Special issue article

Journal of Physical Organic Chemistry

Received: 23 October 2015, Revised: 4 December 2015, Accepted: 9 December 2015, Published online in Wiley Online Library: 25 January 2016

(wileyonlinelibrary.com) DOI: 10.1002/poc.3535

Properties of AOT reverse micelle interfaces with different polar solvents†

M. Alejandra Luna[a], N. Mariano Correa[a], Juana J. Silber[a], R. Dario Falcone[a] and Fernando Moyano[a]*

The behavior of polar solvents such as formamide, ethylene glycol, propylene glycol, glycerol, dimethylformamide (DMF), and dimethylacetamide (DMA), entrapped in *n*-heptane/sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT) reverse micelles (RMs) was investigated using absorption, emission, and the red edge excitation shift technique.

We use the solvatochromism behavior of the hemycianine 4-(4-[dimethylamino]-styryl)-1-methylpyridinium iodide (HC) to investigate the physicochemical properties such as micropolarity, microviscosity, and hydrogen bond (H-bond) interaction in the non-aqueous RMs. Our results demonstrate that AOT surfactant interacts through H-bond with formamide, ethylene glycol, propylene glycol, and glycerol,and this interaction is responsible for weakening the electrostatic interaction between HC-AOT when entrapped in *n*-heptane/AOT RMs in absence of a polar solvent. On the other hand, when non-H-bond donor solvents (DMF and DMA) are incorporated inside the RMs, the structure of both pure solvents is destroyed upon encapsulation by the Na^+-DMF or Na^+-DMA interaction at Ws (Ws = [polar organic solvent]/[AOT]) ≤1.5.

Our results show how the physicochemical properties, such as micropolarity, microviscosity, and H-bond interaction, of non-aqueous *n*-heptane/AOT RMs interfaces can be dramatically changed by simply using different non-aqueous polar solvent. Thus, these results can be very useful for employing these RMs, stabilizing enzymes, and using them as nanoreactors.

Keywords: AOT; HC; microenvironment; micropolarity; non-aqueous reverse micelles

INTRODUCTION

Reverse micelles (RMs) are aggregates of surfactants formed in non-polar solvents. The polar head groups of the surfactants point inward, and the hydrocarbon chains point toward the non-polar medium.[1–4] A common surfactant used to form RMs is sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT). AOT has a well-known V-shaped molecular geometry, giving rise to stable RMs without cosurfactant (Scheme 1).[1–4] In addition, some polar organic solvents having high dielectric constants and very low solubility in hydrocarbon solvents can be encapsulated in RMs.[1,5] The polar organic solvents differentiated as hydrogen-bond (H-bond) donor solvents: formamide (FA), ethylene glycol (EG), propylene glycol (PG), glycerol (GY), and non-H-bond donor solvents dimethylformamide (DMF) and dimethylacetamide (DMA) can be incorporated into RMs.[1,5–11] The amount of solubilized polar organic solvents inside RMs can be expressed as the molar ratio Ws (Ws = [polar organic solvent]/[AOT]).[12,13]

Studies shown [1,5–11] that these polar solvents are confined to the nanometer–scale core of the AOT RMs, where they behave completely different from the bulk solvents as a result of specific interactions and confined geometries.[14] In others words, when a polar solvent is sequestrated inside the RMs, there is a competition between polar solvent–polar solvent interactions with polar solvent–surfactant interactions. Furthermore, we have shown [5] that GY, EG, DMF, DMA, and FA/AOT/*n*-heptane RMs droplet sizes depend on the different polar solvent–AOT interactions and not on their molar volume. It was shown that the key for the RMs droplet size values is the polar solvent–surfactant interaction.[5]

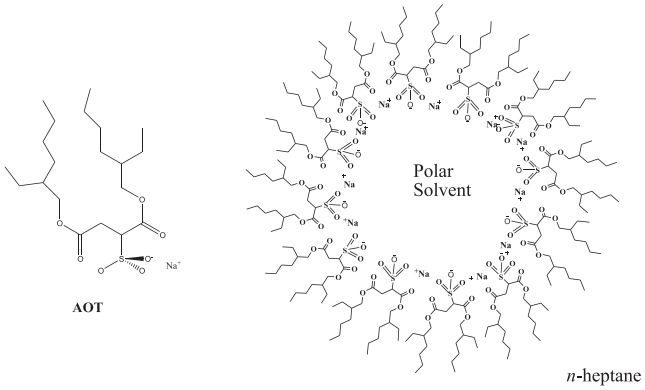
The importance of the investigation of RMs with different organic polar solvents encapsulated for using them as nanoreactor lays in that they can change different properties to the RMs interfaces at the same time. Small content of organic polar solvent can produce big changes in the interfaces properties modifying chemical reactions.[15–17] Therefore, in order to acquire valuable information on the physicochemical properties such as micropolarity, microviscosity, and hydrogen bond (H-bond) interaction of the RM interfaces different molecular probes can be used.[1] Particularly, the molecular probe: 4-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, HC, is interesting because it has a unique behavior (Scheme 2).[18–33] The anomalous behavior of HC [18] on its solvatochromism consists in that the absorption band shifts to higher energy while the emission band shifts to lower energy when the polarity of the media increases. This particular property was attributed to the intramolecular charge transfer (CT) process in the excited state and to different interactions with the environment. Thus, the asymmetrical solvatochromism was

