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Probing the microenvironment of unimicelles constituted of amphiphilic hyperbranched polyethyleneimine using 1-methyl-8-oxyquinolinium betaine

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In this work, the microenvironment of the core of different unimicelles of hyperbranched polyethyleneimine (HPEI) capped with different aliphatic chains (stearate, palmitate, and laurate) dissolved in toluene has been investigated. To achieve this goal we have used 1-methyl-8-oxyquinolinium betaine (QB) as a molecular probe due to its solvatochromic behavior to monitor the micropolarity and hydrogen bond donor ability of the unimicelle cores. QB shows that the micropolarity and the hydrogen bond donor capability of the polar core of reverse unimicellar media are very different than toluene and similar to the one obtained with traditional surfactants that form reverse micellar media but at a very low unimicelle concentration. Particularly, our results show that the hydrogen bonding ability of the core is the driving force for QB to partition toward the unimicellar media.

Introduction

In recent years, core–shell amphiphilic macromolecules (CAMs) based on hyperbranched polymers have attracted much attention because of their impact in supramolecular host–guest chemistry.[1–4] Their encapsulation and controlled release properties open several opportunities in various fields like biomedical research,[5–7] catalytic synthesis and stabilization of nanoparticles.[8–10] The first examples of structures with such properties were illustrated by the use of dendrimers. Seminal studies of Meijer and coworkers[11,12] described the potential of amphiphilic dendrimers as host materials. However, the complex multistep synthesis involved in the production of dendrimers results in expensive products, limiting their practical applications.[13] Nowadays, hyperbranched polymers seem to be excellent candidates to substitute the role of dendrimers in host–guest supramolecular chemistry because of their large scale availability at reasonable costs.

The micellar properties are very well known and desired in the field of CAMs. For this reason these entities are called unimolecular micelles (unimicelles).[14,15] Unlike traditional micelles (multimeric micelles) whose integrity is dictated by the existence of a critical micelle concentration (CMC), unimicelles can act in a wide range of scenarios because all the entity is covalently assembled and in consequence does not exceed a CMC value.[16,17]

When surfactants assemble in non-polar media they form what is known as reverse micelles (RMs), a spatially ordered supramolecular assembly with the polar or charged groups of surfactants located in the interior (core) of the aggregates, while their hydrocarbon tails extend into the bulk organic solvent. RMs are interesting examples of tailorable supramolecular architectures since they provide model systems for interfaces with unique properties.[18] Along these lines, one common approach is to use hyperbranched polyethyleneimine (HPEI) modified with peripheral aliphatic chains as nanoscale building blocks resembling the properties of conventional RMs.[17,19] In this case HPEI represents the hydrophilic core whereas the aliphatic chains constitute the hydrophobic shell, which is ultimately responsible for the solubility of such systems in organic solvents. Scheme 1 shows a schematic representation of these unimicelles. HPEI-C*n* unimicelles (*n* denotes the number of carbons in the carboxylic acid) have been increasingly used in a myriad of fields: encapsulation of dyes,[3,4,17,19,20] nanocarriers for polar drugs,[21] catalysis[22] and stabilization of nanoparticles[9,10] in non-polar media. It is important to note that the boundary between the core and the shell is rather diffuse because of the

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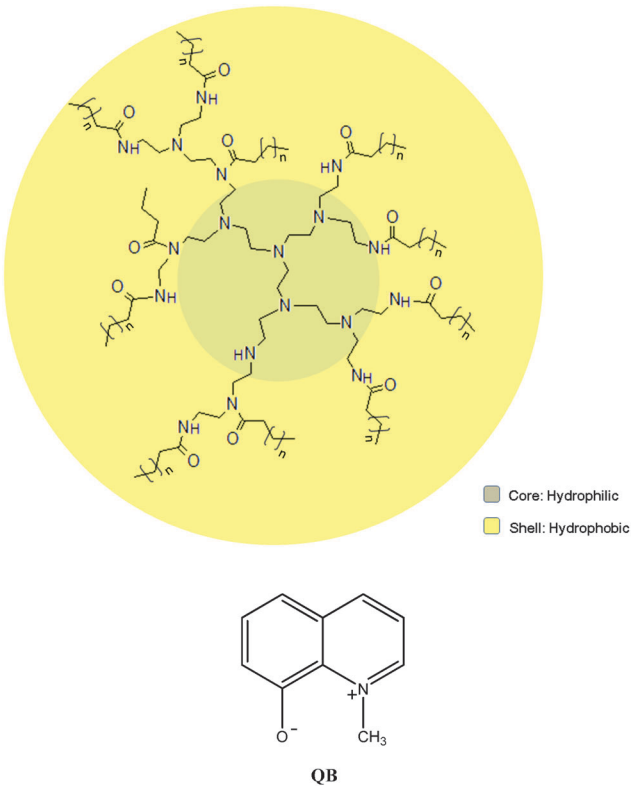

