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EFFECTS INDUCED BY ETHOXYLATED NONIONIC SURFACTANTS ON PYRENE-LABELED HYDROXYPROPYL CELLULOSE IN AQUEOUS SOLUTION

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The work presents the fluorescence investigations on aqueous solutions of pyrene-labeled hydroxypropyl cellulose in presence of octaethylene glycol mono-*n*-dodecyl ether ($C_{12}E_8$), octaethylene glycol mono-*n*-tetradecyl ether ($C_{14}E_8$) and nonaethylene glycol monononylphenyl ether (NPE_9). Surfactant titrations reveal a sharp decrease of the excimer to monomer emission intensity (I_E/I_M) at a concentration lower than the critical micellar concentration and denoted as critical aggregation concentration (CAC). The analysis of excitation and electronic spectra in surfactant-free polymer solutions and below CAC shows different monomer and excimer emission. Their general aspect is similar, but the latter is red-shifted in comparison with the former, and the excimer spectrum corresponds with the electronic spectrum. Above CAC, the excitation spectra are identical. These features reveal that the surfactants disintegrate the aggregates formed in water by the pyrene groups of the labeled polymers.

INTRODUCTION

Cellulose is the most abundant polymer in the nature. Its crystalline structure by multiple hydrogen bondings confers mechanical strength and insolubility in water and in organic solvents. Cellulose can be converted into soluble matter by etherification of parent hydroxyls. Beside solubility, cellulose ethers (CES) are efficient thickening agents, and have remarkable properties of thermoplasticity, surface activity, spreading, wetting, etc. These properties made CES useful in paints,[1] inks,[2] drugs,[3] foods,[4] ceramics,[5] industrial fluids,[6] suspensions and emulsions,[7,8] enhanced the oil recovery,[9] and other applications.[10-14]

Because of nonionic character, the cellulose ethers are compatible with all kinds of chemicals, being often mixed with surfactants to obtain synergistic effects although only the ionic surfactants produce detectable effect on CES.[15-19] Early studies on nonionic surfactant (NS)-CES mixtures showed no interaction,[20] but the hydrophobically modified hydroxyethylcellulose (HMHEC) does interact with *n*-dodecyl octaethylene glycol monoether ($C_{12}E_8$)[20] or with $C_{12}E_5$ and $C_{12}E_9$.[21] In the latter case, it was observed that both the zero-shear viscosity (ZSV) and the shear-thickening index (STI) have a maximum at a definite surfactant concentration. To explain it, the authors admitted that the hydrophobic side-chains of HMHEC aggregate into a network when the polymer dissolves in water. Addition of surfactant produces mixed micelle-like aggregates with the hydrophobic side chains of HMHEC. As the amount of surfactant increases, the number of mixed aggregates grows and strengthens the network. The phenomenon lasts until the maximum. Beyond it, aggregates containing a single polymer side-chain do form, the network connectivity is lost and the viscosity drops.

However, it should be stressed that the previous data are obtained by methods requiring large amounts of material,[20,21] and are not appropriate for dilute systems. A suitable approach in such situations is fluorescence spectroscopy that needs minute amounts of material, and fluorophors like

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pyrene are used as probes or labels. Moreover, the labeled polymers are often used as model for the hydrophobically modified counterparts. The label reports on polymer conformation, the polarity and viscosity of micro medium it experiences and how it is affected by external stimuli like pH, ionic strength, surfactants, etc.[22-28] The literature contains many studies on fluorescently labeled polymer (FLP) – surfactant systems, and a review covering the topic has been recently published.[29] However, the data on FLP – nonionic surfactant mixtures are scarce, and to the best of our knowledge, there is only a paper dealing with the systems of *n*-octyl β-D-thioglucopyranoside (OTG) or n-octyl β-D-glucopyranoside (OG) and pyrene-labeled hydroxypropyl cellulose (Py-HPC).[30] It unveils that the surfactants interact with the labeled polymer at a critical aggregation concentration (CAC) situated just before the critical micelle concentration (CMC) of surfactants alone.

Because OTG, OG and Py-HPC all contain the glucopyranoside ring, it might be possible that the observed interaction to be due to this peculiarity. To verify this hypothesis, we undertake the present study, examining the effect of homogeneously ethoxylate fatty alcohols and alkylphenols on a different batch of Py-HPC. The study is carried out by steady-state fluorescence using as experimental tool the ratio of pyrene monomer emission intensity to the pyrene excimer emission intensity (I_E/I_M) and its changes as a function surfactant concentration. To get a better insight on the phenomena happening at molecular level in the investigated systems, the information from I_E/I_M was corroborated with data from excitation and electronic spectra.