* *Correspondence to: Dr. Fernando Moyano, Departamento de Química. Universidad Nacional de Río Cuarto. Agencia Postal # 3. C.P. X5804BYA Río Cuarto. Argentina E-mail: fmoyano@exa.unrc.edu.ar*

† *This article is published in Journal of Physical Organic Chemistry as a special issue on New Latin American Conference at Villa Carlos Paz, Córdoba, Argentina, 2015 by Elba I. Buján (Universidad Nacional de Córdoba)*

a *M. A. Luna, N. M. Correa, J. J. Silber, R. D. Falcone, F. Moyano Departamento de Química, Universidad Nacional de Río Cuarto, Agencia Postal # 3. C.P. X5804BYA, Río Cuarto, Argentina*

Journal of Physical Organic Chemistry



Scheme 1. Molecular structures of the surfactant AOT and schematic representation of n-heptane/AOT/polar solvent RMs

explained considering that the excitation process starts from a ground state (GS), where the positive charge is located mainly on the pyridinium ring and the emission decay from an excited state, where the positive charge is mainly located on the aniline ring (CT in Scheme 2).[14] Additionally, we demonstrated that HC undergoes specific interactions with solvents that have good electron donor ability (β solvent parameter [34–36]). Thus, the absorption band shifts bathocromically when the β value increases while the emission band shifts hypsochromically.[21] It seems that the positive charge located at the pyridinium ring of the HC in the GS interacts with the electrons in a different way than the positive charge located in the aromatic dialkylamino group in the CT excited state (Scheme 2).

In general, for a fluorophore in a bulk non-viscous solvent, the dipolar relaxation of the solvent molecules around the fluorophore in the excited state is much faster than the fluorescence lifetime.[37] In this way, the wavelength of the maximum emission usually is independent on the excitation wavelength. However, it shows excitation wavelength dependence if the dipolar relaxation of the solvent molecules around the excited state is slow such that the relaxation time is comparable to or longer than the fluorescence lifetime.[37] Such a shift in the wavelength of maximum emission toward higher wavelengths, caused by a shift in the excitation wavelength toward the red edge of the absorption band, is known as the red edge excitation shift (REES).[37,38] Wavelength–selective fluorescence comprises a set of approaches based on the red edge effect in fluorescence spectroscopy. This approach can be used to directly monitor the microenvironment and dynamics around a fluorophore in a motionally restricted media such as organized media like RMs or vesicles.[39,40]

In this work, we utilize HC to characterize the *n*-heptane/AOT RMs interfaces in presence of different organic polar solvents (DMF, DMA, FA, PG, EG, and GY) by absorption, emission, and the REES techniques.

Through the solvatochromism of HC, anchored at the interface of *n*-heptane/AOT/polar solvent RMs, we sensed the different microenvironments created. The electrostatic interaction between HC–AOT is responsible for the hypsochromic shifting, and thus the interaction is attenuated when the polar solvents are incorporated. The results from absorption and emission techniques show that the encapsulated H-bond donor solvents make the RMs interfaces more rigid in comparison with the non-H-bond donor solvents at the same Ws. Furthermore, the REES values obtained demonstrate that the RMs interfaces are more fluid when polar solvents (H-bond and non-H-bond donor solvents) are added in comparison with RMs without polar solvent, Ws = 0. Then, the microenvironment detected never reaches the REES values found for pure polar solvents, and it indicated that the electrostatic interaction between HC–AOT is present.

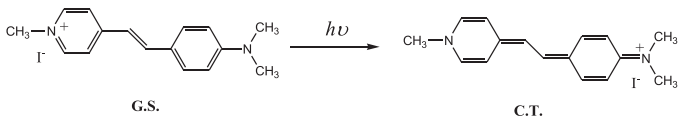
RESULTS AND DISCUSSION

It seems that the tendency to aggregate of cationic dyes such as HC is enhanced when their positive charge is poorly solvated in polar solvents.[18,21] Figs. 1 and 2 show typical absorption and emission spectra of HC in GY and DMF (H-bond donor and non-H-bond donor solvents), respectively. Also, the HC concentration was varied in both solvents. All spectra consist in a single absorption and emission band wherein the maximum wavelength absorption and emission were summarized in Table 1. Thus, the wavelength emission maxima are independent of excitation wavelength and HC obeys the Lambert–Beer's law. This indicates that only one species is present in these polar solvent and HC does not experience an aggregation process.

