

Characterization of Multifunctional Reverse Micelles' Interfaces Using Hemicyanines as Molecular Probes. II: Effect of the Surfactant

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In this work, we have investigated the behavior of the cationic hemicyanine *trans*-4-[4-(dimethylamino)-styryl]-*N*-methylpyridinium iodide (HC) in benzene/benzyl-*n*-hexadecyl dimethylammonium chloride (BHDC)/water reverse micelle media using absorption and emission spectroscopy in addition to the steady-state and time-resolved fluorescence emission techniques and compare the results to those obtained in benzene/sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT)/water reverse micelle media (Moyano, F.; et al. *J. Phys. Chem. B* 2009, 113, 4284.) in order to gain more insight about reverse micelle interface properties. Our results show that HC spectroscopic behavior is completely different when dissolved in AOT or in BHDC reverse micelle media. While the dye experiences an intramolecular charge-transfer process upon excitation in the former media, in BHDC, this process is inhibited because of the cationic nature of the surfactant. Interestingly, we also show that the water properties are different for water molecules sequestered inside of an anionic and cationic reverse micelle system. This comes out because the water molecules entrapped inside of the BHDC reverse micelle media appear to be non-electron-donating because of its interaction with the cationic surfactant polar head group. On the other hand, the water molecules sequestered inside of the AOT reverse micelle systems show its electron-donor ability enhanced in comparison with its water bulk structure. These results could also explain the lack of nucleophilicity shown by the water molecules entrapped in BHDC reverse micelle media reported in previous kinetic studies.

Introduction

Several surfactants are able to aggregate in nonaqueous solvents to yield reverse micellar systems. Small solute particles can be located in three different compartments, (a) the external organic solvent, (b) the micellar interface formed by a surfactant monolayer, and (c) the internal polar core.^{1–4}

Among the anionic surfactants that form reverse micelles, the best known are the systems derived from the AOT (sodium-1,4-bis-2-ethylhexylsulfosuccinate) in different nonpolar media. AOT has a well-known V-shaped molecular geometry, giving rise to stable reverse micelles without cosurfactant. In addition, AOT has the remarkable ability to solubilize a large amount of water with values of W , ($W = [\text{H}_2\text{O}]/[\text{surfactant}]$), as large as 40–60 depending on the surrounding nonpolar medium, the solute, and the temperature. However, the droplets size depends only on W .^{1,2,5} The cationic surfactant, benzyl-*n*-hexadecyl dimethylammonium chloride (BHDC), also forms reverse micelles in benzene without addition of a cosurfactant, and water can be solubilized up to $W \sim 25$.^{6–8} The BHDC reverse micelles seem to have properties that are characteristic of other reverse micellar systems. This is brought out by the nature of the water pool in the BHDC reverse micelles, which shows properties similar to that of the bulk water only after there is enough water for the surfactant solvation.^{6,7}

Among small molecules, dyes based on the hemicyanine (aminostyryl pyridinium) chromophore have been investigated in the past to establish the relationship between molecular structure and their solvatochromism.^{9–16} Today, they are studied

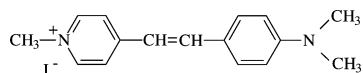
not only for the effect of solvent polarity on their optical properties but also because of possible applications in the field of nonlinear optics.^{17,18}

Previously, we have performed a solvatochromic study on the hemicyanine *trans*-4-[4-(dimethylamino)-styryl]-*N*-methylpyridinium iodide (HC) (see Scheme 1) in homogeneous media in order to gain more insight about its spectroscopic behavior. The results demonstrate, for the first time, that the cationic hemicyanines undergo a specific interaction with the medium through the electron-donor ability of the solvents as measured by the β solvent parameter.¹⁹

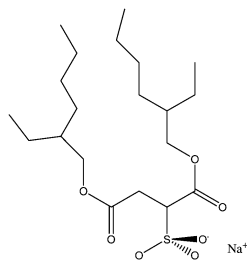
Because we found that hemicyanines are interesting dyes to monitor both polarity and electron-donor properties of the microenvironment where they are solubilized,¹⁹ we performed a detailed investigation of its behavior in different reverse micelle systems; in the first part of our work, we reported results on two different hemicyanines in the anionic benzene/AOT/water reverse micelle media.²⁰ In this work, we have investigated the behavior of the cationic hemicyanine HC in benzene/BHDC/water reverse micelle media using absorption and emission spectroscopy in addition to the steady-state and time-resolved fluorescence emission techniques and compare the results to those obtained in benzene/AOT/water reverse micelle media²⁰ in order to gain more insight about reverse micelle interfacial properties.