EXPERIMENTAL

Octaethylene glycol mono-*n*-dodecyl ether ($C_{12}E_8$) and octaethylene glycol mono-*n*-tetradecyl ether ($C_{14}E_8$) were purchased from Nikko Chemicals Company Ltd., and used as received. Nonaethylene glycol monononylphenyl ether (NPE_9) was obtained in our laboratory by semipreparative HPLC as previously described.[31] Hydroxypropyl cellulose (HPC) from Sigma-Aldrich, average M_W 100,000 was used to prepare the pyrene-labeled polymer (HPC-Py/37) as described.[32] It contains 7.14 x 10^{-5} mol of Py/g of polymer or on average 1 pyrene for 37 glucose units. The solutions were prepared with ultrapure water (resistivity 18.2 MΩ.cm at 25°C), produced by a Simplicity UV Millipore system.

The fluorescence measurements were done with a Fluoromax 4P (Horiba Jobin Yvon) spectrometer. The absorbance spectra were recorded on a Cary 100 (Varian) spectrophotometer. Emission spectra were not corrected. The I_E/I_M was calculated by taking the ratio of the emission intensity at 485 nm to the half-sum of the emission intensities at 378 and 396 nm. Solutions for analysis had a constant HPC-Py/37 concentration of 0.025 g/L. The surfactant concentration changed from 10^{-7} to 10^{-3} M. All the surfactant-polymer solutions were allowed to equilibrate overnight prior to fluorescence measurements. The measurements were done at 25 °C.

RESULTS AND DISCUSSION

The fluorescence spectrum of HPC-Py/37 in water has a well-resolved monomer emission of intensity I_M with the [0,0] band at 378 nm, and a broad excimer emission of intensity I_E centered at 485 nm. The computed I_E/I_M was equal to 0.85. Fig. 1 shows the effect of $C_{12}E_8$ on the I_E/I_M of HPC-Py/37. At low surfactant level, the ratio is hardly affected by the surfactant added, and I_E/I_M describes a plateau starting at the lowest surfactant concentration studied by us (*i.e.*, 1.16 x 10^{-7} M) and ending at 5.80 x 10^{-5} M $C_{12}E_8$. Above 5.80 x 10^{-5} M $C_{12}E_8$, I_E/I_M decreases sharply. At 1.16 x 10^{-4} M $C_{12}E_8$, the decline becomes less steep and flattens at 4.64 x 10^{-4} M $C_{12}E_8$ when a lower plateau is reached (I_E/I_M = 0.27). The sharp decrease of I_E/I_M observed at 5.80 x 10^{-5} M $C_{12}E_8$ is just before the CMC of $C_{12}E_8$ taken from literature,[33,34] and given for comparison in Table 1. It indicates a high cooperative binding of surfactant to the polymer and is designed as the critical aggregation concentration.

Additional information about the effect of surfactant on the pyrene-grafted HPC can be obtained by separate monitoring the emissions of monomer and excimer. The data presented in Fig. 2 show that excimer emission is lower that monomer emission. Both I_E and I_M have plateaus at lower and higher surfactant concentrations. The first plateau begins at 1.16 x 10^{-7} M $C_{12}E_8$ and ends at 5.80 x 10^{-5} M $C_{12}E_8$. Above 5.80 x 10^{-5} M $C_{12}E_8$, IE starts decreasing and I_M precipitously increases a trend that finishes at 3.48 x 10^{-4} M $C_{12}E_8$ when the second plateau situated at higher intensities for I_M, and at lover intensities for I_E becomes visible.

In the aqueous HPC-Py/37 – $C_{14}E_8$ system, similar changes of I_E/I_M, I_E and I_M are produced by surfactant addition. The differences are the lower surfactant concentration at which the changes appear and the smaller CAC. They are in accordance with the higher hydrophobicity of $C_{14}E_8$, which has a lower CMC than $C_{12}E_8$ (see Table 1).

