bromide (AgNO_3 test). Once the salt was eliminated, the dichloromethane was removed by vacuum evaporation. The formation of both catanionic IL-like surfactants was confirmed by ^1H NMR, as we previously reported [37]. Prior to use, AOT-BHD and AOT-CTA were dried under vacuum for 4 h.

2.2. Methods

The stock solutions of AOT-BHD and AOT-CTA in benzene were prepared by weight and volumetric dilution. Both solutions were sonicated for a few minutes until they were optically clear. Different amounts of water were added using a calibrated microsyringe. The W_0 ($W_0 = [\text{Water}]/[\text{Surfactant}]$) parameter was used to express the amount of water dispersed in the RM solutions. RMs without the addition of water correspond to a system with $W_0 = 0$.

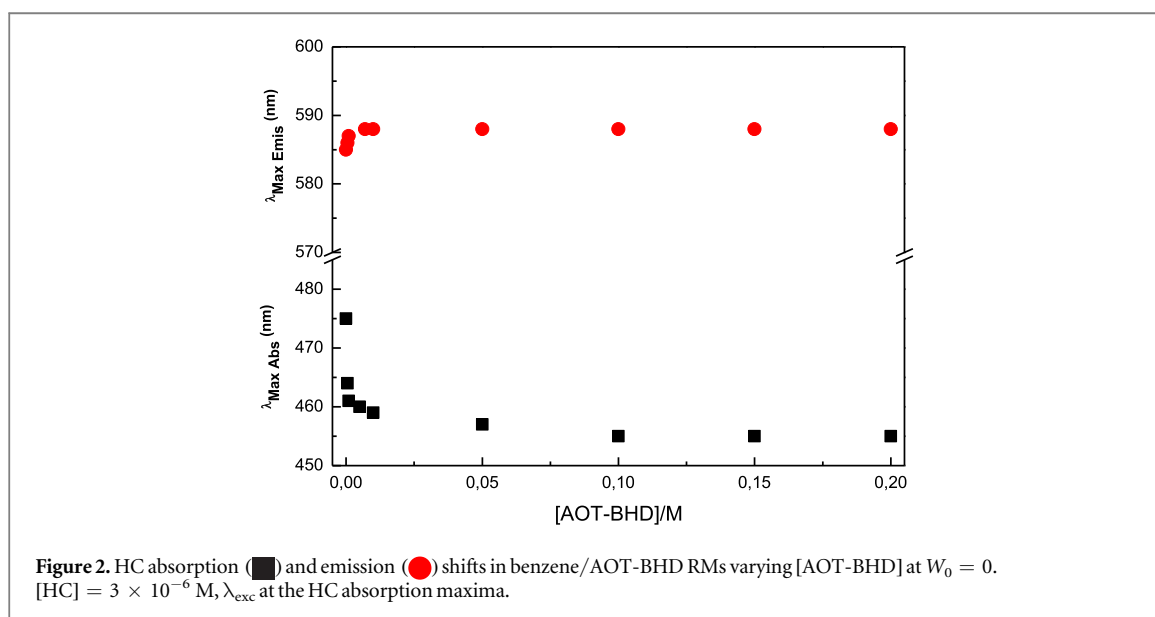
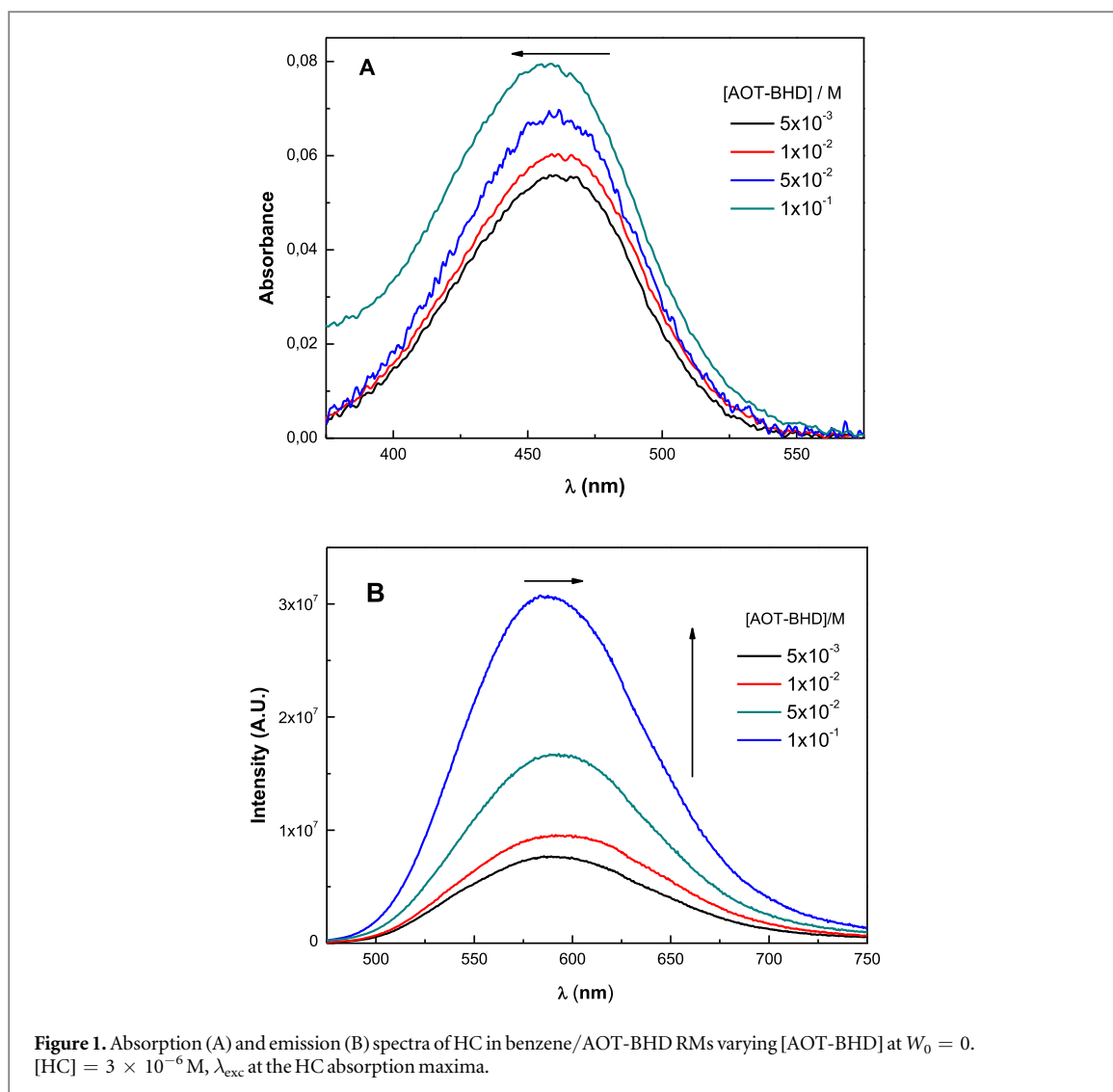
In order to introduce the molecular probe, a 1.5×10^{-3} M solution of HC was prepared in methanol. All the studies were made using an HC concentration of 3×10^{-6} M. Thus the appropriate amount of the HC's stock solution was transferred into a volumetric flask, and the methanol was evaporated by bubbling dry N_2 ; then, the catanionic RM solution was added to the residue to obtain a $[\text{surfactant}] = 0.2$ M. This stock solution containing the surfactant and the molecular probe was agitated in a sonicating bath until the solution was optically clear. An appropriated amount of stock solution was added to a fluorescence cell (1 cm optical path) bearing 2 ml of HC of the same concentration in benzene, in order to obtain a given concentration of surfactant in the micellar media. Therefore, the absorption and emission of the molecular probe was not affected by dilution [44, 45].