Scheme 1 Schematic representation of unimicelles and the molecular structure of QB.

nature of the core which provides the anchoring points for the capping layer.

The most common approach to monitor the micellar characteristics of such systems is the encapsulation of dyes, which can also serve as an adequate framework to study the hosting of several molecules.[4,20,23] The uptake of hydrophilic dyes was vastly studied using extraction protocols, for example, phase transfer of dyes solubilized in aqueous solution to unimicelles dissolved in non-polar solvents or direct solubilization of solid hydrophilic dyes in unimicelles dissolved in non-polar solvents. In addition, various ways to quantify the extraction capability, like "loading capacity" or "transport capacity" were proposed.[19] However, despite the relevance of these unimicellar systems, the study of valuable micellar properties such as micropolarity or partition constants which are essential to use these building blocks as nanoreactors remains almost unexplored.

The micellar properties can be straightforwardly studied in homogeneous media by assessing the partition of probes between the micellar phase and the solvent.[18,35] This methodology differs from the aforementioned examples in the following point: in our case the probe and the unimicelle are soluble in the non-polar solvent, and the study focuses on the changes observed in the spectral features of the photophysical probe. This strategy is well established in traditional micellar physical chemistry and has been thoroughly employed to study reverse and direct micelles. However, this is the first attempt to characterize unimicelles using this experimental approach. The integration of these photophysical tools in unimicelle characterization would greatly facilitate not only the comparison between unimolecular and multimolecular systems, but also the estimation of valuable physicochemical parameters.

In this work, we performed experiments using unimicelles of HPEI capped with different aliphatic chains (stearate, palmitate, and laurate) dissolved in toluene and, 1-methyl-8-oxyquinolinium betaine as the molecular probe (QB, Scheme 1). The choice of the molecular probe relied on its sensitivity to detect subtle changes in the physicochemical properties of the micellar system. In addition, QB is a well-known molecular probe that presents several advantages.[24] Due to its small size, this probe is considered not to cause important perturbations on the interacting micellar systems. This is an important difference from hydrophilic dyes (rose bengal, congo red, eosin Y or methylthymol blue) typically used to characterize unimolecular micelles[4,15,17,19,20,23] which are significantly bigger than QB. QB is a molecular probe that has an UV-vis absorption spectrum with two major features. A band in the visible region, B_1, which is primarily sensitive to polarity and a band located at shorter wavelengths in the UV region, B_2, which reflects the hydrogen bond donor capability of the solvent.[24,25] Thus, the goal of the present contribution is to study the physicochemical properties such as the micropolarity and the hydrogen bond donor capability of the polar core of reverse unimicellar media.

Materials and methods

Hyperbranched polyethyleneimine (HPEI, M_n = 10 000 Da) and fatty acid chlorides (lauryl, palmitoyl and stearoyl chlorides) were purchased from Sigma-Aldrich. Triethylamine (TEA) was purchased from Sintorgan. All chemicals and solvents used were of the maximum purity available in the market. Prior to use, HPEI was kept under vacuum for 2 days. Chloroform and TEA were purified and dried following standard protocols.[26] Toluene and acetonitrile, both of HPLC grade, were purchased from Sigma-Aldrich and Sintorgan, respectively.

1-Methyl-8-oxyquinolinium betaine (QB) was prepared by a procedure previously reported.[25]

The amine distribution of HPEI was determined by 1D-^{13}C-NMR in $CDCl_3$.[27] The primary : secondary : tertiary amine ratio determined was 31 : 41 : 28.