Our results show that reverse micelle interfaces can be a unique media to control some charge-transfer processes of molecules that have a complicated photophysics, and because the water properties can be significantly changed depending on

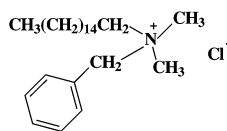
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SCHEME 1: Molecular Structures of HC and the Surfactants AOT and BHDC

HC



AOT



BHDC

the kind of surfactant used to create reverse micelles, those media can be an excellent choice to use as nanoreactors.

Experimental Section

Sodium-1,4-bis-2-ethylhexylsulfosuccinate (AOT) (Sigma >99% purity) was used as received. Benzyl-*n*-hexadecyldimethylammonium chloride (BHDC) from Sigma (>99%) was recrystallized twice from ethyl acetate.⁸

Both surfactants were kept under vacuum over P₂O₅ to minimize water absorption. The absence of acidic impurities was confirmed through the 1-methyl-8-oxyquinolinium betaine (QB) absorption bands.²¹

trans-4-[4-(Dimethylamino)-styryl]-*N*-methylpyridinium iodide (HC) was synthesized through a modification of a known method.^{14,19,22}

Ultrapure water was obtained from Labonco equipment model 90901-01.

The stock solutions of AOT and BHDC in the hydrocarbon solvent were prepared by mass and volumetric dilution. To obtain optically clear solutions, they were shaken in a sonicating bath. To introduce the probe, a concentrated solution of HC was prepared in acetonitrile (Sintorgan, HPLC quality). The appropriate amount of these solutions to obtain the desired final concentration of hemicyanines in the micellar system was transferred into a volumetric flask, and the acetonitrile was removed by bubbling dry N₂. Benzene (Sintorgan, HPLC quality) was added to the residue, and the resulting solution was used to prepare the surfactant-containing samples. The appropriate amount of stock surfactant solution to obtain a given concentration of surfactant in the micellar media was transferred into the cuvette, and the water was added using a calibrated microsyringe. The amount of water present in the system is expressed as the molar ratio between water and the surfactant ($W = [\text{H}_2\text{O}]/[\text{surfactant}]$). The lowest value of W (called $W = 0$) corresponds to a system with no addition of water, and its presence corresponds to the intrinsic humidity of the system

($W = 0.3$) as it was previously determined using QB as molecular probe²¹ and the Karl Fischer titration method.²³

The absorption spectra were measured by using Shimadzu 2401 equipment at 25 ± 0.1 °C unless otherwise indicated. A Spex fluoromax apparatus was employed for the fluorescent measurements. Corrected fluorescence spectra were obtained using the correction file provided by the manufacturer. The path length used in the absorption and emission experiments was 1 cm. The λ_{max} was measured by taking the midpoint between the two positions of the spectrum where the absorbance is equal to $0.9A_{\text{max}}$. The uncertainties in λ_{max} are about 0.1 nm.

Fluorescence decay data were measured with the time-correlated single-photon counting technique (Edinburgh Instrument FL-900) with a PicoQuant subnanosecond pulsed LED PLS 450 (emitting at 450 nm) with <600 ps fwhm, collecting a total number of 10000 counts. Fluctuations in the pulse and intensity were corrected by making an alternate collection of scattering and sample emission. The choice between a single- or a double-exponential fit was made on the basis of the presence or absence of any observed deviation from random fluctuation in residual plots and the values of the chi-squared parameter (χ^2).²⁴ For the best fit, χ^2 must be around 1.0–1.2.²⁵ It must be noted that in the case of single-exponential fit, we have tried to perform a multiexponential fitting, but the statistics of the decays were not improved or became worse. In all cases, we did not observe negative amplitude in the fitting at any detection wavelength, which means that there are no rise components for HC inside of AOT reverse micelles. In other words, HC does not exhibit an excited-state process leading to a new emitting state different from the initially excited state.²⁶

Results and Discussion

HC in Benzene/AOT and Benzene/BHDC Reverse Micelles Systems. $W = 0$. We have demonstrated in part I of our work²⁰ that HC is prompted to aggregate in benzene at $[\text{HC}] > 10^{-5}$ M because of its low solubility. Moreover, we have shown that HC forms a J-aggregate with a fluorescence lifetime value higher than the monomer lifetime. In AOT reverse micelles, the situation is different because HC exists as a monomer at the reverse micellar interface. Since here we are interested in investigating the properties of different reverse micelle interfaces using HC as a molecular probe, we work at dye concentrations below 10^{-5} M in both reverse micelle media.