HC in *n*-heptane/AOT RMs. Ws = 0

Fig. 3(a) shows the absorption spectra of HC in *n*-heptane/AOT RMs varying the HC concentration, and the inset shows the HC absorbance varying the molecular probe concentrations at Ws = 0. Fig. 3(b) shows the variation of HC emission maxima (λ_{em}) as a function of the excitation wavelength (λ_{exc}). As shown in Fig. 3(a), the HC absorbance at λ = 430 nm does not obey the Lambert–Beer law over the concentration range studied. Moreover, Fig. 3(b) shows that the λ_{em} values increase as the λ_{exc} values change from 600 to 645 nm (the red edge of their emission bands). The tendency to increase the maxima of the fluorescence emission with the excitation wavelength is observed for fluorophores that exist in environments of restricted mobility.[37–41]]

Because HC has a positive charge in their moiety and AOT bears a negative charge in its polar head group (Schemes 1 and 2) it is very likely that the coulombic interaction between the dye and the surfactant head group has an influence on the HC solvatochromic behavior. As the AOT polar head is a good electron donor environment,[18] this possibility should also be taken into account in conjunction with the coulombic attraction interaction. We postulated that the coulombic interaction between HC and AOT is responsible for the fact that HC does not obey the Lambert–Beer law. This interaction was invoked before to explain anomalous behavior of similar hemicyanines inside *n*-heptane/AOT RMs.[42,43] Then, some interesting observations of the RM interfaces with different polar solvents encapsulated can be analyzed.



Scheme 2. Representative HC structures as it is explained in the text

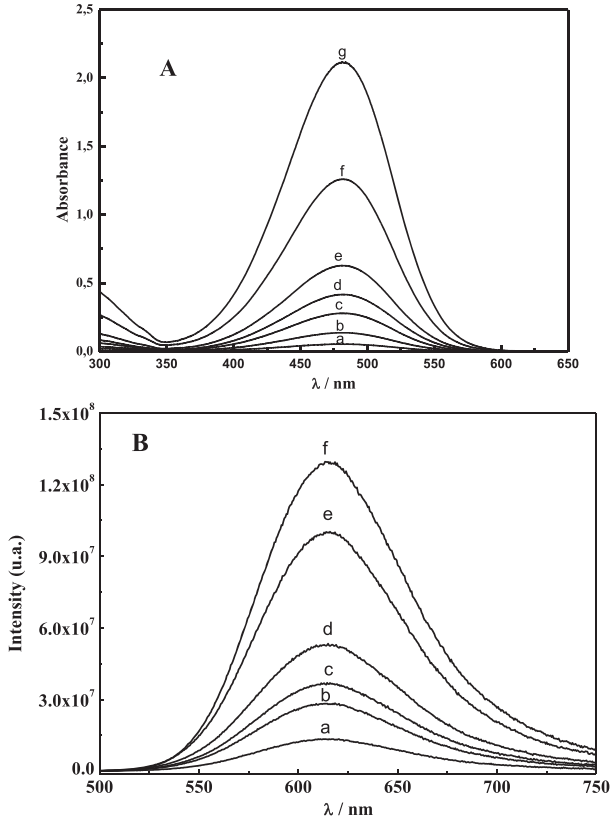


Figure 1. (A) Absorption spectra of HC in GY at different concentrations of HC. [HC]: (a) 9.3×10^{-7} M, (b) 2.7×10^{-6} M, (c) 5.3×10^{-6} M, (d) 8.5×10^{-6} M, (e) 1.2×10^{-5} M, (f) 2.4×10^{-5} M, (g) 4.0×10^{-5} M. (B) Emission spectra of HC in GY at different concentrations of HC. [HC]: (a) 2.7×10^{-6} M, (b) 5.3×10^{-6} M, (c) 8.5×10^{-6} M, (d) 1.2×10^{-5} M, (e) 2.4×10^{-5} M, (f) 4.0×10^{-5} M. $\lambda_{exc}=390$ nm