The synthesis of HPEI capped with aliphatic chains *via* amide bonds was accomplished according to well-established protocols.[12,19] All the compounds were synthesized with a degree of capping of 52% (ratio between acid bound *via* amide bonds and total amines on HPEI). Briefly, HPEI was dissolved in chloroform and TEA was added in a 1.3/1 molar ratio relative to the expected amount of carboxylic acid to be used. The whole system was degassed and filled with nitrogen or argon. The corresponding amount of carboxylic acid chloride (1.05/1 molar ratio in respect of the stoichiometric amount necessary to achieve the desired capping degree) was added dropwise and kept at room temperature for 2–3 days under stirring. The opalescent mixture was filtered and the organic phase was washed several times with

2% Na_2CO_3 and NaCl aqueous solutions. The organic phase was dried using Na_2SO_4, and the solvent was evaporated. The solid was kept under vacuum until constant weight (2–3 days).

All the products were characterized by ^1H, ^{13}C NMR and FTIR spectroscopy. The NMR spectra were recorded on a Bruker ARX 300 (300.1 MHz for ^1H, 75.5 MHz for ^{13}C) using $CDCl_3$ as solvent and $Si(CH_3)_4$ as internal reference. The infrared spectra were recorded on a Nicolet–Nexus FT-IR spectroscope and a Varian 660 FT-IR spectroscope. As an example, HPEI-C12: ^1H NMR ($CDCl_3$) δ = 3.31 (br, $-CH_2CH_2NHCO-$, $-CH_2CH_2NCO-$); 2.52 (m, $-CH_2CH_2NH-$, $-CH_2CH_2N-$); 2.37–1.97 (br, $-NCOCH_2-$); 1.53 (br, $-NCOCH_2CH_2-$); 1.19 (br, $-NCOCH_2CH_2(CH_2)_{12}CH_3$); 0.81 (t, $-NCOCH_2-CH_2(CH_2)_{12}CH_3$). IR ν = 1640 cm^{-1} (amide bond).

Spectroscopic experiments were performed using a constant concentration of QB and variable concentrations of HPEI-C18, HPEI-C16 or HPEI-C12. Solutions of unimicelles were prepared by weight and volumetric dilution. To incorporate the molecular probe, a 0.01 M solution of QB was prepared in acetonitrile. To obtain a given concentration (5×10^{-4} M) of the probe in the unimicellar medium the appropriate amount of this solution was transferred into a volumetric flask, and the acetonitrile was evaporated by bubbling dry N_2; then, the unimicellar solution was added to the residue to obtain [HPEI-C18, C16 or C12] = 10 g l^{-1}. The stock solution of unimicelles and the molecular probe was sonicated to obtain a clear solution. To a cell containing 2 ml of QB of the same concentration in toluene was added the appropriate amount of unimicelles and molecular probe stock solution to obtain a given concentration of unimicelles. In this way, the absorption of the molecular probe was not affected by dilution.

All experimental points were measured three times using different prepared samples. The pooled standard deviation was less than 5%. In all the cases, the temperature was kept at 25 °C ± 0.2 °C.

The UV/visible spectra were recorded using a Shimadzu 2401 spectrophotometer with a thermostated sample holder. The path length used in the absorption experiments was 1 cm. λ_{max} was measured by taking the midpoint between the two positions of the spectrum where the absorbance is equal to 0.90 × A_{max}. The uncertainties in λ_{max} are about 0.10 nm. In all the cases, the corresponding unimicellar solution with the appropriate concentration and without the molecular probe was used as a blank sample.

Results and discussion

QB is a very well-known solvatochromic probe used to test the traditional reversed micellar systems.[24,25] It presents two absorption bands, one in the visible (B_1) and the other in the UV region (B_2) which are sensitive to different environmental properties. It was shown that the position of the maxima in band B_1 correlated well with the π^* parameter (index of dipolarity/polarizability of the media)[28] and the absorbance of the B_2 band is highly sensitive to the hydrogen bonding ability (α, index of the hydrogen bond donor ability of the media, HBD)[28] of the environment. Since the absorbance of the B_1 band has no dependence on the α parameter, the ratio of the absorbances of B_2 to B_1 ($AbsB_2/AbsB_1$) provides an effective method to determine the HBD ability of the microenvironment surrounding the probe. Thus, this ratio in combination with the shifts in absorption bands can be used to determine the micropolarity and the HBD ability of the media at the same time.[24] On the other hand, QB is soluble in toluene, allowing studying partition coefficients between different pseudophases: the external organic solvent and the unimicellar media, and important interfacial properties are deduced.[24,25]