2.3. General

A spectrophotometer, Shimadzu 2401, with a thermostated sample holder and a Spex Fluoromax apparatus were used to obtain the absorption and emission spectra, respectively. Corrected fluorescence spectra were obtained using the correction file provided by the manufacturer. The path length used in both experiments was 1 cm. λ_{max} was measured by taking the midpoint between the two positions of the spectrum where the absorbance (or intensity) is equal to $0.9 \times$ maximum absorbance (intensity). The uncertainties in λ_{max} are about 0.1 nm. All experimental points were measured three times with different prepared samples and the pooled standard deviation was less than 5%. All the experiments were carried out at $35 \text{ }^\circ\text{C} \pm 0.5 \text{ }^\circ\text{C}$.

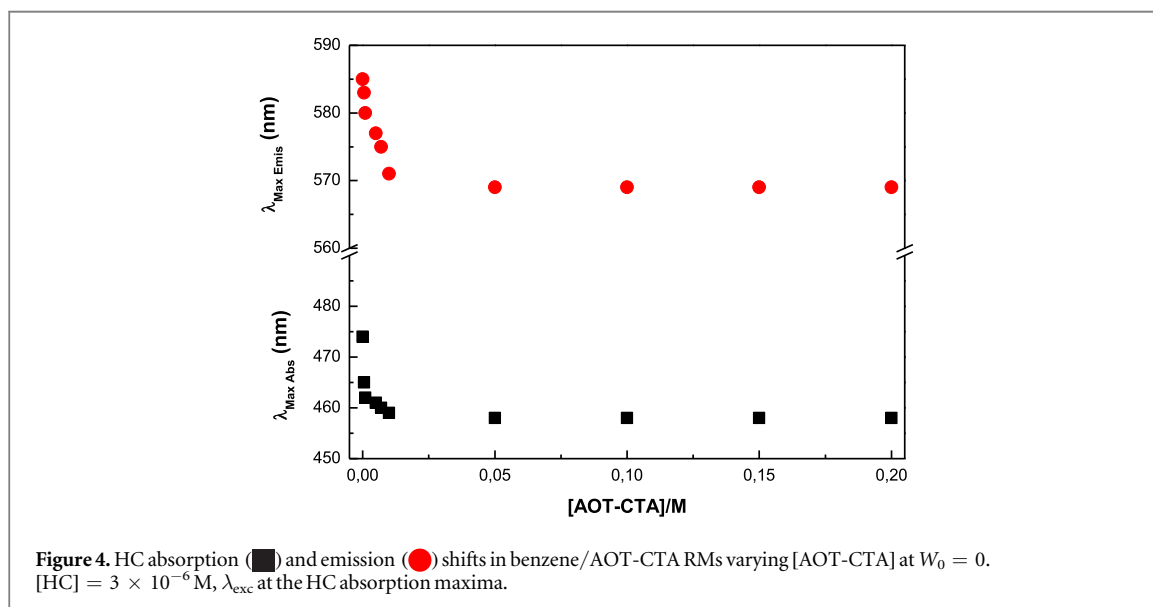
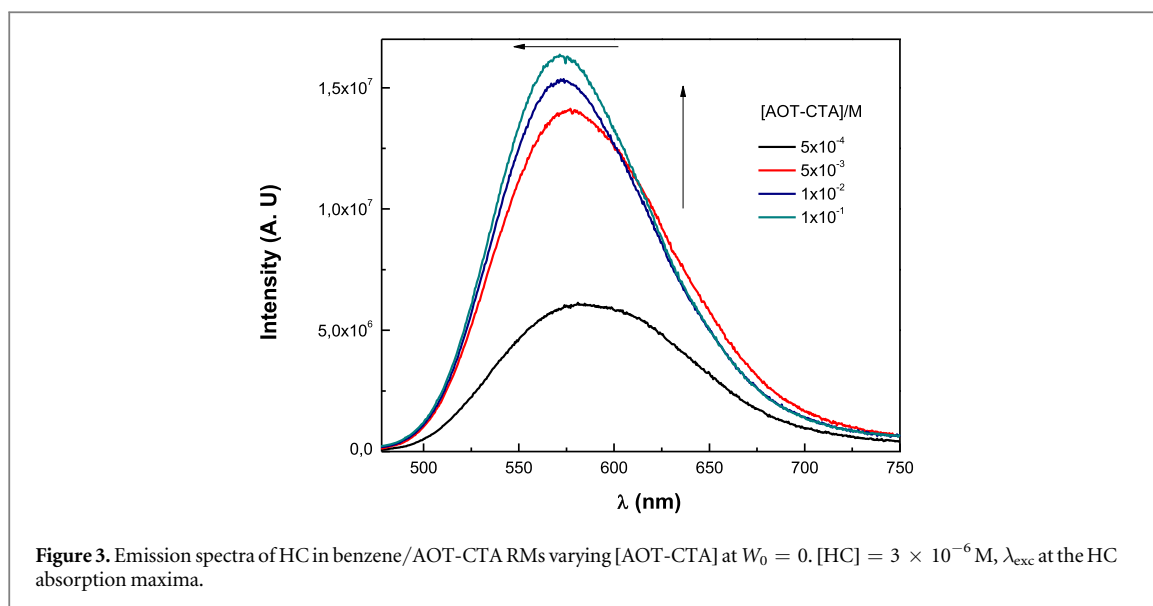
3. Results and discussion

As we want to explore the HC behavior in different types of RM, all the experiments are performed



varying the cationic surfactant concentration from 0 (pure benzene) to 0.2 M at different water contents. Thus, in the first part we show the experiments

performed in the absence of water addition, and in the second part we show the effect of the entrapped water.



3.1. HC in benzene/AOT-BHD and benzene/AOT-CTA RMs at $W_0 = 0$

Figures 1(A) and (B) show the absorption and emission spectra of HC in benzene/AOT-BHD RMs, respectively, as a function of the surfactant concentration at $W_0 = 0$. Figure 2 shows the HC absorption and emission shifts when the surfactant concentration increases. As can be seen, when AOT-BHD surfactant is added, the absorption spectra of HC shifts 20 nm hypsochromically in comparison to benzene. In contrast, the emission spectra shift bathochromically only 3 nm, and the emission spectrum increases its intensity (figure 1(B)), showing that HC emission is not quenched by the surfactant. The increment on the emission intensity, when the surfactant concentration increases, can be attributed to a quantum yield change of the HC. Thus, the fluorescent quantum yield of HC in the RMs would be larger than in neat benzene.