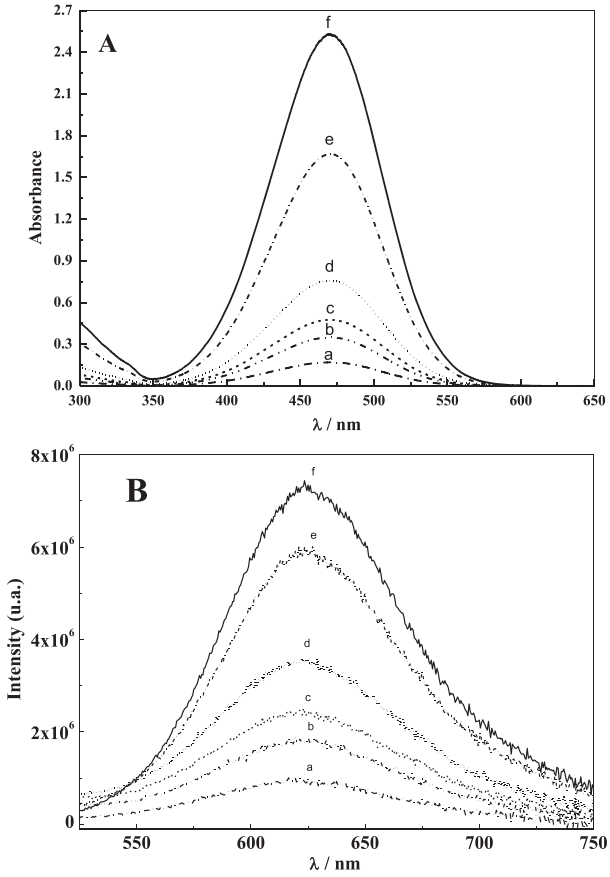


Figure 2. (A) Absorption spectra of HC in DMF at different concentrations of HC. [HC]: (a) 3×10^{-6} M, (b) 6.1×10^{-6} M, (c) 8.3×10^{-6} M, (d) 1.3×10^{-5} M, (e) 2.8×10^{-5} M, (f) 4.3×10^{-5} M. (B) Emission spectra of HC in DMF at different concentrations of HC. [HC]: (a) 3×10^{-6} M, (b) 6.1×10^{-6} M, (c) 8.3×10^{-6} M, (d) 1.3×10^{-5} M, (e) 2.8×10^{-5} M, (f) 4.3×10^{-5} M. $\lambda_{exc}=390$ nm

HC in *n*-heptane/AOT/polar solvent RMs.

Herein, we show results for the following polar solvents encapsulated: DMF, DMA, FA, PG, EG, and GY. In order to present the discussion, we classified the polar solvents into two categories: as H-bond donor solvents: FA, PG, GY, and EG, and as non-H-bond donor solvents: DMF and DMA. Previously, we have demonstrated [5] that all these polar solvents are encapsulate in *n*-heptane/AOT RMs using DLS technique. The RMs formed with H-bond donor solvents have similar droplets sized values, and they are larger than the ones created using non-H bond donor solvents. Therefore, the question that can be made is if the physicochemical properties of the interfaces of non-aqueous *n*-heptane/AOT/polar solvent RMs such as micropolarity, microviscosity, and H-bond interaction could be changed simply using different non-aqueous polar solvents.

Fig. 4(a) shows the HC absorption maxima shifts in *n*-heptane/AOT/polar solvent RMs as a function of the polar solvent content. From Fig. 4(a), it is possible to observe that the absorption maximum wavelength $\left(\lambda_{max}^{Abs}\right)$ remains constant up to Ws~1.5 and then starts to increase slightly when either DMF or DMA are used as polar solvent. The situation is different when H-bond donor solvents are encapsulated inside *n*-heptane/AOT RMs because there is a constant hypsochromic shift when the polar solvent content increases in the whole Ws range investigated.

Herein, we interpret that when non-H-bond donor solvents inside RMs are encapsulated, the RM interfaces are weakly solvated by these solvents and the HC–AOT interaction is not perturbed at low Ws values. Thereafter, the sequestrated polar solvents interact with the polar head of AOT and weaken the HC-AOT interaction. It is known [44,45] that the non-H-bond donor solvents DMF and DMA have a large affinity for solvating cations, which can disrupt their weakly bulk associated structures.[46–49] Therefore, DMF and DMA encapsulated inside AOT RMs could preferentially solvate the Na^+ counterions without interacting with the sulfonate group as reflected in the shifting shown for the HC absorption spectra.

For H-bond donor solvents encapsulated inside RMs, it seems that they solvate the AOT RM interface through H-bond

Table 1. HC absorption λ_{max}^{Abc} and emission maxima $\left(\lambda_{max}^{Em}\right)$ in different polar solvents

Polar solvent	Absorption emission	
	λ_{max}^{Abs} (nm)	λ_{max}^{Em} (nm)
DMF	470	631.5
DMA	470	631.0
FA	478	627.0
PG	480	616.5
EG	477	623.0
GY	482	619.5

Journal of Physical Organic Chemistry

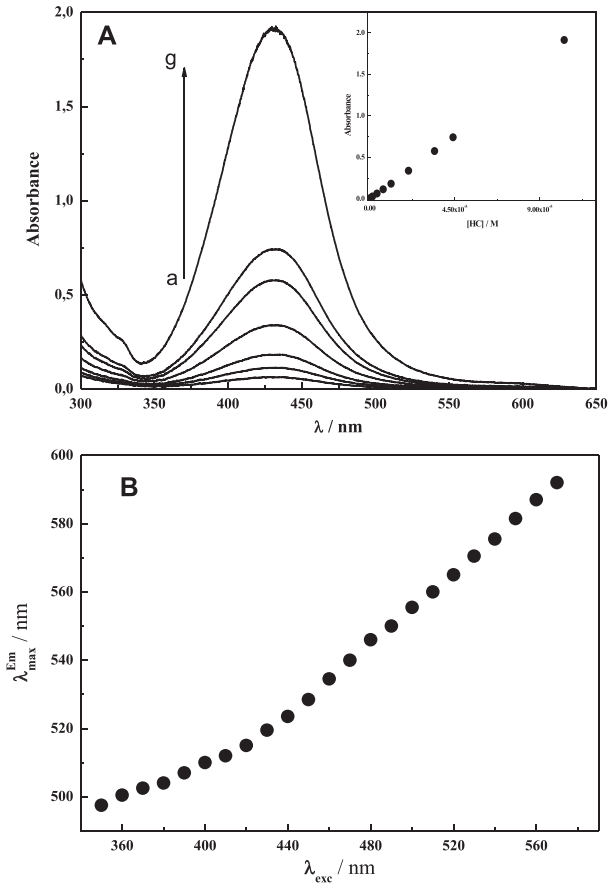


Figure 3. (A) Absorption Spectra at Ws = 0 in n-heptane/AOT at different HC concentrations. [HC]: (a) 3.9×10^{-6} M, (b) 7.2×10^{-6} M, (c) 1.1×10^{-5} M, (d) 2.1×10^{-5} M, (e) 3.4×10^{-5} M, (f) 4.4×10^{-5} M, (g) 1×10^{-4} M. Inset: HC Absorbance as the function of HC concentration. (B) HC emission maxima $\left(\lambda^{Em}_{max}\right)$ as a function of. the excitation wavelength (λ_{exc})