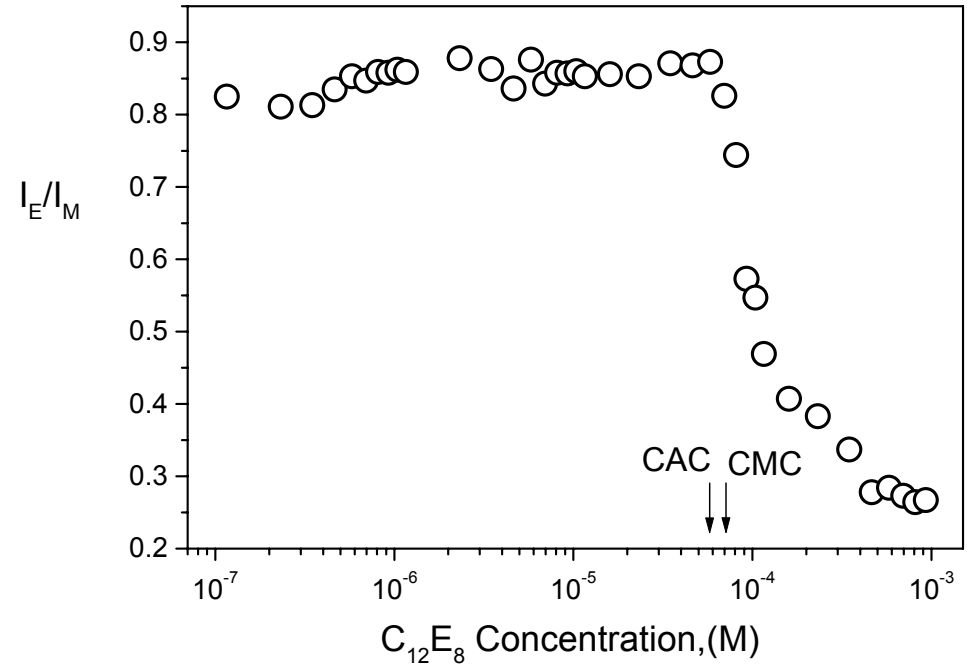

Fig. 1 – The change of I_E/I_M of HPC-Py/37 *vs.* the concentration of $C_{12}E_8$. [HPC-Py/37] = 0.025 g/L. The arrows indicate the critical aggregation concentration (CAC) and respectively the critical micelle concentration (CMC).

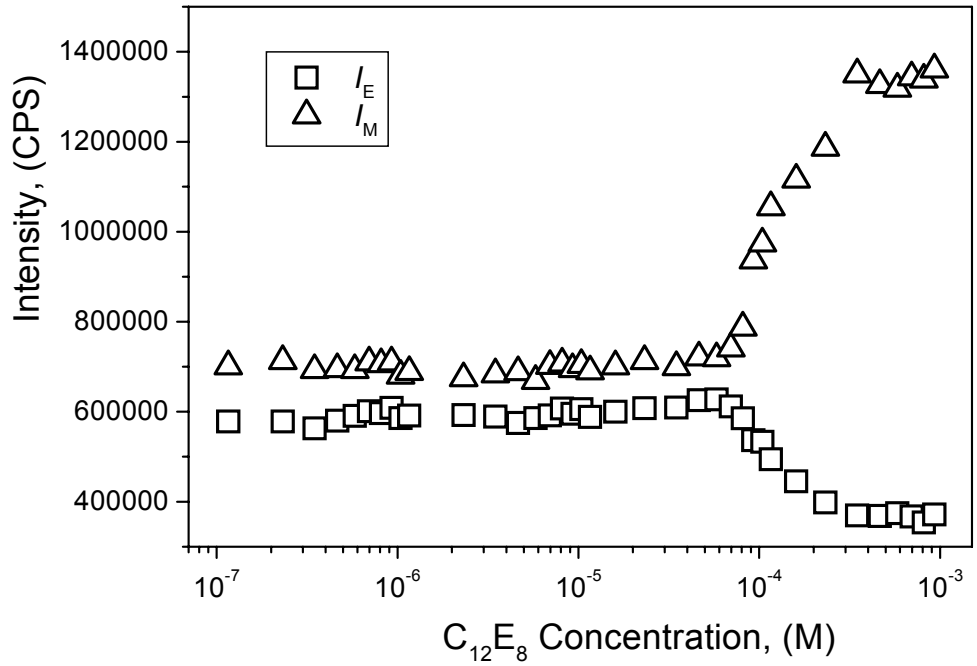

Fig. 2 – The dependence of I_E and I_M on $C_{12}E_8$ concentration; [HPC-Py/37] = 0.025 g/L.

Table 1

The CAC of HPC-Py/37 (0.025 g/L) – nonionic surfactant systems and the CMC of the surfactants, at 25 ^oC.