However, when HC is dissolved in AOT-CTA RMs a different behavior is observed, particularly in the emission feature. Figure S1 is available online at stacks.iop.org/MAF/5/044001/mmedia in the supporting information section and figure 3 shows the absorption and emission spectra of HC in AOT-CTA RMs varying the AOT-CTA concentration at $W_0 = 0$, respectively. Figure 4 shows the absorption and emission maxima of HC as a function of AOT-CTA concentration. As can be seen in this figure, both absorption and emission maxima values shift hypsochromically as the concentration of surfactant is increased. While the absorption shifts 16 nm, the emission maxima change by 17 nm, in contrast to the very small bathochromic shift (3 nm) observed in AOT-BHD RMs.

In order to understand these results, initially it must be taken into consideration that in homogeneous media HC absorption maxima shift hypsochromically

as the polarity π^* parameter of the media increases [46]. Thus, our results (figures 2 and 4) indicate that HC senses a more polar environment as the concentration of AOT-BHD and AOT-CTA are increased, denoting the formation of the organized system in the organic solvent and consequently the incorporation of the molecular probe from the non-polar solvent (benzene) into a more polar region, the RMs.

In contrast to the absorption behavior, in homogeneous media the HC emission band shows an opposite shift as π^* increases and/or β decreases [46]. Thus, it would be expected that the emission band show bathochromic shifts increasing the surfactant concentration in both AOT-BHD and AOT-CTA RMs. However, the behavior of HC's emission band is different and dependent on the surfactant used. Shifts of 3 nm to the red and 17 nm to the blue are observed (figures 2 and 4) for AOT-BHD and AOT-CTA, respectively.

To explain the dissimilar emission obtained in the two catanionic RMs, it is necessary to consider the behavior of HC in RMs formed by BHDC and Na-AOT. In BHDC RMs, the emission band of HC was practically insensitive to the surfactant concentration, shifting around 3 nm to higher wavelengths when the [BHDC] was increased [44] in comparison with pure benzene. This fact was explained by taking into account that the BHDC RM interface offers a polar and a non-electron donor environment [16] in which HC is dissolved as a monomer. In the absence of an electron donor environment, the HC emission occurs from the LE state, because the positive charge of the excited state cannot be stabilized by the microenvironment [46]. Due to the small bathochromic shift observed in figure 2, our results indicate that a similar phenomenon happens in AOT-BHD RMs, and HC emission occurs also from the LE state as if it is dissolved in a non-electron donor environment. This is quite interesting because if the catanionic AOT-BHD interface is formed by both AOT anions and BHD⁺ cations (see scheme 1), it is not expected to be a completely non-electron donor environment as the BHDC RM interface is. Thus, even in the presence of the AOT anion, the behavior of HC is dominated by the BHD⁺ cation, meaning that in the AOT-BHD RM interface, HC's π electrons cloud interacts with the positive charge of BHD⁺. This specific interaction is a powerful driving force for aromatic molecular probes to interact mainly with BHDC surfactants and to be located exclusively at the cationic part of the RM interface [13, 52, 53]. We conclude then, that in the catanionic RMs BHD⁺ interacts weakly with AOT moiety and strongly with the dye through cation- π interaction.

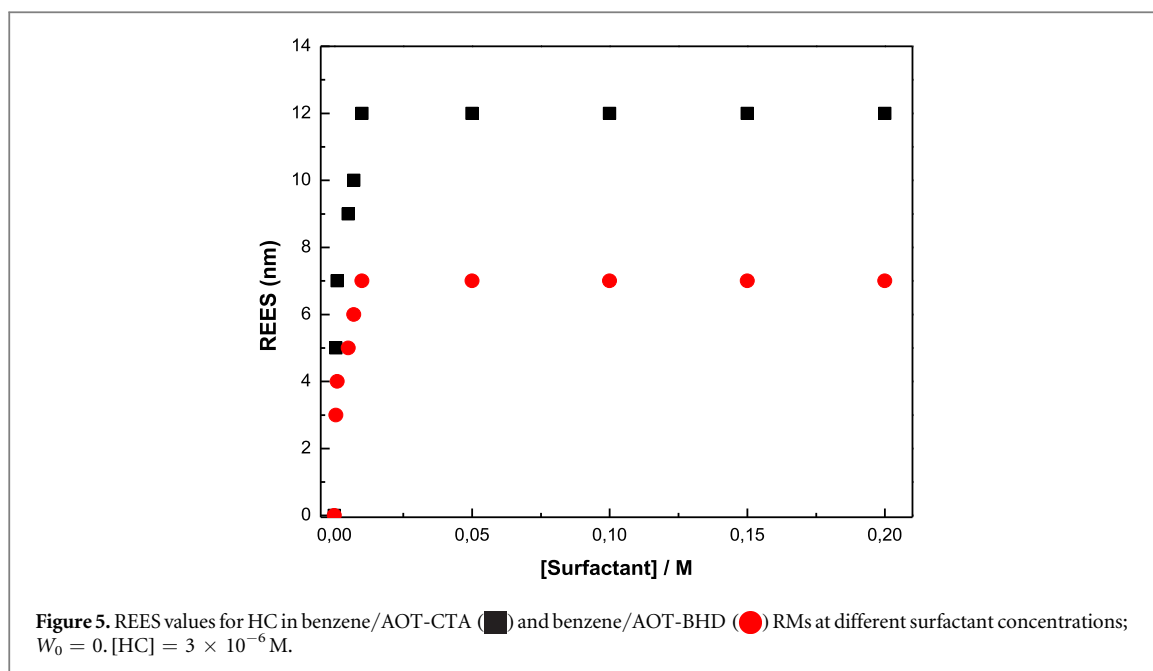
However, the behavior of HC in AOT-CTA RMs is similar to that previously reported in Na-AOT RMs [45]. In the anionic RMs and in the absence of water, both the absorption and emission band shifted hypsochromically as the surfactant concentration was increased. This behavior was attributed to an