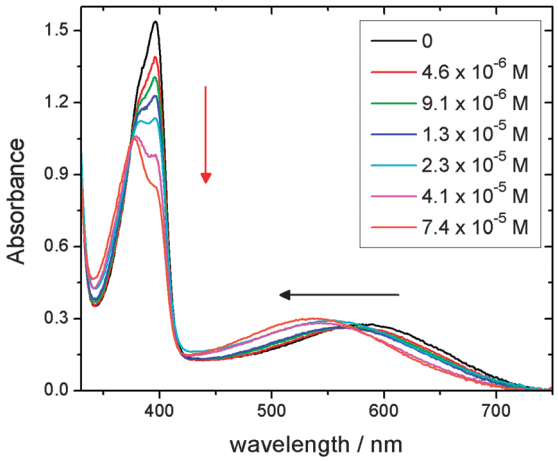

Fig. 1 Evolution of absorption spectra of QB with increasing concentrations of HPEI-C18. The inset indicates the concentrations used. The black arrow shows the shift of band B_1 and the red arrow denotes the decrease in band B_2 (at 396 nm).

Fig. 1 shows the spectra of QB recorded with varying concentrations of HPEI-C18 at 25 °C in toluene. It can be seen that the B_1 band presents a hypsochromic shift with the concentration of the unimicelles, while the B_2 band exhibits a pronounced decrease of the absorbance at λ = 396 nm.

Fig. 2 summarizes the data collected from Fig. 1 and, presents the variation in the position of the maxima of band B_1 (Fig. 2A) and the $AbsB_2/AbsB_1$ ratio (Fig. 2B) with increasing HPEI-C18 concentrations. In the concentration range studied, the B_1 band shows an important hypsochromic shift ($\approx$44 nm) indicating a more polar microenvironment when the concentration of HPEI-C18 increases. This can be explained if we consider the nature of the core and the interface between the core and the shell in the unimicelles. The core is a polyaminated structure while the diffuse interface presents a large number of amide bonds. These two regions are clearly more polar than toluene, a fact that accounts for the shift observed. The transition energy of the B_1 band (in kcal mol^{-1}) can be used as a polarity parameter, E_{qb},[24a] and this E_{qb} can be correlated with the well-known Dimroth and Reichardt polarity parameter, $E_T(30)$[29] using the linear relationship found by Ueda and Schelly:[25a]

$$E_T(30) = 1.712\ E_{QB} - 49.7 \quad (1)$$

For example, at [HPEI-C18] = 7.4×10^{-5} M, the last point of the concentration range studied presents the B_1 band centered at λ = 540.5 nm, E_{qb} = 52.91 kcal mol^{-1} and $E_T(30)$ = 40.88 kcal mol^{-1}

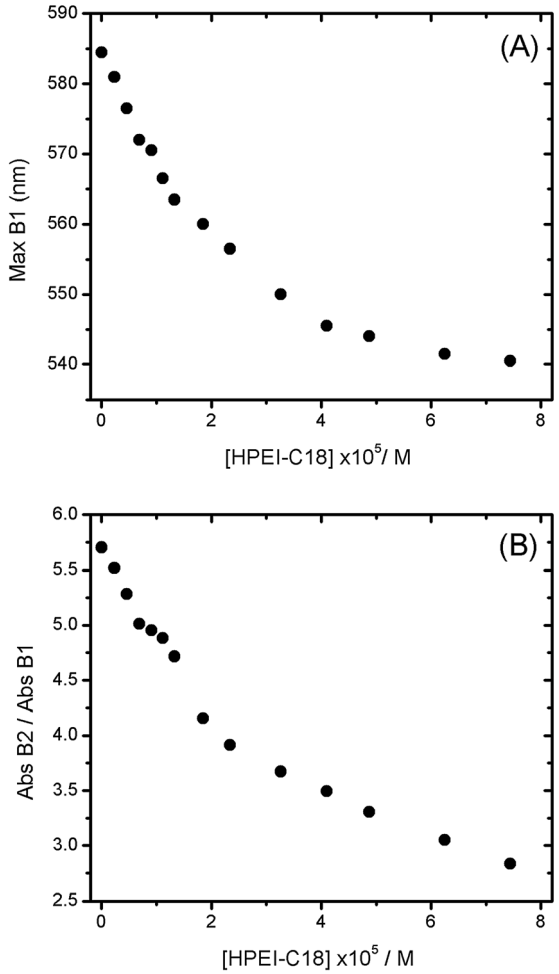

Fig. 2 (A) Evolution of maxima in B_1 band with increasing concentrations of HPEI-C18. (B) Evolution of the ratio of $AbsB_2$ (at 396 nm)/$AbsB_1$ (in maxima) with increasing concentrations of HPEI-C18.