Surfactant	CAC, (M)	CMC, (M) [Ref.]
$C_{12}E_8$	5.8×10^{-5}	7.1×10^{-5} [33]
$C_{14}E_8$	6.0×10^{-6}	9.0×10^{-6} [33]
NPE_9	1.0×10^{-5}	6.0×10^{-5} [34]

In the system containing HPC-Py/37 and NPE_9 the decline of I_E/I_M starts at a surfactant concentration of 1.0 x 10^{-5} M, but is rather smooth. The curve has a steep drop after 3.6 x 10^{-5} M NPE_9, which ends at 1.0 x 10^{-4} M when the lower I_E/I_M plateau emerges. This behavior can be explained with the aid of data for I_E and I_M. Apparently they are similar to those in Fig. 2. However, a careful inspection reveals that this holds true only for I_E. I_M starts to increase slightly at a surfactant concentration of 1.0 x 10^{-5} M, which is smaller than that of the I_E decrease (*i.e.*, 1.0 x 10^{-4} M). The increase of I_M becomes sharp after 3.6 x 10^{-4} M NPE_9, which corresponds to the decrease of I_E. It means that the underlying mechanism of NPE_9 interaction with HPC-Py/37 is different from that for the C_iE_j surfactants. A possible reason is that although the hydrophilic part of NPE_9 is homogeneous, that hydrophobic is not. It contains a large number of isomers of nonene, the propene trimer used to alkylate the phenol, and the attachment of the alkyl chain to the aromatic ring is both in the *ortho* and *para* positions. The last account is based on previous HPLC data revealing in the parent surfactant used to obtain the NPE_9 about 10 % (mole) *ortho* isomer.[31]

On the other hand, it is well documented that excimer emission of pyrene-labeled HPC in water originates from preformed pyrene dimers or higher aggregates stabilized by hydrophobic bondings.[35] The aggregates may occur between pyrenes belonging to the same polymer chain or to different chains. There is evidence that addition of ionic surfactants to aqueous solutions of pyrene-labeled HPC causes disruption of pyrene aggregates, producing the decrease of pyrene excimer emission and a concomitant increase of pyrene monomer emission.[36] Hence, the sharp transition in the plot of I_E/I_M as a function of surfactant concentration signalizes surfactant binding to the pyrene label and the interaction with the polymer. Corroborating the data of I_E/I_M one might affirm that the CAC taken as the first decline of I_E/I_M versus the surfactant concentration is always lower than the critical micelle concentration of the surfactant alone (see Table 1).

Compelling information about the studied systems are obtained from excitation (see Figs. 3 and 4) and electronic spectra (see Fig. 5). The normalized excitation spectra in Fig. 3 obtained at a surfactant concentration below the CAC are clearly different. Their general features are similar, but the spectrum for excimer is red-shifted in comparison with that for monomer ($\Delta\lambda$ = 2.5 nm). The peak-to-valley parameters P_E and P_M have quite different values. They represent the ratios between the maximum corresponding to the (0,0) transition in the ^1L_a band and the adjacent minimum situated at lower wavelength viewed from excimer and monomer position, respectively. In our case, P_E = 1.63 and P_M = 2.49. For aggregated ground-state pyrenes, P_E is always smaller that P_M and $\Delta\lambda = \lambda_{max}$ (excimer) – λ_{max} (monomer), the shift in the wavelength maxima of the (0,0) transition in the two excitation spectra is positive and has a value from 1 to 4 nm,[37] but higher shifts were also reported.[38] Moreover, we noticed that the excitation spectrum of excimer corresponds to the UV absorption spectrum of HPC-Py/37 in water and a strong hypochromic effect appears in the UV spectrum at low surfactant level (see Fig. 5). All these observations indicate static excimers formed by direct excitation of pyrene dimmers or higher aggregates.

A totally different situation is revealed by the spectra shown in Figure 4 recorded at a surfactant concentration above CAC. In this case, P_E is almost equal to P_M, $\Delta\lambda$ decreases to 0.5 nm, the spectra almost superimpose each-other, and the emission band of excimer is narrow. Moreover, the electronic spectrum from Fig. 5 has in turn narrow bands, P_A increases to 1.80, and becomes 2.00 at the highest surfactant concentration used in this study (9.3 x 10^{-4} M $C_{12}E_8$). Although they are lover that 3, the value for dynamic pyrene excimers,[37] the decrease of static excimer populations is obvious. All these data are evidences attesting that the surfactant reduces the pre-association of pyrene.

The obtained results will be interpreted in the following section taking into account that surfactant addition decreases the aggregation state of pyrenes grafted on HPC. This statement is obvious because at a particular surfactant concentration the monomer emission increases and that of excimer drops. Assuming that the increase of I_M is equal to the decrease of I_E, then the I_E/I_M should be constant. In fact, none of the investigated systems show such a behavior. At low surfactant levels, I_E/I_M has a high plateau; thereafter it drops and finally stabilizes on a lower plateau.