Figure 1 shows the HC's absorption and emission maxima shift in benzene/AOT and benzene/BHDC reverse micelles (A and B, respectively) and the HC emission spectra in benzene/BHDC (C) as a function of the surfactant concentration, $[\text{HC}] = 3 \times 10^{-6}$ M. Figure 1A shows that as the $[\text{AOT}]$ increases, both the absorption and the emission bands clearly shift hypsochromically, even though it is well-known that the AOT reverse micelle micropolarity increases as the AOT concentration increases.² The absorption shift is around 25 nm, while the emission shift is around 40 nm in the whole $[\text{AOT}]$ range studied. We want to remark that the HC's absorption band shifts hypsochromically while the emission band shifts bathochromically when the polarity of the medium increases.^{19,20} These results inside of the AOT reverse micelle media were explained²⁰ by considering that other effects rather than the medium polarity dominate the HC photophysics in the microheterogeneous media. Since HC bears a positive charge in its moiety and AOT has a negative charge in its polar head group, the electrostatic interaction between the dye and the surfactant head group should have an influence on the hemicyanine solvatochromic behavior. Moreover, we have explained the HC solvatochromism behavior

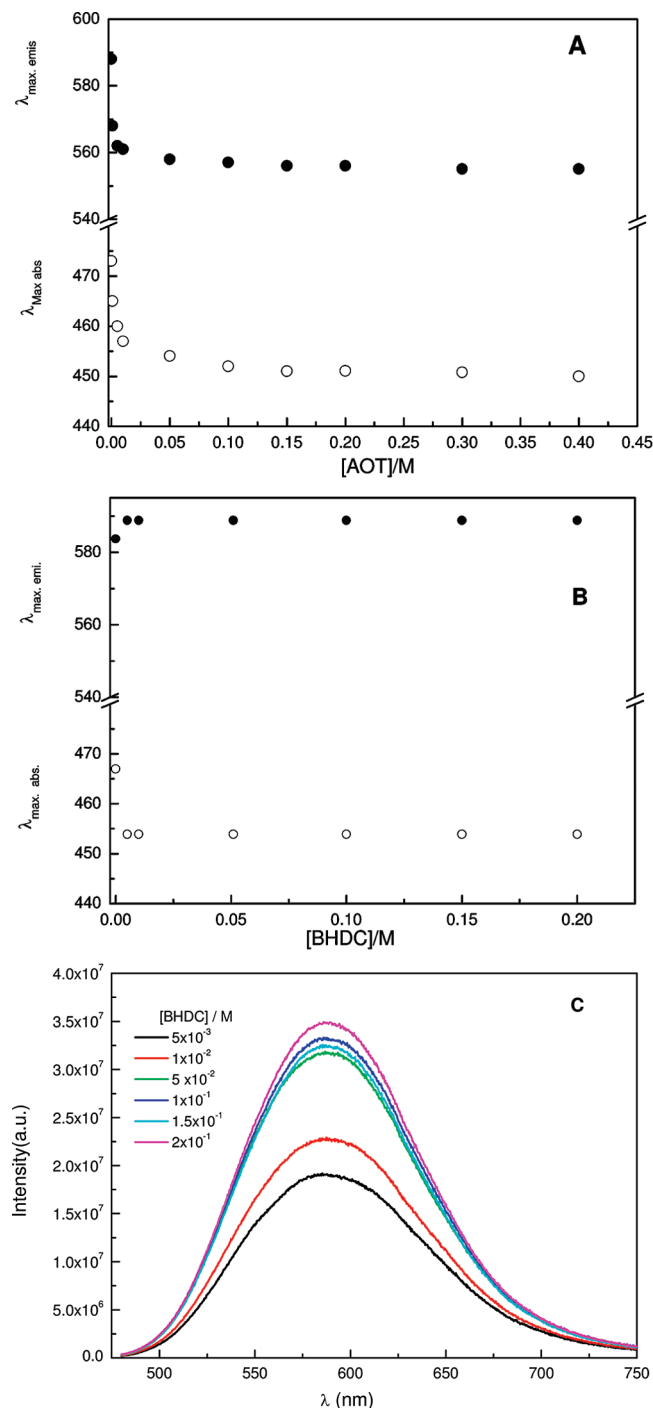
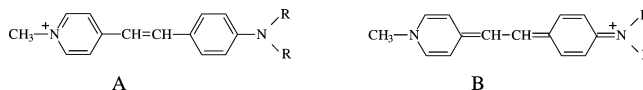


Figure 1. (A) HC absorption (O) and emission (●) shift in the benzene/AOT reverse micelle system with varying [AOT]. (B) HC absorption (O) and emission (●) shift in the benzene/BHDC reverse micelle system with varying [BHDC]. [HC] = 3×10^{-6} M, λ_{exc} = 470 nm, and $W = [\text{H}_2\text{O}]/[\text{surfactant}] = 0$. (C) Emission spectra of HC in the benzene/BHDC reverse micelle system with varying [BHDC]; [HC] = 3×10^{-6} M, λ_{exc} = 470 nm, and $W = 0$.