values can be obtained through eqn (1). It is interesting to note that the value obtained for the $E_T(30)$ parameter is very similar to those reported by Correa *et al.*[30] for benzyl-*n*-hexadecyl-dimethyl-ammonium chloride (BHDC) RMs in benzene but lower than sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT) in the same solvent. It must be noted that in the aforementioned experiments on AOT and BHDC RMs, the surfactant concentration was 600 times higher than the unimicelle concentration employed in our work. This difference clearly illustrates the very strong affinity of QB for the unimicellar pseudophase. That is, with this new system similar properties to the one obtained with traditional surfactants can be achieved but at very low unimicelle concentration, which is very exciting for using it as a nanoreactor.

Fig. 2 describes a pronounced decrease in the $AbsB_2/AbsB_1$ ratio upon increasing the concentration of unimicelles in solution. At the highest concentration of HPEI-C18 the ratio $AbsB_2/AbsB_1 \approx 2.8$, which implies that the magnitude of this decrease ($\Delta AbsB_2/AbsB_1$) within the experimental concentration range is close to 2.9 units (see Table 1). The results reflect that QB senses a microenvironment within the unimicelle core with high H-bond donor capabilities. Considering that the degree of

Table 1 Parameters obtained for the systems studied in the experimental concentration range

Compound	K_p (M^{-1})	ΔB_1[a]	$AbsB_2/B_1$*[b]	$\Delta AbsB_2/AbsB_1$[c]
HPEI-C18	3.11×10^4	43.5	2.82	2.93
HPEI-C16	2.65×10^4	41.0	2.97	2.64
HPEI-C12	2.87×10^4	38.0	3.12	2.53

K_p, partition constant obtained using eqn (6). [a] ΔB_1 refers to shift of the maxima of B_1 band in a unimicelle concentration range between 0 and $\approx 7.4 \times 10^{-5}$ M. [b] $AbsB_2/AbsB_1$* refers to the value of this $AbsB_2/AbsB_1$ ratio obtained for the highest concentration of CAM within the concentration range. [c] $\Delta AbsB_2/AbsB_1$ refers to the magnitude of the decrease of the $AbsB_2/AbsB_1$ parameter within the experimental concentration range.

capping of the unimicelles is 52% and the percentage of primary plus secondary amines in the starting HPEI core is around 72%, one can conclude that nearly 50% of secondary amines still remain unaltered after covalently linking the capping layer. Hence, this population of secondary amines is responsible for conferring H-bond donicity to the unimicelle core. In addition, amide bonds at the interface (amides derived from the primary amine still possess a hydrogen), could also contribute to the HBD ability of the core. Interestingly the $AbsB_2/AbsB_1$ ratio value is lower than the one obtained for AOT and BHDC RMs[30] reflecting the larger HBD donicity of the unimicelle core in comparison with the traditional ionic RMs.

In order to gain more insights into the interaction of QB with the reverse unimicellar media, the partition of QB between the unimicellar RMs and the external solvent was treated within the framework of the pseudophase model.[31–35] This model considers the RMs as distinct pseudophases whose properties are independent of the surfactant concentration. Thus, only two solubilization sites are considered, that is: the external solvent and the RM interface (*i.e.* all the surfactant molecules). In this way, the distribution of QB between the micelles and the external solvent pseudophase defined in eqn (2) can be expressed in terms of the partition constant K_p shown in eqn (3):

$$QB_f \rightleftarrows QB_b^{\#} \quad (2)$$

$$K_p = \frac{[QB]_b^{\#}}{[QB]_f} \quad (3)$$

The terms in brackets represent free (f) and bound (b) molecular probes in terms of the local micellar concentration. If $[QB]_b$ is the analytical (bulk) concentration of the molecular probe bound to the micelle, eqn (4) holds.

$$[QB]_b^{\#} = \frac{[QB]_b}{[\text{Unimicelle}]} \quad (4)$$

and hence K_p can be expressed as in eqn (5)

$$K_p = \frac{[QB]_b}{[QB]_f[\text{Unimicelle}]} \quad (5)$$

where $[QB]_f$ is the concentration of the substrate in the organic solvent and [unimicelle] is the unimicelle concentration.