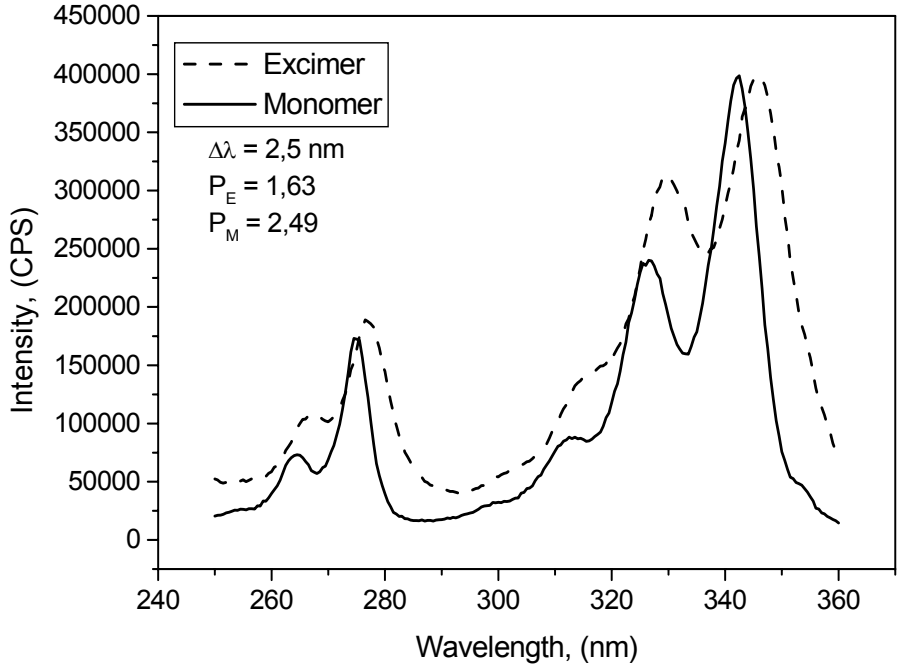

Fig. 3 – Normalized excitation spectra of HPC-Py/37 (0.025 g/L) monitored at 378 nm (monomer) and at 485 nm (excimer) at a $C_{12}E_8$ concentration below CAC (2.3 x 10^{-6} M).

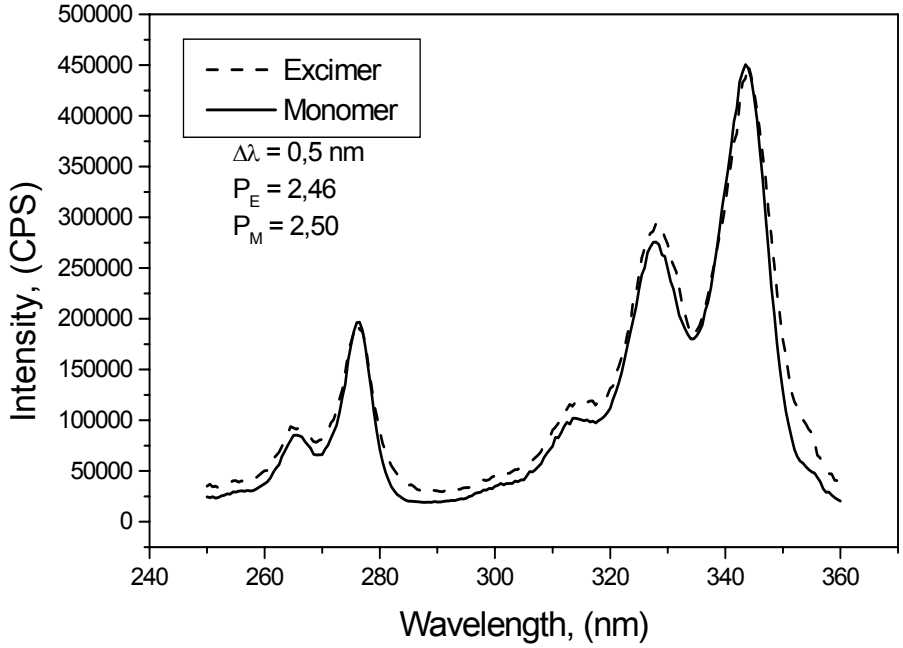

Fig. 4 – Normalized excitation spectra of HPC-Py/37 (0.025 g/L) monitored at 378 nm (monomer) and at 485 nm (excimer) at a $C_{12}E_8$ concentration above CAC (5.8 x 10^{-4} M).