in AOT reverse micelles by considering that HC also engages in a specific interaction with the electron-donating environment that the AOT polar head offers, as occurs with other electron-donor solvents, measured through the β solvent parameter.¹⁹ In this way, the absorption band shifts bathochromically as β increases while, the emission band shifts hypsochromically.¹⁹ We suggested²⁰ that in the ground state, the positive charge is located in the hemicyanine's *N*-pyridinium atom (Scheme 2, structure A), and it interacts with the AOT sulfonate negative

SCHEME 2: Representative HC Structures As Explained in the Text



charge through electrostatic interaction. Thus, as the surfactant concentration increases, the HC inside of AOT reverse micelles exhibits this interaction as being closer to the AOT sulfonate group rather than the more electron-donating succinate ester group (higher β).¹⁹ Upon excitation, the hemicyanine's excited-state holds the positive charge localized at the *N*-anilinium atom (see Scheme 2, structure B). Thus, now, the excited-state microenvironment of the fluorophore is near the succinate ester and the tail region of the AOT reverse micelle interface. This interface region offers a lower polarity and a higher electron-donor environment in comparison with the environment that surrounds the hemicyanine ground state.

On the other hand, the situation is quite different when HC is dissolved inside of benzene/BHDC reverse micelles. Figure 1B shows that as the BHDC concentration increases, the absorption maxima shifts around 13 nm hypsochromically in comparison with benzene, while the emission maxima shift bathochromically only 3–4 nm. Also, the HC emission spectrum increases its intensity (Figure 1C), showing that HC emission is not quenched by the surfactant. These results are very interesting and unexpected because it is known that the micropolarity of the BHDC reverse micelle media is higher than the benzene value.⁶ Our homogeneous studies performed on the absorption and emission HC solvatochromism¹⁹ showed that both bands sense the changes in the microenvironment properties. Thus, we were expecting a shift not only in the absorption but also in the emission maxima as was found in the AOT reverse micelle media (Figure 1A). The observed behavior of HC in benzene/BHDC media is difficult to explain; however, our experimental results were elucidated as follows. It is known that the emission of HC-type dyes is related to different states, a planar locally excited state (LE), originating directly from the $S_0 \rightarrow S_1$ transition, which shows a short fluorescence lifetime value; a second emitting state that is planar with a significant charge-transfer character, the ICT state; and, a third one, the TICT state, for example, a twisted intramolecular charge-transfer excited state which usually is nonradiative.^{10,17} The observation of these emission states depends on the medium characteristics such as polarity and viscosity. It has been shown in homogeneous media^{10–13} that upon enhancing the solvent's polarity, the absorption band shifts to a higher energy while the emission band shifts to lower energy. The effects were assigned to the intramolecular charge transfer (ICT) in the processes of the dyes excitation and to the interaction of this charge shift with the environment. Thus, the symmetrical solvatochromism was rationalized using a Born–Marcus-type theory of reversible charging for the positive chromophore alone, which was described using an electrical point charge and an electrical point dipole in the center of a sphere. In other words, the solvatochromism is what would be expected for a neutral molecule with a reversal of the dipole moment upon electronic excitation.^{10–13}

The excitation starts from a ground state where the positive charge lies mainly on the pyridinium ring of the dyes, and the emission starts from an ICT state excited state, where the positive charge lies mainly on the aniline ring where the positive charge holds after excitation (see Scheme 2, structures A and B, respectively). Recently, we have shown that HC spectroscopic features also depend on the electron-donor capac-

ity of the environment (β value).¹⁹ It must be pointed out that in all of the homogeneous media studies performed on different hemicyanines^{10–13} and HC,¹⁹ the set of solvents used has considerable polarity/polarizability (π^*) and β parameter values where the emission comes mainly from the ICT state. On the other hand, quantum chemical calculations show that the dipole moment of the first excited state (LE) is lower than that of the ground state.²⁷ Thus, an increase in the solvent polarity stabilizes more the ground state than the excited LE state with the corresponding hypsochromic shifts of the absorption band^{9,28} and the insensitivity of the LE state to the properties of the environment. Nevertheless, it is very difficult to detect experimentally emissions only from the LE state because the dyes tend to aggregate or cannot be dissolved in solvents where the β parameter is null or low.¹⁹