The values of K_p can be determined from the absorbance changes (at a given wavelength) in the QB absorption spectra

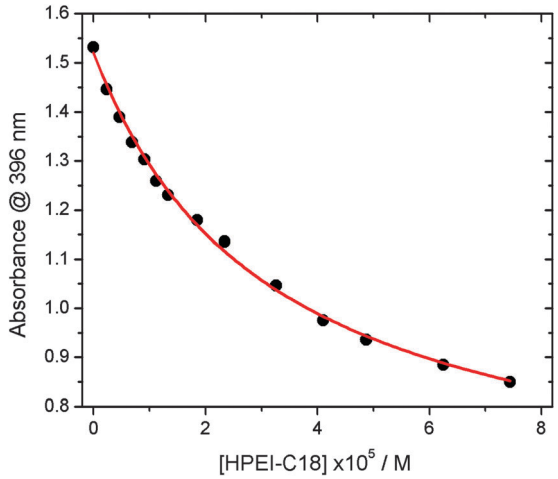

Fig. 3 Evolution of the absorbance values at λ = 396 nm with increasing concentrations of HPEI-C18. The red curve depicts the fitting of the experimental data using eqn (6).

upon varying the surfactant concentrations. Thus, for QB, K_p was determined using eqn (6)[36]

$$A^{\lambda} = \frac{(\varepsilon^{f} + \varepsilon^{b}[\text{Unimicelle}]K_p)[\text{QB}]_T}{(1 + K_p[\text{Unimicelle}])} \quad (6)$$

where A^{λ} is the absorbance at different surfactant concentrations, ε^{f} and ε^{b} are the molar extinction coefficients of QB obtained in toluene and in the unimicellar media, respectively, and $[\text{QB}]_T$ is the total dye concentration.

Fig. 3 shows the representative plots of QB absorbance values recorded at λ = 396 nm as a function of HPEI-C18 concentration. Data at [HPEI-C18] = 0 corresponding to QB in the pure toluene is also plotted for comparison. Data shown in the figure were fitted to eqn (6) using a non-linear regression method and, the K_p value obtained is 3.11 × 10^4 M^{-1} (Table 1), revealing a strong interaction between QB and the unimicelle. It must be noted that for molecular probes that are sensitive to hydrogen bonding interaction, such as different nitroanilines[37a] and amines[37b] and, PRODAN,[36] values of K_p between 1 and 1000 were obtained in traditional RMs.

With the aim of studying the effect of the chain length of the capping layer, we performed similar experiments using HPEI-C16 and HPEI-C12 unimicelles. It is evident that the evolution of the B_1 band and the $AbsB_2/AbsB_1$ ratio of QB upon increasing the unimicelle concentration follows a trend similar to that observed in HPEI-C18 systems (Fig. 4).

Fig. 5 shows the QB absorbance values recorded at λ = 396 nm as a function of HPEI-C16 and HPEI-C12 concentrations, respectively. Fitting of experimental data according to eqn (6) prompted the estimation of K_p values which are summarized in Table 1.

There is no clear tendency in the experimental data to attribute any significant influence of the chain length to the hypsochromic B_1 shift and the absorbance ratio variation. Moreover, in all the cases, the K_p values are quite large (in the range of 2.6–3.1 × 10^4 M^{-1}) regardless of the chain length. It can be hypothesized that as one increase the chain length of the capping layer, the larger is the hydrophobicity of the shell with the consequent decrease in K_p values. Our data do not confirm this assumption and, the fact that we do not observe tendencies with the chain length could be interpreted if one considers that the interaction between QB and the unimicelle is