What happens at nanometric level in these systems can be explained taking into account that by dissolving the HPC-Py/37 in water the pyrenes encounter a hostile environment. They tend to protect from water by bringing together and surrounding by the hydrophilic polymer backbone. Therefore, the fluorescence spectrum of HPC-Py/37 in water contains both the emission of monomer and excimer. Introduction of surfactant into the aqueous HPC-Py/37 solution does not initially affect the I_E and I_M, and I_E/I_M is constant. This happens because all the surfactant

accumulates on the hydrophobic pyrene aggregates of HPC-Py/37. At a threshold value of surfactant concentration, I_E/I_M suddenly drops and further stabilizes on a lower plateau at higher surfactant levels. The trend of I_E/I_M results from those of I_E and I_M. For the C_iE_j surfactants, the decrease of excimer emission coincides on the concentration scale to the increase of monomer emission. For the NPE_9, the decrease of I_E/I_M is initially gradual and corresponds with the surfactant concentration when I_M starts the gradual increase, while I_E is constant. The sudden drop of I_E/I_M appears at a higher surfactant concentration and is consistent with the fall of I_E. The obvious inference from these data is that the excimer governs the behavior of the HPC-Py/37 – C_iE_j systems, whereas the monomer plays the key role for the HPC-Py/37 – NPE_9 mixture. In the latter, one may recall that the surfactant does not have a homogeneous hydrophobic part and is possible to interact differently with the ground-state pyrenes. On the other hand, in all the studied cases, the monomer emission increases much more that decreases the excimer emission. This means that the energy given to the system by excitation is not retrieved by emission. This is because only a part of excitation energy produces fluorescence emission. Some energy goes to radiationless processes, thermal dissipation, system intercrossing or internal conversion, but a major part is lost by the self-quenching existing in the pyrene aggregates.[25]

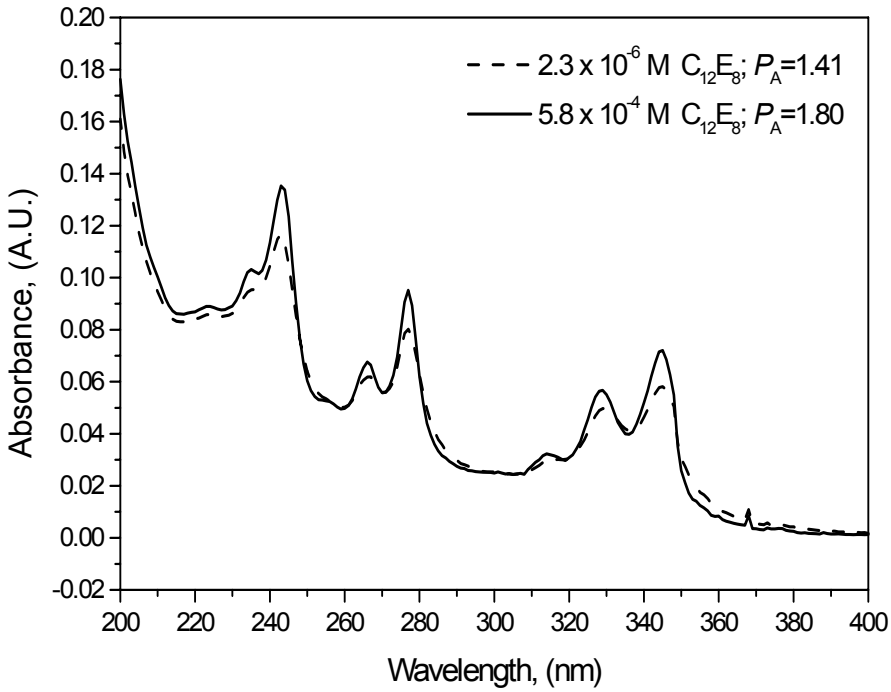

Fig. 5 – The UV spectra of HPC-Py/37 (0.025 g/L) + $C_{12}E_8$ at concentrations below and above CAC.

Fig. 6 schematically depicts the situation at molecular level into the studied systems. In the upper left corner there are drawn two segments of cellulose ether with pendant pyrenes in the absence of surfactant. For convenience, the ground-state aggregated pyrenes are marked by a circle. Because the cellulose ethers are stiffer in comparison with polymers with simple carbon-carbon bondings, the free rotation is restricted, the random coil is extended and the pyrene aggregates are mostly intermacromolecular. The added surfactant goes primarily to the pre-associated pyrenes and forms mixed aggregates. This is the region before CAC, where I_E, I_M and I_E/I_M are constant. By further surfactant addition, one reaches the point where the number of surfactant molecules surrounding one pyrene from the ground-state aggregate is high enough to take it apart. This is the reason why the excimer drops and the monomer arises. The leveling of both emissions at higher surfactant level is due to the destruction of the majority of ground-state pyrene aggregates, and excimer emission is controlled by diffusion. However, in the excitation spectra $\Delta\lambda$ does not become equal to zero, and the other parameters do not have values corresponding to un-aggregated pyrenes. All these are proofs that the system still contains static excimers.