Benzene/BHDC reverse micelles offer a unique microenvironment for HC to be dissolved as a monomer in a non-electron-donating (i.e., without appreciable β value) but polar environment. This is quite different from the benzene/AOT reverse micelle media where the interface offers a polar and also a very rich electron-donating environment (higher β).²⁹ In light of our results shown in Figure 1B in the benzene/BHDC reverse micelle media, the HC's ICT state is destabilized probably due to the positive charge and the lack of electron-donating environment that the BHDC reverse micelle interface has. Hence, the HC emission occurs mainly from the LE state because its emission is almost unaffected by the micropolarity changes in the benzene/BHDC media. This interesting result also shows how reverse micelle interfaces can control the charge-transfer processes of dyes that exist at the interface, as it was recently demonstrated for the aromatic molecular probe 6-propionyl-2-(*N,N*-dimethyl)aminonaphthalene, (PRODAN) in different nonaqueous AOT reverse micelles systems.³⁰

The HC counterions are iodide, which is a fairly efficient fluorescent quencher, as was discussed previously.²⁰ It can be thought that because the effective I^- concentration near the chromophore is high at $W = 0$, there could be an effective hemicyanine quenching by I^- inside of the BHDC reverse micelles. Surprisingly, Figure 1C shows a dramatic intensity increase for HC as the BHDC concentration increases, which discounts the possibility of such a quenching process. Probably, the strong BHDC–HC interaction showed below avoids this phenomenon. In part I, we have discussed the different scenarios that can be considered to explain the HC's intensity increases.²⁰

Interestingly, Figure 1B shows the independence of the HC absorption and emission maxima with [BHDC]. This feature indicates that HC does not experience a partition process between the organic and the reverse micelle pseudophases, despite the HC benzene solubility.^{2,6,8} It is known that specific interaction between surfactant-bearing tetraalkylammonium heads and aromatic compounds has frequently been suggested to explain anomalous results in these systems.^{6,8,21,31–34} We have shown previously⁶ that this kind of interaction is the principal reason for the aromatic probe 1-methyl-8-oxyquinolinium betaine (QB) to exist exclusively at the benzene/BHDC reverse micelle interface while QB partitions between the organic and the micellar pseudophase in the benzene/AOT reverse micelle system.²³ We have shown⁸ that the partition constant value of PRODAN in the benzene/BHDC system is almost 4 times higher than the value obtained for the *n*-heptane/AOT reverse micelle media. The result also reflects the specific interaction between the cationic polar head of the surfactant and the PRODAN aromatic ring invoked before. In light of the discussion presented, it is very likely that the HC's aniline ring aromatic

TABLE 1: Fluorescence Lifetimes (τ , ns) of HC in Benzene/BHDC Reverse Micelles at Different $W = [H_2O]/[BHDC]$ ($\lambda_{exc} = 450$ nm, $[HC] = 3 \times 10^{-6}$ M)

Benzene/BHDC; $W = 0$	
[BHDC] = 0.10 M	
$\lambda_{emi} = 585$ nm	$\lambda_{emi} = 670$ nm
$\tau = 0.49 \pm 0.05$	$\tau = 0.72 \pm 0.06$
$\chi^2 = 1.15$	$\chi^2 = 1.10$
Benzene/BHDC/Water; $W = 10$	
[BHDC] = 0.10 M	
$\lambda_{emi} = 585$ nm	$\lambda_{emi} = 670$ nm
$\tau = 0.32 \pm 0.05$	$\tau = 0.40 \pm 0.05$
$\chi^2 = 1.20$	$\chi^2 = 1.13$

π electron cloud interacts with the tetraalkylammonium BHDC head group, this specific interaction being a powerful driving force for the molecular probe to reach the cationic reverse micelle interface without experiencing a partition process to the organic pseudophase. Consequently, HC exists exclusively at the BHDC reverse micelle interface.

The interaction between small molecules and interfaces has also been investigated in other organized systems such as micelles^{35,36} and vesicles.³⁷ Simonis et al. have explored the interaction between several porphyrinic compounds with different interfaces using different spectroscopic techniques. They clearly demonstrate that the interactions of the porphyrin with the membranes depend not only in the surfactant but also on the molecule structure, and they suggest that such studies are essential to characterize complex drug–membrane interactions for developing clinically useful porphyrin drugs.^{35–37}

Table 1 shows the fluorescence lifetime of HC in benzene/BHDC reverse micelles at [BHDC] = 0.1 M and at different emission wavelengths. HC exhibits a monoexponential decay with τ values that are emission-wavelength-dependent at $W = 0$. The fluorescence lifetime serves as a sensitive indicator for the local microenvironment where a solute exists because the differential extent of solvent relaxation around a given fluorophore could be expected to give rise to differences in its fluorescence lifetime. Observation at shorter wavelengths of the emission spectra selects the unrelaxed fluorophores with shorter lifetimes because this population decays both at the rate of fluorescence emission at the given excitation wavelength and at the rate of the emission at longer (nonobserved) wavelengths. On the other hand, the observation at longer wavelength (red edge) of the emission selects the more relaxed fluorophores, which have spent enough time in the excited state to allow a larger extent of solvent relaxation.^{19,26,41} Thus, in a motion-restricted media such as organized systems like reverse micelles or vesicles, lifetime values are expected to be dependent on the excitation and emission wavelengths.¹⁹