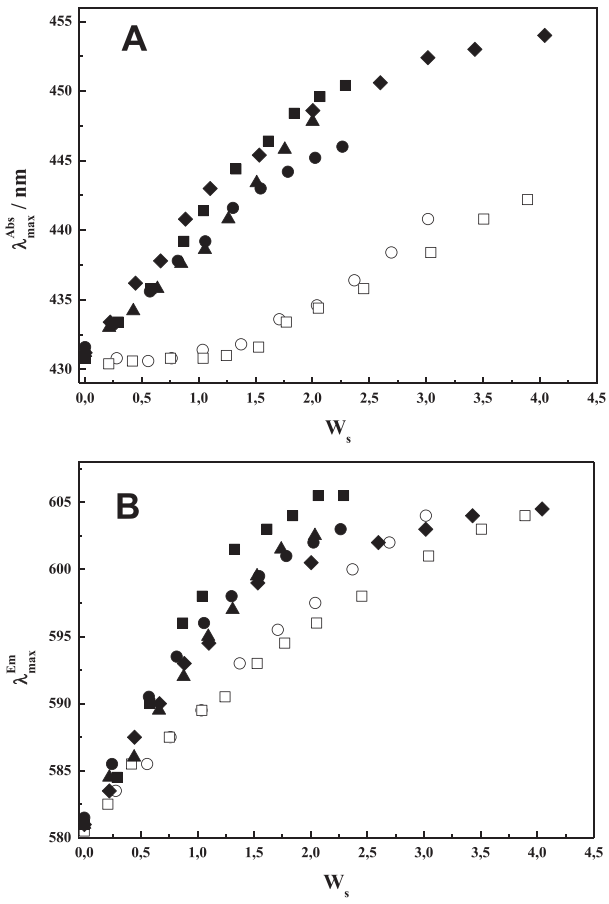


Figure 4. (A) Variation of HC absorption maxima in n-heptane/AOT with different polar solvents as a function of Ws. (▲) PG, (■) EG, (♦) GY, (●) FA, (□) DMF, (○) DMA. [AOT] = 0.15 M. (B) Variation of HC absorption maxima in *n*-heptane/AOT with different polar solvents as a function of Ws. (▲) PG, (■) EG, (♦) GY, (●) FA, (□) DMF, (○) DMA. [AOT] = 0.15 M. λ_{exc} = 550 nm

interaction when Ws increases and consequently start to weaken the HC–AOT interaction. The greater absorption maximum shifts found in H-bond donor solvents indicate that the interaction HC–AOT is more disrupted in comparison with the non-H-bond donor solvents. In other words, as H-bond donor solvents are a kind of solvents similar to water in the way that they can interact through H-bond with the sulfonated group of AOT, they compete to solvate the AOT polar head and can interact specifically in the interface of AOT RMs. It is also important to note that all the systems with polar solvents sequestrated into RMs have the λ^{Abs}_{max} different than in homogeneous media (Table 1), reflecting the strong specific interactions that HC–AOT has.

Fig. 4(B) shows the HC maxima emission shifts (λ^{Em}_{max}) in *n*-heptane/AOT/polar solvent RMs as a function of Ws at λ_{exc} = 550 nm. When the polar solvents are encapsulated inside *n*-heptane/AOT RMs there is an unexpected bathochromic shift of the emission band when the polarity of the interface increases.[18,21] Unlike the absorption shifts, all the emission shifting have similar tendency. A possible explanation can be that the HC charge translocate in the excited state upon excitation. That is, in the HC excited state the positive charge shifts toward the N of the aniline group and far from the negative charge of the sulfonate group. Thus, HC senses a similar environment independently of the polar solvent encapsulated so, the charge in the excited state of HC is near the succinate ester group and the tails region of the AOT RMs interface. Note that for all systems, the λ^{Em}_{max} tends to the value of 605 nm at the W_{max}. In summary, the RMs interface offers a lower polarity (π^*) and a higher electron donor (β) environment in comparison with the one that surrounds the hemicyanine GS.

Study of REES in non-aqueous RMs

Previously, we described the REES,[37–40] and this tool can be used to directly monitor the microenvironment and dynamics around a fluorophore in a motion restricted media such as organized media like RMs [50] or vesicles.[20,21] We want to explore the dynamics of the AOT RMs using HC as molecular probes and REES, which can be defined as the difference in the emission peak maximum when exciting at 550 and 350 nm, as Eqn 1 shows.

$$REES = \Delta\lambda_{em} = \lambda_{em}(excitation = 550nm) - \lambda_{em}(excitation = 350nm) \quad (1)$$

Our results suggest that HC resides anchored at the non-aqueous RMs interface, which prompted us to explore it using REES according to Eqn 1.