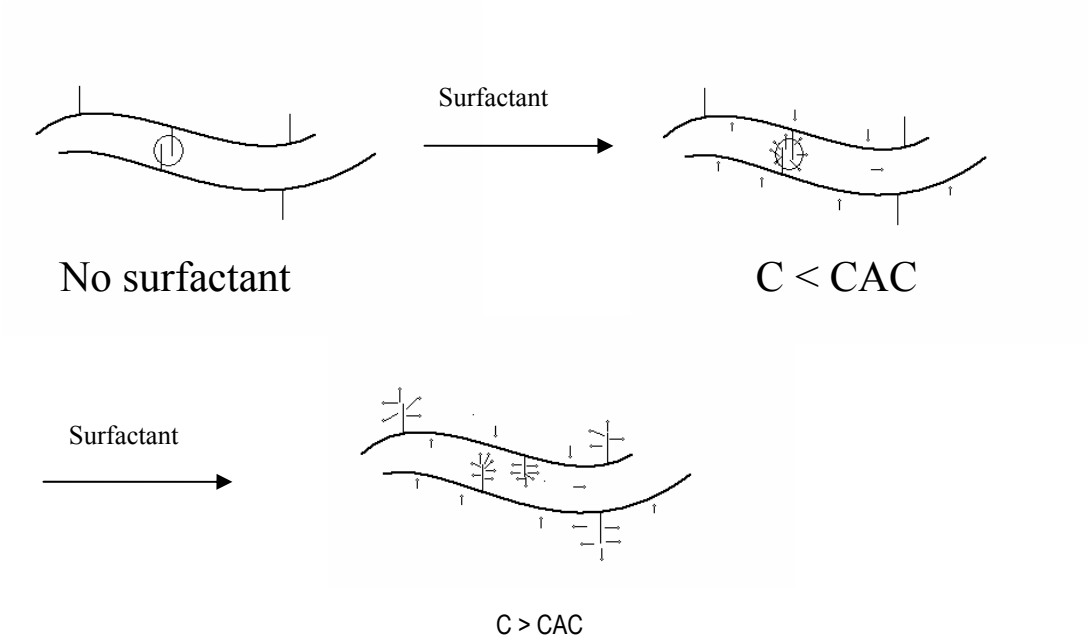

Fig. 6 – Conceptual model illustrating the effect of nonionic surfactant on pyrene-labeled cellulose ethers.

CONCLUSIONS

This study unveils that pyrene-labeled cellulose ethers interact with ethoxylated nonionic surfactants no matter the nature of their hydrophobic part. The reported data demonstrate that CAC is smaller than CMC. Besides that, the use of fluorescently labeled polymers yields information at molecular level concerning the surfactant effects on the polymer. The surfactants added into the system affect profoundly the pre-associated pyrenes grafted onto the polymer. They annihilate the pyrene-pyrene aggregates and modify the macromolecular chain conformation. Evidences that attest this are the observed changes of monomer and excimer emission in presence of surfactant, and prove the formation of polymer-surfactant complexes. At the same time, the fact that ethoxylated nonionic surfactants interact with the pyrene-labeled HPC attests that the phenomenon is governed by the hydrophobic forces, with no contribution from the hydrophilic part. Hydrophobic interactions are frequent in biological systems and are essential in the transport of matter through membrane cells. Therefore, investigations on model systems like those in the present study are important because they contribute to the better understanding of phenomena in molecular biology, medicine, material sciences and other important fields of nowadays life.