Our results demonstrate that HC exists at the BHDC reverse micelles interface and not in the benzene pseudophase as was previously discussed (Figure 1B). Moreover, the fact that the τ value is higher in the reverse micelle than that in pure benzene ($\tau = 0.20$ ns)²⁰ also reflects the specific interaction between HC and BHDC. In part I,²⁰ we discussed the HC's lifetime values in benzene/AOT reverse micelles, and at [AOT] = 0.2 M, the features are quite similar to those found in benzene/BHDC reverse micelles.

We use the shift in the maximum fluorescence emission toward higher wavelengths caused by a shift in the excitation wavelength toward the red edge of absorption band, the red

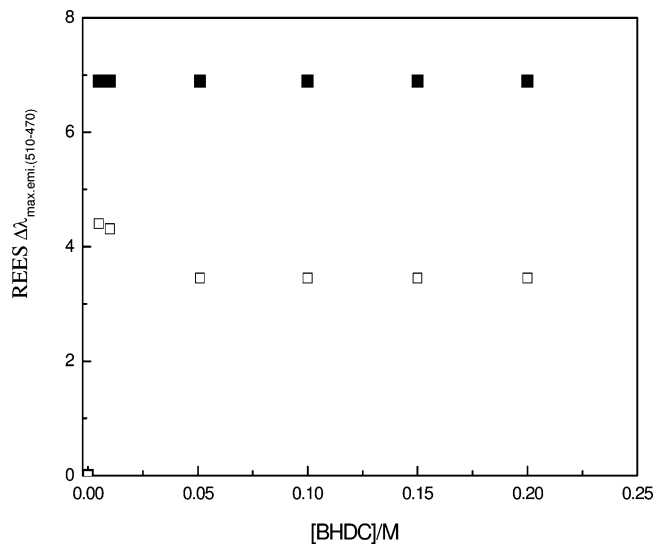


Figure 2. REES ($\lambda_{\text{max,em}}$ at λ_{exc} 510 nm $-\lambda_{\text{max,em}}$ at λ_{exc} 470 nm) values for HC in benzene/BHDC reverse micelles at different BHDC concentrations; (■) $W = [\text{H}_2\text{O}]/[\text{BHDC}] = 0$, (□) $W = 10$; $[\text{HC}] = 3 \times 10^{-6}$ M.

edge excitation shift (REES),^{26,38–41} to monitor the dynamics around HC inside of reverse micellar media. In the benzene/AOT system, the huge REES value found (around 25 nm) was not attributed only to the solvent relaxation processes,^{14,20,26,40} and we have suggested that also the electrostatic interaction between HC and the AOT polar head is included in the REES magnitude.²⁰ On the other hand, the result is different for HC in benzene/BHDC reverse micelles. Figure 2 shows the shift in the maxima of the HC fluorescence emission in the cationic reverse micelle media at $W = 0$ as a function of the excitation wavelength at different BHDC concentrations, being $\Delta\lambda_{\text{em}} = (\lambda_{\text{em(exc 510nm)}} - \lambda_{\text{em(exc 470nm)}})$. As can be observed, upon surfactant addition, the REES magnitude increases around 7 nm compared to the benzene value, which also confirms that HC exists at the benzene/BHDC reverse micelle interface, a motion-restricted environment where there is no electrostatic interaction.

HC in Benzene/AOT/Water and Benzene/BHDC/Water Reverse Micelle Systems. $W > 0$. Figure 3 shows typical HC absorption and emission maxima shifts in benzene/AOT/water (A) and in benzene/BHDC/water reverse micelles (B) as a function of the surfactant concentration at $W = 10$; $[\text{HC}] = 3 \times 10^{-6}$ M. The trend is the same for the different W values investigated, 5, 10, and 14 for AOT and 5, 10, 15, and 20 for BHDC. Figure 3A shows that when water is added to the AOT reverse micellar system, the absorption and emission band shifts are expected for hemicyanines emitting from their ICT state;^{11–13,19} the absorption band shifts hypsochromically, and the emission band shifts bathochromically as the AOT concentration increases. Taking into account previous results in homogeneous media,¹⁹ those shifts indicate that HC experiences a more polar and a less electron-donating environment as the water content increases. It seems that HC senses the presence of water because water penetrates the interface to hydrate the AOT succinate group when benzene is the organic solvent.^{2,6} Thus, HC is being solvated by the water molecules, which are more polar (higher π^*) and less electron-donating (lower β) molecules than the AOT succinate ester group.^{42–44}