Fig. 5 shows the REES for HC as a function of Ws for all RMs system studied. It is necessary to clarify that the value typical for regular relaxation phenomena in movement-restricted microenvironments is around 10 nm.[37] However, we observe that the

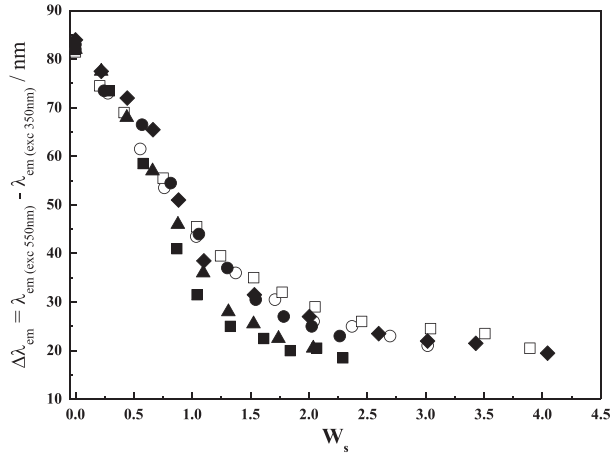


Figure 5. Variation of REES values of HC in n-heptane/AOT RMs with different polar solvents as a function of Ws. (▲) PG, (■) EG, (♦) GY, (●) FA, (□) DMF, (○) DMA. [AOT] = 0.15 M. REES = $\Delta\lambda_{em} = \lambda_{em}$(excitation = 550nm)-$\lambda_{em}$(excitation = 350 nm)

REES value is around 85 nm at Ws = 0, and we think that this reflects the HC–AOT electrostatic interaction invoked before. On the other hand, as we expected [1,20] when the polar solvent content increases the interface should be more fluid, similarly to the behavior observed previously when using water as polar solvent. Correa et al. [50] observed that the larger REES value obtained using the coumarin C343 as molecular probe in EG/AOT/isooctane RMs at small Ws was because of the strong interactions between EG and AOT polar head. Thus, the C343 molecule anchored in the interfaces senses the most motionally restricted medium of RMs. This behavior differs from other results found using acridine orange base as molecular probe.[51] Acridine orange base senses a less rigid environment in DMF/AOT RMs than it does for EG sequestered inside the RM systems.[51]

Considering that HC is anchored at the interface *n*-heptane/AOT RMs [18,20] is interesting to remark the magnitude of REES in the RMs sequestering organic polar solvents.

Table 2 shows the values of REES in RMs at Ws = 1 and Ws = 2 of all solvents encapsulated. For the non-H-bond donor solvents, the values of REES are around 43 nm at Ws = 1 in contrast to the H-bond donor solvents for which the REES value is around 33 nm at the same Ws. The lower value of REES (33 nm) found using H-bond donor solvents indicates that the H-bond donor solvents interact with the AOT RMs through H-bond and weakens HC–AOT electrostatic interaction. On the contrary, for non-H-bond donor solvents where the REES value is larger (43 nm) probably indicates that the HC–AOT interaction is not being completely removed. Therefore, HC senses an environment more restricted of movement using non-H-bond donor solvents, results that could be very interesting to explore thinking the non-aqueous RMs as nanoreactors for enzyme catalysis.

Table 2. REES values of HC in *n*-heptane/AOT/polar solvent RMs at different Ws. [AOT] = 0.15 M

Polar solvent	Empirical solvent Parameter[1] π^*	REES (nm)	
		Ws = 1	Ws = 2
DMF	0.88	45.5	29
DMA	0.88	43.5	26
FA	0.97	44	25
PG	0.92	36	20.5
EG	0.92	31.5	20.5
GY	0.62	34	21

[1]Values taken from references 34 and 36.

CONCLUSIONS

The solvatochromic behavior of HC, anchored in the interface *n*-heptane/AOT RMs, is dominated by the microenvironment that it senses in different polar solvents. The electrostatic interaction between HC–AOT is responsible by higher hypsochromic shifting, and thus the interaction is attenuated when polar solvents are incorporated.

The HC excited states shift the positive charge toward the N of the aniline group then, HC far from sulfonate group of AOT, senses the similar environment independently the polar solvent encapsulated. This interface domain offers a lower polarity and a higher electron donor medium in comparison with the environment that surrounds the hemicyanine GS.

When the non-H-bond donor solvents are encapsulated in RMs, the interfaces are weakly solvated in comparison with H-bond donor solvents. The H-bond donor solvents can diminish the electrostatic interaction AOT–HC, and thus, the interfaces are more restricted of movement making these systems very interesting to employ as nanoreactors.