electrostatic interaction between HC's positive charge and the sulfonate group of AOT [45]. In the GS, the positive charge is located in HC's N-pyridinium atom (scheme 2) and it can interact with the AOT sulfonate negative charge. Upon excitation, the hemicyanine's excited state holds the positive charge localized at the N-anilinium atom (CT state in scheme 2). Thus, the positive charge in the excited-state microenvironment of the fluorophore is now close to the succinate ester and the tails region of the Na-AOT RM interface [45]. This interfacial region offers a lower polarity and a higher electron donor environment responsible for the hypsochromic shift in the emission, in comparison with the environment that surrounds the hemicyanine ground state. The same emission behavior (figure 3) is observed for HC in AOT-CTA RMs, indicating that the probe emits from CT state and it senses the more electron donor but less polar environment of the succinate ester of the AOT anion. This result also denotes a stronger interaction between the anion AOT and CTA⁺ than AOT with BHD⁺, where the benzylic cation dominates the HC's photophysical. Thus, our results suggest that the type of cationic component in the interfacial region is crucial to the phenomenon that HC senses.

Taking into account that HC emission is very sensitive to the microenvironment, we examined the solvation dynamic around HC when the molecular probe is inside the catanionic RMs. To do that, the shift in the maximum fluorescence emission caused by a shift in the excitation wavelength toward the red edge of the absorption band, called the red edge excitation shift (REES) effect, was performed [46, 48, 54–60]. This phenomenon is commonly observed with polar fluorophores in a motion restricted media [48, 50, 51, 53] such as very viscous solutions, condensed phases or organized systems such as RMs and vesicles; and it arises from the slow rates of solvent relaxation around the excited state of the fluorophore, imposed on the microenvironment in the immediate vicinity of the molecular probe [50]. Thus, the REES effect can be determined and compared between different organized media, revealing, for example, whether the fluorophore is in a restricted media or in bulk solution [46, 61–63]. In our case, the REES phenomenon is used as an indicator of the interfacial fluidity of the catanionic RMs explored, and it can be defined as the difference in the emission peak maximum when exciting at the red edge of the absorption band and at the absorption maxima, as equation (1) shows.

$$\text{REES}(\text{nm}) = \lambda_{\text{em}(\text{exc red edge})} - \lambda_{\text{em}(\text{exc absorption maxima})} \quad (1)$$

Figures S2(A) and (B), in the supporting information section, show the emission spectra of HC varying the surfactant concentration in both catanionic RMs at $W_0 = 0$ and $\lambda_{\text{exc}} = 515$ nm (red edge of absorption band). Additionally, as an example, figure S2(C) shows



the normalized emission spectra of HC at surfactant concentration equal to 0.1 M in AOT-BHD RMs at $W_0 = 0$ and λ_{exc} at the absorption maxima and 515 nm. Figure 5 shows the REES values obtained using equation (1) in both AOT-BHD and AOT-CTA RMs at $W_0 = 0$ as a function of surfactant concentration. As can be observed, the REES magnitudes for both systems increase upon surfactant addition, reaching constant values around 12 nm and 6 nm in the AOT-CTA and AOT-BHD RMs, respectively. These REES values suggest that when the RM is formed, HC is located in a motion restricted environment, that is, the cationic RM's interface in comparison with the benzene pseudophase where the REES is equal to zero. It was mentioned previously that HC's emission occurs from the LE state in AOT-BHD RMs while in AOT-CTA RMs it occurs from the CT state. As the excited states are not the same it is not pertinent to compare the REES magnitudes obtained for the two cationic systems.

For the AOT-BHD system, the REES magnitude obtained in this system (7 nm) is similar to that reported for the BHDC RMs [44], showing that the cationic moiety exerts the main influence on the HC behavior. In AOT-BHD and BHDC RMs systems, HC does not show electrostatic interaction with the micellar interface and the emission occurs from the LE state.