Figure 3B shows that HC in the BHDC reverse micelle system has a similar trend in the absorption and emission shift, but the magnitudes of the shifting are quite different. The HC's

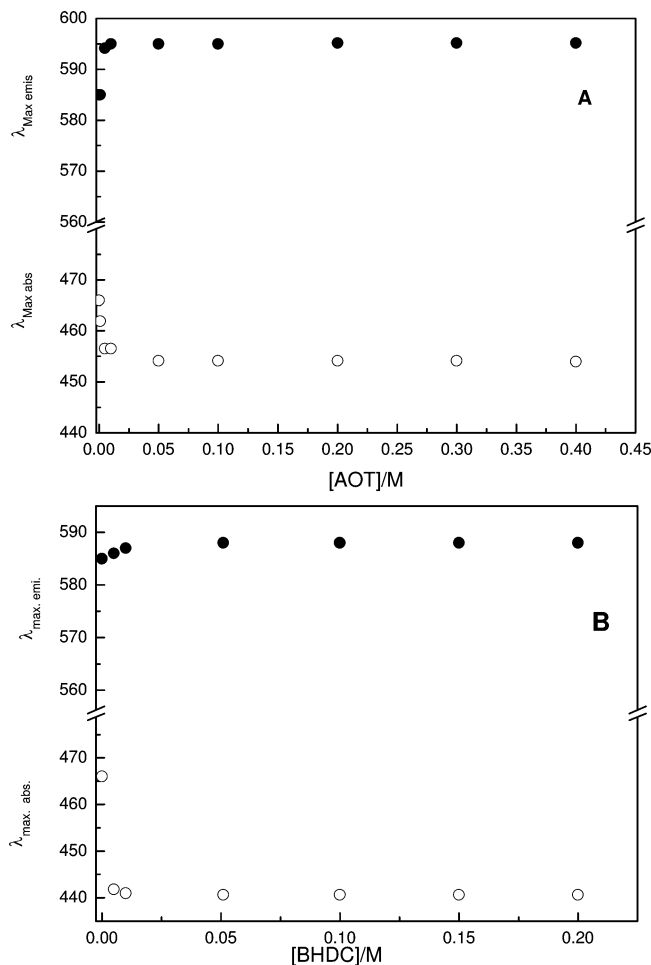


Figure 3. (A) HC absorption (○) and emission (●) shift in the benzene/AOT/water reverse micelle system with varying $[\text{AOT}]$; $[\text{HC}] = 3 \times 10^{-6}$ M; $\lambda_{\text{exc}} = 470$ nm; $W = [\text{H}_2\text{O}]/[\text{surfactant}] = 10$. (B) HC absorption (○) and emission (●) shift in the benzene/BHDC/water reverse micelle system with varying $[\text{BHDC}]$; $[\text{HC}] = 3 \times 10^{-6}$ M; $\lambda_{\text{exc}} = 470$ nm; $W = 10$.

absorption maxima shifting is around 25 nm, in comparison with the benzene value (more than the value at $W = 0$), while the HC's emission maxima shifting is around 2 nm (similar to $W = 0$). As it was observed at $W = 0$ (Figure 1B), HC's excited state is almost insensitive to the changes in its microenvironment properties even though its ground state senses the increase in the BHDC reverse micelle interface micropolarity upon the water addition. Similar to the result found at $W = 0$, HC's ICT state is not formed upon excitation, although water has an electron-donating capacity. The HC absorbance shifting shows an increase in the micropolarity of the reverse micelle interface but also shows that there is a non-electron-donor environment in the benzene/BHDC/water interface in comparison with benzene. Moreover, the absorbance maximum peaks at around 441 nm in the cationic reverse micelles, while in water, it peaks at 450 nm.¹⁹ This result suggests that water sequestered by BHDC reverse micelles preserves its polarity, but its nonbonding electron pair is not available to interact with HC. Probably, the water oxygen nonbonding electron pairs are completely involved in the solvation of the cationic BHDC polar head group through the ion–dipole interaction producing the water-entrapped non-electron donor. This novel result shows that the water properties are completely different if the molecules are sequestered by AOT or BHDC reverse micelle systems. In the AOT reverse micelle, water interacts with the surfactant polar head through