EXPERIMENTAL SECTION

Sodium 1,4-bis (2-ethylhexyl) sulfosuccinate (AOT) (Sigma >99% purity) was used as received. AOT was kept under vacuum over P_2O_5 to minimize H_2O absorption. The absence of acidic impurities was confirmed through the 1-methyl-8-oxyquinolinium betaine absorption bands.[52]

Trans-4-(4-[dimethylamino]-styryl)-N-methylpyridinium iodide (HC) was synthesized through a modification of a known method.[42,53] 4-Picoline (Sigma) was dissolved in acetone (0.5 M) with an excess of methyl iodide (Fluka), and the mix was refluxed for 14 h. The crystals were purified with absolute ethanol (Sintorgan) and then were added to a solution of *N*,*N*-dimethyl amino benzaldehyde (0.5 g), piperidine (2 mL), and ethanol (30 mL). The mixture was refluxed under N_2 atmosphere for 4 h. The solution was cooled until the HC crystals precipitate from the solution. The crystals were recrystallized in a 1:1 ethanol:*n*-heptane solution, and the purity checked by silica gel 250 μm TLC plates (Analtech) in a chloroform–methanol 2:1 v/v mixture where the $R_f = 0.76$.[53]

n-Heptane (Merck spectroscopic quality), FA, EG, PG, GY, DMF, DMA were used as received.

The stock solutions of AOT in the hydrocarbon solvent (*n*-heptane) 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 hemicyanine in the micellar system was transferred into a volumetric flask, and the acetonitrile was removed by bubbling dry N_2. *n*-Heptane 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 polar solvent was added using a calibrated microsyringe. The amount of polar solvent present in the system is expressed as the molar ratio between polar solvent and the AOT (Ws = [polar solvent]/[AOT]).

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 uncertainties in λ_{max} are about 0.1 nm.

Acknowledgments

Financial support from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional de Río Cuarto, and Agencia Nacional de Promoción Científica y Técnica is gratefully acknowledged. NMC, JJS, RDF, FM, hold a research position at CONICET. MAL thanks CONICET for a research postdoctoral fellowship.