When the REES values obtained for Na-AOT and AOT-CTA RMs are compared the following differences are observed. Moyano *et al* [45] reported that as the concentration of Na-AOT in benzene/Na-AOT is increased, the REES magnitude of HC increases up to 25 nm with respect to the value in pure benzene (REES = 0 nm). This large value (25 nm) cannot be attributed only to the solvent relaxation processes and it was suggested that the electrostatic interaction between HC and the anionic AOT polar head group is

the main cause for the REES magnitude [45]. Nevertheless, as the REES magnitude observed in the AOT-CTA system is smaller than in Na-AOT RMs, we believe that HC shows electrostatic interaction with the anionic moiety on the AOT-CTA RM's interface. We believe that the differences in the REES values can be explained by taking into account the chemical nature of the AOT counterions. In AOT-CTA RMs, the amphiphilic counterion CTA^+ is forced to be part of the RM's interface and cannot be easily displaced from the AOT polar head group vicinity. Therefore a weaker interaction between HC and the sulfonate group of the AOT anion is expected. In this case the magnitude of REES (12 nm) would be sensing only the restricted media offered by the AOT-CTA interface. On the other hand, in Na-AOT RMs the counterion is a small cation (Na^+) that can be moved from the sulfonate head group vicinity and probably be solvated by the π -electrons of HC. This movement allows a stronger interaction between the cationic moiety of HC and the sulfonate group of the surfactant than in AOT-CTA RMs.

3.2 HC in benzene/AOT-BHD/water and benzene/AOT-CTA/water RMs at $W_0 > 0$

Figures 6(A) and (B) show the emission spectra of HC as a function of the surfactant concentration and with water addition ($W_0 > 0$), in benzene/AOT-BHD/water and benzene/AOT-CTA/water RMs, respectively. Additionally, figures S3(A) and (B) show plots of the typical absorption spectra of HC in both cationic RMs. Figures 7(A) and (B) show HC absorption and emission maxima shifts in benzene/AOT-BHD/water and in benzene/AOT-CTA/water RMs as a function of the surfactant concentration at $W_0 = 1.5$ and $W_0 = 2$, respectively.