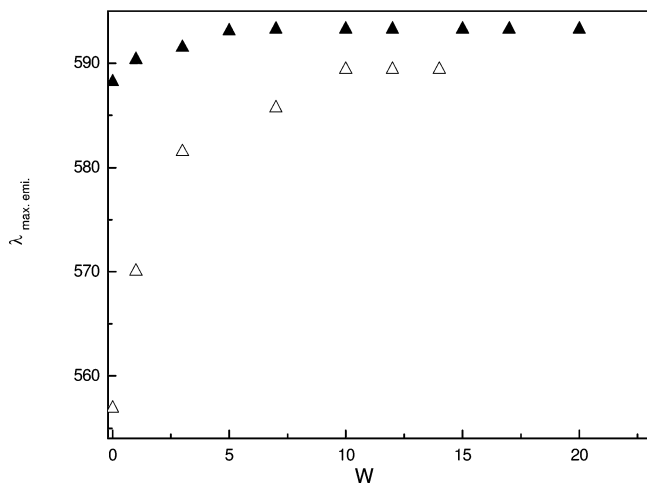


Figure 4. HC emission maximum shift in (Δ) benzene/AOT/water and (▲) benzene/BHDC/water reverse micelles varying the water content ($W = [\text{H}_2\text{O}]/[\text{surfactant}]$); $[\text{HC}] = 3 \times 10^{-6} \text{ M}$; $\lambda_{\text{exc}} = 470 \text{ nm}$.

a hydrogen-bond interaction, the bulk hydrogen bond network is destroyed,^{2,21} and the water oxygen nonbonding electron pairs are available, making the molecule more nucleophilic.⁴⁵ In BHDC reverse micelles, water solvates the cationic polar head group through its nonbonding electron pairs, making the water almost non-nucleophilic and more electrophilic when sequestered inside of the cationic reverse micelle. We have investigated the mechanism of the nucleophilic aromatic substitution ($\text{S}_{\text{N}}\text{Ar}$) reaction between 1-fluoro-2,4-dinitrobenzene and piperidine (PIP) in benzene/AOT and benzene/BHDC reverse micelle systems. There were observed differences in the reaction rate when water was added to both reverse micelles. The reaction rate increased at $W = 10$ in comparison with that at $W = 0$ in the benzene/AOT/water reverse micelle, while the opposite was observed for the benzene/BHDC/water reverse micelle.^{46,47} These results could also indicate that water entrapped inside of the benzene/BHDC reverse micelle is more electrophilic than that inside of the AOT reverse micelle, lowering the PIP nucleophilicity by the hydrogen-bond interaction in the solvation process.

Figure 2 shows the REES values for HC in the cationic reverse micelle media at different BHDC concentrations at $W = 10$. As can be seen, the REES value is lower than the one obtained in the absence of water, which shows that HC is located in a more fluid interface when water is present in the benzene/BHDC/water reverse micelle. Also, the fluorescence lifetime value gathered in Table 1 at $W = 10$ confirms that HC senses the water presence because the τ value diminishes due to the water quenching process.¹⁵ Moreover, the lifetimes at $W = 10$ are independent of the emission wavelength monitored, which also confirms that the BHDC reverse micelle interface is more fluid than that at $W = 0$.^{19,26,41}

Figure 4 shows the shift in the HC emission maxima as a function of the water content in the AOT and BHDC reverse micelles at $[\text{surfactant}] = 0.1 \text{ M}$. The plot summarizes the discussion presented in this work since it is clear that the HC excited state is more sensitive to the microenvironment changes when it is dissolved in AOT rather than that in BHDC reverse micelle media.

Conclusions

The behavior of the cationic hemicyanine HC was studied in the anionic benzene/AOT/water as well as in the cationic

benzene/BHDC/water reverse micelle media, using absorption, emission, and time-resolved spectroscopies.

Dissolved in the AOT reverse micelles systems, HC experiences a strong electrostatic interaction with the AOT anionic polar head group that cannot be disrupted with the presence of water in the reverse micelles. The molecular probe senses the polar and the electron-donating microenvironment that the AOT reverse micelle interface offers. Moreover, the results suggest that the water entrapped inside of the anionic reverse micelle has its nonbonding electron pairs available to interact with the HC molecule.

HC dissolved in the BHDC reverse micelle system experiences a nonelectrostatic interaction between its aniline aromatic ring and the BHDC polar head group and shows a polar and non-electron-donating environment with and without water sequestration. The results suggest that the BHDC reverse micelle interface inhibits the HC's ICT process upon dye excitation, the HC emission coming mainly from the less polar LE state. This is very interesting and completely different to what is observed for HC in homogeneous media as well as in the AOT reverse micelle media where its emission comes mainly from the ICT states.

HC shows that the water entrapped inside of the BHDC reverse micelles is non-electron-donating because of its interactions with the cationic surfactant polar head group.

We believe that our results show that reverse micelle systems can be a unique media to control the electron-transfer processes for molecules that have a complicated photophysics, and because the water properties can be significantly changed depending on the kind of surfactant used to prepare the reverse micelles, they can be an excellent choice to use as nanoreactors.

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