REFERENCES

[1] N. M. Correa, J. J. Silber, R. E. Riter, N. E. Levinger, *Chem. Rev.* **2012**, *112*, 4569–4602.
[2] J. J. Silber, M. A. Biasutti, E. Abuin, E. Lissi, *Adv. Colloid Interface Sci.* **1999**, *82*, 189–252.
[3] T. K. De, A. Maitra, *Adv. Colloid Interface Sci.* **1995**, *59*, 95–193.
[4] S. P. Moulik, B. K. Paul, *Adv. Colloid Interface Sci.* **1998**, *78*, 99–195.
[5] R. D. Falcone, N. M. Correa, J. J. Silber, *Phys. Chem. Chem. Phys.* **2009**, *11*, 11096–11100.
[6] S. S. Quintana, R. D. Falcone, J. J. Silber, F. Moyano, N. M. Correa, *Phys. Chem. Chem. Phys.* **2015**, *17*, 7002–7011.
[7] P. Lopez-Cornejo, S. M. B. Costa, *Langmuir*. **1998**, *14*, 2042–2049.
[8] H. Shirota, H. Segawa, *Langmuir*. **2004**, *20*, 329–335.
[9] B. B. Raju, S. M. B. Costa, *Spectroc. Acta Part A.* **2000**, *56*, 1703–1710.
[10] C. A. T. Laia, W. Brown, M. Almgrem, S. M. B. Costa, *Langmuir*. **2000**, *16*, 8763–8770.
[11] C. A. T. Laia, S. M. B. Costa, *Langmuir*. **2002**, *18*, 1494–1504.
[12] P. D. I. Fletcher, M. F. Galal, B. H. Robinson, *J. Chem. Soc., Faraday Trans. 1*. **1984**, *80*, 3307–3314.
[13] E. R. Riter, J. R. Kimmel, E. P. Undiks, N. E. Levinger, *J. Phys. Chem. B.* **1997**, *101*, 8292–8297.
[14] S. S. Quintana, F. Moyano, R. D. Falcone, N. M. Correa, *J. Phys. Chem. B*. **2009**, *113*, 6718–6724.
[15] R. D. Falcone, M. A. Biasutti, N. M. Correa, J. J. Silber, E. Lissi, E. Abuin, *Langmuir*. **2004**, *20*(14), 5732–5737.
[16] F. Moyano, E. Setien, J. J. Silber, N. M. Correa, *Langmuir*. **2013**, *29*(26), 8245–8254.
[17] F. Moyano, J. C. Mejuto, R. D. Falcone, J. J. Silber, N. M. Correa, *ChemEur. Journal.* **2010**, *16*, 8887–8893.
[18] F. Moyano, S. S. Quintana, R. D. Falcone, J. J. Silber, N. Mariano Correa, *J. Phys. Chem. B*. **2009**, *113*, 4284–4292.
[19] F. M. Agazzi, J. Rodriguez, R. D. Falcone, J. J. Silber, N. M. Correa, *Langmuir*. **2013**, *29*, 3556–3566.
[20] F. Moyano, M. A. Biasutti, J. J. Silber, N. M. Correa, *J. Phys. Chem. B*. **2006**, *110*, 11838–11864.
[21] F. Moyano, J. J. Silber, N. M. Correa, *J. Colloid Interface Sci.* **2008**, *317*, 332–345.
[22] M. Novaira, M. A. Biasutti, J. J. Silber, N. M. Correa, N. M. , *J.Phys. Chem. B*. **2007**, *111*, 748–759.
[23] Z. R. Grabowski, K. Rotkiewicz, W. Rettig, *Chem. Rev.* **2003**, *103*, 3899–4032.
[24] M. Novaira, F. Moyano, M. A. Biasutti, J. J. Silber, N. M. Correa, *Langmuir*. **2008**, *24*, 4637–4646.
[25] J. Barucha-Kraszewska, S. Kraszewski, P. Jurkiewicz, C. Ramseyer, M. Hof, *Biochim. Biophys. Acta*. **1798**, *2010*, 1724–1734.
[26] E. A. Lissi, E. B. Abuin, M. A. Rubio, A. Cerón, *Langmuir*. **2000**, *16*, 178–181.
[27] W. K. Nitschke, C. C. Vequi-Suplicy, K. Coutinho, H. Stassen, *J. Phys. Chem. B*. **2012**, *116*, 2713–2721.
[28] R. Adhikary, C. A. Barnes, J. W. Petrich, *J. Phys. Chem. B*. **2009**, *113*, 11999–12004.
[29] K. K. Karukstis, C. A. Zieleniuk, M. J. Fox, *Langmuir*. **2003**, *19*, 10054–10060.
[30] E. K. Krasnowska, L. A. Bagatolli, E. Gratton, T. Parasassi, *Biochim. Biophys. Acta*. **2001**, *1511*, 330–340.
[31] B. Mennucci, M. Caricato, F. Ingrosso, C. Cappelli, R. Cammi, J. Tomasi, G. Scalmani, M. J. Frisch, *J. Phys. Chem. B*. **2007**, *112*, 414–423.
[32] L. Cwiklik, A. J. A. Aquino, M. Vazdar, P. Jurkiewicz, J. Pittner, M. Hof, H. Lischka, *J. Phys. Chem. A*. **2011**, *115*, 11428–11437.
[33] B. Sengupta, J. Guharay, P. K. Sengupta, Spectrochim. *Acta, Part A.* **2000**, *56*, 1433–1441.
[34] Y. Marcus, *Pure Appl. Chem.* **1990**, *62*, 2069–2076.
[35] M. J. Kamlet, J. L. M. Abboud, M. H. Abraham, R. W. J. Taft, *J. Org. Chem.* **1983**, *48*, 2877–2887.
[36] J. L. M. Abboud, R. Notario, *Pure Appl. Chem.* **1999**, *71*, 645–718.
[37] J. R. Lakowicz, in: *Principles of Fluorescence Spectroscopy*(Eds: K. Academic), 2nd edn. New York, New York, **1999**.
[38] J. Milhaud, *Biochim. Biophys. Acta*. **1663**, *2004*, 19–51.
[39] A. Chattopadhyay, *Chem. Phys. Lipids*. **2003**, *122*, 3–17.
[40] A. Chattopadhyay, S. Murkherjee, H. Raghuraman, *J. Phys. Chem. B*. **2002**, *106*, 13002–13009.
[41] A. Chattopadhyay, S. Mukherjee, *Biochemistry*. **1993**, *32*, 3804–3838.
[42] M. Hof, P. Lianos, A. Laschewsky, *Langmuir*. **1997**, *13*, 2181–2183.
[43] J. Kim, M. Lee, *J. Phys. Chem. A*. **1999**, *103*, 3378–3382.
[44] Y. P. Puhovski, L. P. Safanova, B. M. Rode, *J. Mol. Liquid.* **2003**, *15*, 103–104.
[45] J. Barthel, R. Buchner, B. Wurm, *J. Mol. Liquid.* **2002**, *51*, 98–99.
[46] C. M. Criss, E. Luksha, *J. Phys. Chem.* **1968**, *72*, 2966–2970.
[47] H. Kobara, A. Wakisaka, K. Takeuchi, T. Ibusuki, *J. Phys. Chem. B*. **2003**, *107*, 11827–11829.
[48] W. A. Alves, C. A. Tellez Soto, E. Hollauer, R. B. Faria, *Spectrochim. Acta A*. **2005**, *62*, 755–760.
[49] M. Holz, C. K. Rau, J. Chem, *Soc. Faraday Trans. 1*. **1982**, *78*, 1899–1910.
[50] N. M. Correa, N. E. Levinger, *J. Phys. Chem. B*. **2006**, *110*, 13050–13061.
[51] R. D. Falcone, N. M. Correa, M. A. Biasutti, J. J. Silber, *J. Colloid Interface Sci.* **2006**, *296*, 356–364.
[52] N. M. Correa, M. A. Biasutti, J. J. Silber, *J. Colloid Interface Sci.* **1995**, *172*, 71–76.
[53] K. Lunkenheimer, A. Laschewsky, *Prog. Colloid Polym. Sci.* **1992**, *89*, 239–242.