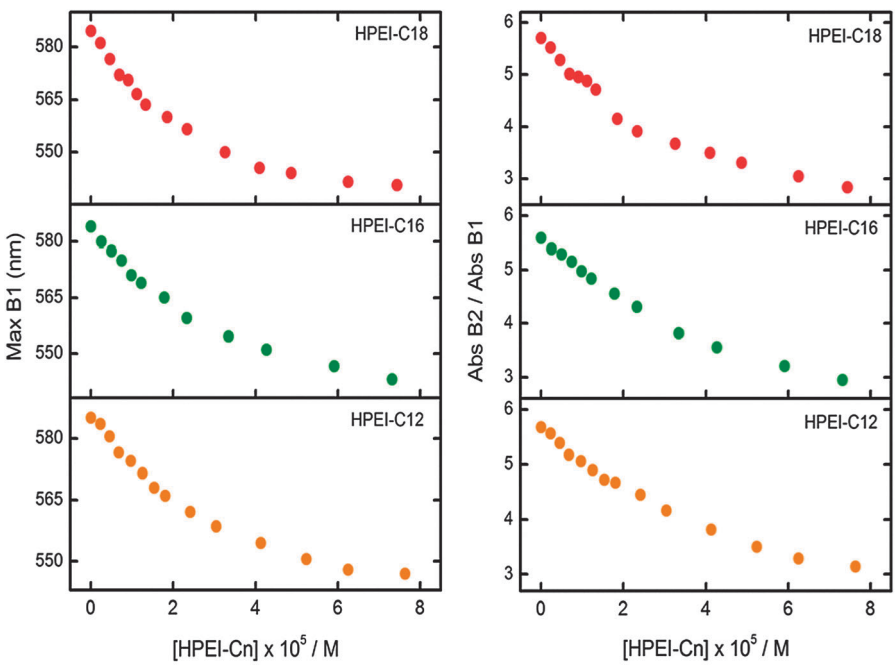

Fig. 4 Evolution of maxima in B_1 band with increasing concentrations of HPEI-C*n* (left) and $AbsB_2/AbsB_1$ ratio values with increasing concentrations of HPEI-C*n* (right).

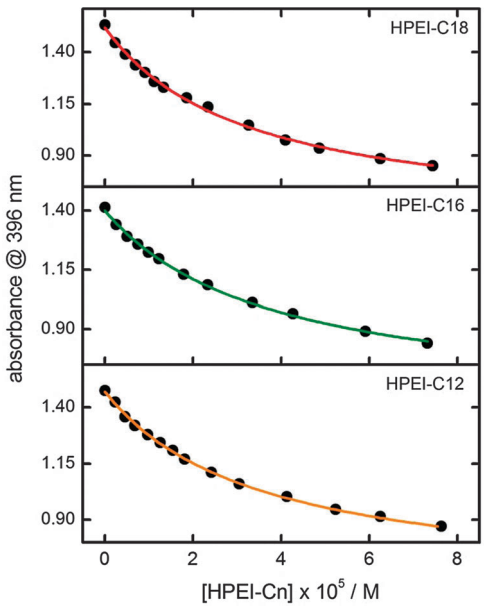

Fig. 5 Evolution of the absorbance values at λ = 396 nm with increasing concentrations of HPEI-C*n*. Solid curves depict the fitting of the experimental data using eqn (6).

focused on the core of the unimicelles. In other words, the unique hydrogen bond donor ability of the core can be considered to be the driving force that makes QB to penetrate the unimicellar media. In this situation, QB shows that the aliphatic tails in the structure solely act as solubilization agents facilitating the dissolution of the unimicelles in non-polar solvents but do not offer specific interaction sites as the core does. Interestingly, very recently the role of H-bonds in the hierarchical structure of an aggregating amphiphile–oil solution containing a coordinating metal complex was shown by means of atomistic molecular dynamics simulations and X-ray techniques. For the first time, the authors showed that H-bonds not only stabilize the metal complex in the hydrophobic environment, but also affect the growth of such reverse micellar aggregates.[38]

Conclusions

We have addressed the microenvironment of unimicelles, constituted by HPEI and long chain aliphatic acids, using the very well-known probe QB. The partition constants and data for the micropolarity and hydrogen bond donicity were obtained. These parameters are very useful in order to understand the behavior of CAMs although their investigation is not very common in the field of unimicelles derived from hyperbranched polymers. All the CAMs studied present large K_p (over 10^4 M^{-1}) values which are independent of the chain length, demonstrating a strong specific interaction between the hyperbranched core and the probe. QB is located in a polar microenvironment with high hydrogen bond donicity, which is consistent with the structure of the HPEI core.

We think that the approach used in this work is powerful and could make a substantial contribution to the study of the properties of CAMs especially if they will be used as nanoreactors or in molecular recognition.

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