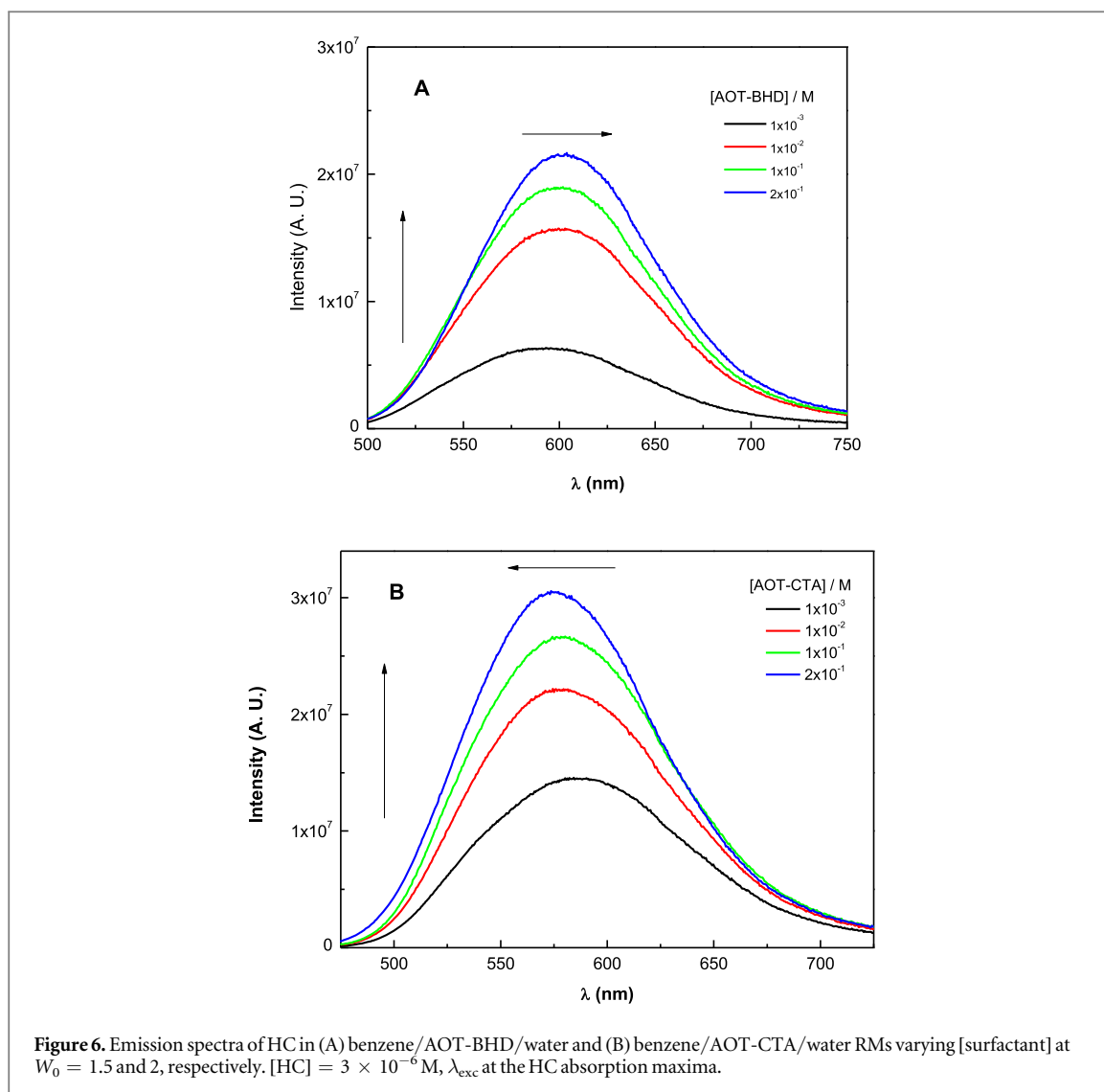


Figure 7(A) shows that when water is added to the AOT-BHD RMs, the maximum absorption band shifts hypsochromically, and the emission band shifts bathochromically as the surfactant concentration is increased. In particular, the important bathochromic emission shift (20 nm) corresponds to the one expected from the hemicyanine emitting from the CT state. This result is different to the very small shift observed in the same RMs but in the absence of water (figure 2). It seems that the water present at the AOT-BHD interface breaks down the specific interaction between HC and the BHD⁺ cation observed at $W_0 = 0$. Therefore, HC is solvated by water molecules and, upon excitation, the hemicyanine's excited state holds the positive charge localized at the N-anilinium atom and the emission is from the CT state. The behavior of the water molecules can be explained considering that in the benzene/AOT-BHD system, the entrapped water interacts strongly with the interface, disrupting its bulk structure and being able to interact with other solutes like HC present in the interface. These results agree with our assumptions invoked in a previous work [37]. In contrast, in figure 7(B) it is shown that in

the benzene/AOT-CTA/water system both the absorption and emission band shift hypsochromically as the surfactant concentration is increased, a similar behavior to the one observed at $W_0 = 0$ (figure 4). These results indicate that HC is still involved in an electrostatic interaction with the polar head group of the AOT anion which produces a hypsochromic shift on the emission. We believe that the water entrapped in the benzene/AOT-CTA RMs interacts weakly with the micellar interface as was suggested by our previous work [37]. In this situation, the water molecules appear more bulk-like and they cannot break the electrostatic interaction between positively charged HC and the AOT anion. Therefore, similar behavior of the absorption and emission bands at both W_0 values (0 and 2) is observed.

Figures S4(A) and (B), show the emission spectra of HC in both cationic RMs varying the surfactant concentration at $W_0 > 0$ and $\lambda_{exc} = 515$ nm. Table 1 shows the REES values of HC in the cationic RMs studied at different W_0 and at a fixed surfactant concentration of 0.2 M. In AOT-BHD RMs the REES values changed from 6–4 nm when the water content