REFERENCES

1. U. Kastner, *Colloids Surf. A*, **2001**, *193-185*, 805-821.
2. E. S. Abdel-Halim, H. E. Emam and M. H. El-Rafie, *Carbohydr. Polym*., **2008**, *74*, 938-941.
3. A. Ludwig, *Adv. Drug Deliv. Rev*., **2005**, *57*, 1595-1639.
4. G. A. Burdock, *Food Chem. Toxicol*., **2007**, *45*, 2341-2351.
5. J. Beusen, M. K. Van Bael, H. Van den Rul, J. D'Haen and J. Mullens, *J. Eur. Ceram. Soc*., **2007**, *27*, 4529-4535.
6. E. Akiyama, T. Yamamoto, Y. Yago, H. Hotta T. Ihara and T. Kitsuki, *J. Colloid Interface Sci*., **2007**, *311*, 438-446.
7. V. Mutalik, L. S. Manjeshwar, A. Wali, M. Sairam, K. V. S. N. Raju and T. M. Aminabhavi, *Carbohydr. Polym.*, **2006**, *65*, 9-21.
8. M. Karlberg, K. Thuresson and B. Lindman, *Colloids Surf. A*, **2005**, *262*, 158-167.
9. A. L. Kjoniksen, N. Beheshti, H. K. Kotlar, K. Z. Zhu and B. Nystrom, *Eur. Polym. J.*, **2008**, *44*, 959-967.
10. U. Kästner, *Colloids Surf. A*, **2001**, *183-185*, 805-821.
11. G. S. Chauhan, B. Singh, S. Chauhan, M. Verma and S. Mahajan, *Desalination*, **2005**, *181*, 217-224.
12. R.S. Veerapur, K.B. Gudasi and T.M. Aminabhavi, *J. Membr. Sci*., **2007**, *304*, 102–111.
13. W. J. Liu, Z. H. Zhang, H. R. Liu, W. D. He, X. W. Ge and M. H. Wang, *Mater. Lett*., **2007**, *61*, 1801–1804.
14. Y. Song, Q. Zheng and C. Liu, *Ind. Crops Prod*., **2008**, *28*, 56-62.
15. J. Djuve, R. J. Pugh and J. Sjoblom, *Colloids Surf. A*, **2001**, *186*, 189-202.
16. B. Wittgren, M. Stefansson and B. Porsch, *J. Chromatogr. A* , **2005**, *1082*, 166-175.
17. A. L. Kjoniksen, K. D. Knudsen and B. Nystrom, *Eur. Polym. J*., **2005**, *49*, 1954-1964.
18. A. Maestro, C. Gonzalez and J. M. Gutierrez, *J. Colloid Interface Sci*., **2005**, *288*, 597-605.
19. M. R. Rojas, A. J. Muller and A. E. Saez, *J. Colloid Interface Sci*., **2008**, *322*, 65-72.
20. K. Sivadasan and P. Somasundaran, *Colloids Surf.*, **1990**, *49*, 229-239.
21. G. Q. Zhao and S. B. Chen, *J. Colloid Interface Sci*., **2007**, *316*, 858-866.
22. F. M. Winnik, in "Interactions of Surfactants with Polymers and Proteins", E. D. Goddard and K. P.

Ananthapadmanabhan (Eds.), CRC Press, Boca Raton, 1993, p. 367-394.
23. F. M. Winnik and S. T. A. Regismond, *Colloids Surf. A*, **1996**, *118*, 1-39.
24. F. M. Winnik and S. T. A. Regismond, in "Polymer-Surfactant Systems", J. C. T. Kwak (Ed.), Dekker, New York, 1998, 267-315.
25. D. F. Anghel, V. Alderson, F. M. Winnik, M. Misuzaki and Y. Morishima, Y., *Polymer*, **1998**, *39*, 3035-3044.
26. F. M. Winnik, S. T. A. Regismond and D. F. Anghel, in "Associative Polymers in Aqueous Solutions", J. E. Glass (Ed.), ACS Symposium Series No. 765, American Chemical Society, Washington DC, 2000, p. 286-302.
27. K. Schillen, D. F. Anghel, M. Miguel and B. Lindman, *Langmuir*, **2000**, *16*, 10528-10539.
28. D. F. Anghel, J. L. Toca-Herrera, F. M. Winnik, W. Rettig and R. v. Klitzing, Langmuir, **2002**, *18*, 5600-5606.
29. D. F. Anghel, in "Focus on Ionic Polymers", S. E. Dragan (Ed.), Research Signpost, Kerala, India, 2005, p. 203-222.
30. F. M. Winnik, *Langmuir*, **1990,** *6*, 522-524.
31. D. F. Anghel, M. Balcan, A. Voicu and M. Elian, *J. Chromatogr. A*, **1994**, *668*, 375-383.
32. F. M. Winnik, *Macromolecules*, **1987**, *20*, 2745-2750.
33. D. F. Anghel, S. Saito, A. Baran and A. Iovescu, *Langmuir*, **1998**, *14*, 5342-5346.
34. D. F. Anghel, S. Saito, A. Ionescu and A. Bălan, *Colloids Surf. A*, **1994**, *90*, 89-94.
35. F. M. Winnik, M. A. Winnik, S. Tazuke and C. K. Ober, *Macromolecules*, **1987**, *20*, 38-44.
36. F. M. Winnik, M. A. Winnik, and S. Tazuke *J. Phys. Chem*., **1987**, *91*, 594-597.
37. F. M. Winnik, *Chem. Rev*., **1993**, *93*, 587-614.
38. M. A. Winnik, S. M. Bystryak, Z. Liu and J. Siddiqui, *Macromolecules*, **1998**, *31*, 6855-6864.