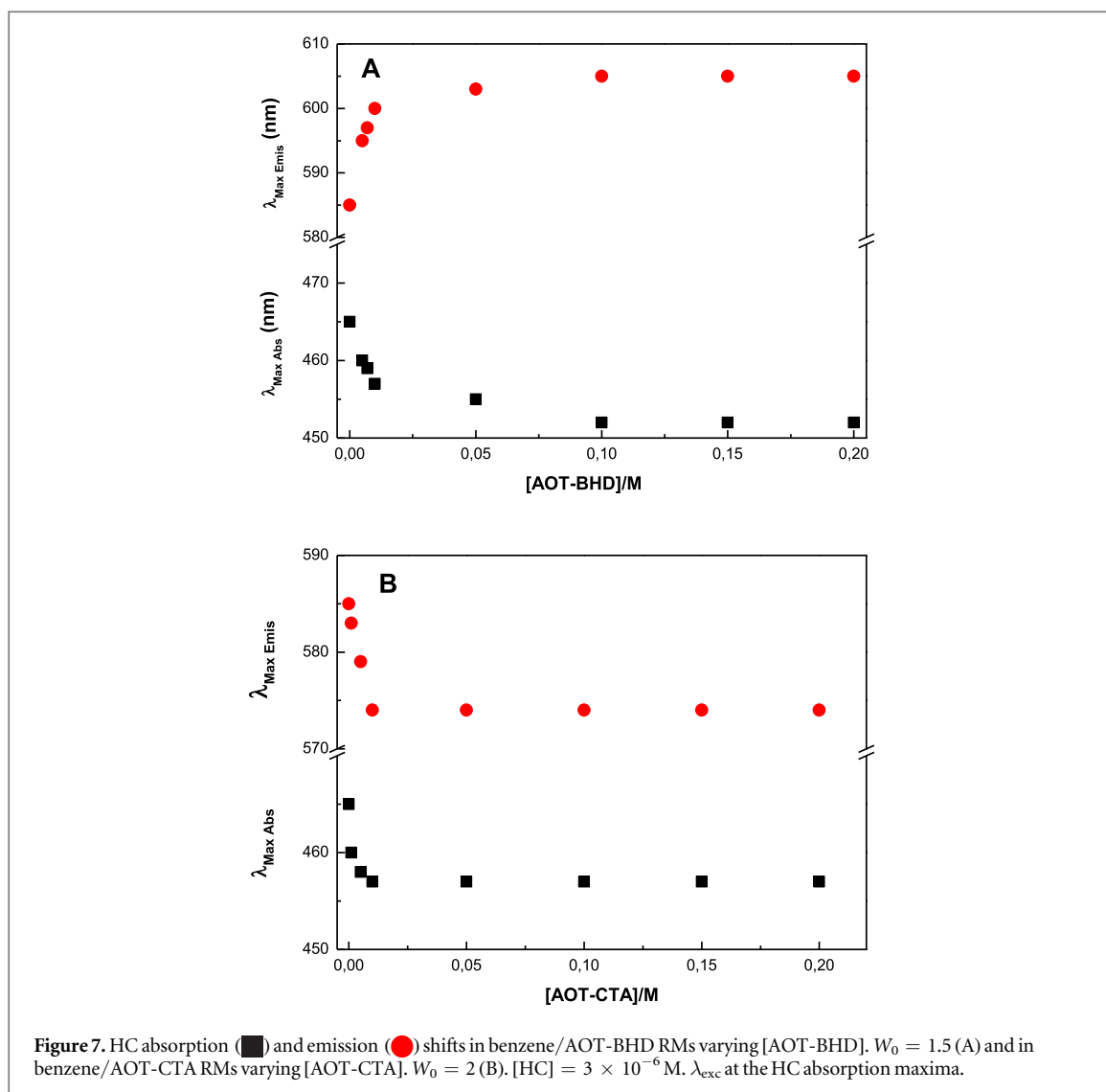


Table 1. REES values of HC in different catanionic RMs. $[Surfactant] = 0.2$ M. $[HC] = 3 \times 10^{-6}$ M.

RMs	W_0	REES (nm) ^a	HC specie emitting
benzene/AOT-BHD	0	7	LE
benzene/AOT-BHD/ water	1.5	4	CT
benzene/AOT-CTA	0	12	CT
benzene/AOT-CTA/ water	2.0	6	CT

^a REES = $\lambda_{em}(exc\ 515\ nm) - \lambda_{em}(exc\ absorption\ maxima)$.

increased from $W_0 = 0$ to 1.5, respectively. The small decrease in the REES value indicates that HC is still sensing a restricted environment when water is added, a fact that is explained considering that water molecules strongly interact with the interface which provides a less fluid region. On the other hand, in the AOT-CTA RMs the REES value decreases from 12–6 nm when the W_0 value varies from 0–2. In this case, HC senses a more fluid environment as water is

added to the RMs, a result that corroborates the weak water–interface interaction invoked above, with the consequent increase in the water–water interaction, making a real pool with higher fluidity.

4. Conclusions

In the present work we show differences between two catanionic RMs (AOT-BHD and AOT-CTA) by monitoring the absorption and emission behavior of the molecular probe, HC, dissolved in the systems. The chemical structure of the CTA⁺ and BHD⁺ cations has a great impact on the excited state from which the HC emission occurs, indicating that in the catanionic RMs it is possible to control charge transfer processes by modifying one of their components. Additionally, the structural difference between the cations impacts on the water–interface interaction, making it possible to control the solvation process in these RMs, which is not easy to do when the RMs are formed with the traditional Na-AOT or BHDC surfactants. Furthermore, as the

REES values show, differences in the interfacial fluidity between the two cationic RMs is observed, a result that is particularly interesting with regard to these systems being used as nanoreactors.

Acknowledgments

Financial support from Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, PIP CONICET 112-201101-00204), Universidad Nacional de Río Cuarto, Agencia Nacional de Promoción Científica y Técnica (PICT 2012-0232, PICT 2012-0526 and PICT 2015-0585), and Ministerio de Industria, Comercio, Minería y Desarrollo Científico Tecnológico de Córdoba (PID-2013) is gratefully acknowledged. N.M.C., J.J.S. and R.D.F. hold a research position at CONICET. C.C.V. thanks CONICET for a research fellowship.

Conflicting interests

The authors have declared that no conflicting interests exist.

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