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Fluorescent probes for detection of amphiphilic polymer hydrophobic microdomains: A comparative study between pyrene and molecular rotors

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Abstract Cationic amphiphilic polymers (e.g. polyvinylpyridinium bromides and polyvinylimidazolium bromides) adopt a compact coiled form in aqueous solutions. In the case of former polymers, the resulting hydrophobic microdomains are evidenced only by fluorescence spectroscopy if a molecular rotor (DMAC) is used as a fluorescent probe, while the behaviour of the latter can be studied in aqueous solution by using both types of fluorescent probes, i.e., pyrene and the molecular rotor. The purpose of the present investigation deals with a comparative study between the magnitude of the local viscosity and the polarity of the hydrophobic microdomains generated by poly(3-hexadecyl-1-vinylimidazolium bromide) in an aqueous medium using pyrene and DMAC as fluorescent probes. Moreover, the results are compared with the data obtained with micelles of conventional surfactants such as the homopolymer repetitive unit model and CTAB.

Key words Pyrene – molecular rotor – cationic amphiphilic polymers – cationic surfactants – fluorescence spectroscopy

Introduction

Among the various water-soluble polymers, cationic amphiphilic polymers are of great interest due to their physico-chemical properties [1], possibility of self-aggregation due to hydrophobic interactions allowing the use of the micelle-like pseudo-phase for dissolution and transport of lipophilic substances, adsorption at interfaces (e.g. water/air and water/organics). A subclass of these polymers (according Berger's classification [1]) is established each time the cationic charge is located on an atom belonging to a chain pendent to the polymer backbone (external cationic polymers). In this subclass are ranked the polymers derived from basic polyheterocycles (imidazole, pyridine) in which the nitrogen atom is quaternized with a long alkyl chain (12 and 16 carbon atoms). The polyalkylvinylimidazolium and polyalkylvinylpyridinium salts are classified as polysoaps belong to this category [2].

In order to study the aggregation way of this kind of polymers in aqueous medium, a widely used technique is the fluorescence spectroscopy with pyrene as a probe [3]. This polarity probe, particularly well-suited in the case of polyalkylvinylimidazolium salts [4], is proved ineffective for polyalkylvinylpyridinium salts [5], because the long alkyl chain quaternized pyridine rings are responsible of pyrene quenching.

In order to circumvent the quenching process, molecular rotors as fluorescent probes (sensitivity to solvation, polarity and molecular mobility changes) were chosen, particularly for their very low excited state lifetimes (from 0.01 to 5 ns). Indeed, a cinnamylidene rotor has been proven to be a powerful polarity and cohesion probe, both to detect and characterize hydrophobic microdomains in poly(1-hexadecyl-3-vinylpyridinium bromide) and in poly (methylvinylpyridinium-*co*-hexadecylvinylpyridinium dibromide) in aqueous solutions [5].

For an in-depth study, we would like to confront the polarity information of a system obtained with a molecular rotor to those provided with pyrene as a probe. Indeed this comparison can be only quantified with systems which do not present quenching processes, as for example the imidazolium derivatives, but requires at first, a study on the behaviour of the two probes in solvents of different polarities, so as to establish polarity scales.

In this paper, we report on the first results regarding a comparative study using either pyrene or a cinnamylidene molecular rotor as probes in order to detect in an aqueous medium the polarity of hydrophobic microdomains resulting form intra- and/or intermolecular associations in the case of the cationic amphiphilic polymer, polyhexadecylvinylimidazolium bromide. The polarity measurements of this system will be compared, for each of the two probes, with that of conventional surfactants, of HMIB (an analogue of the polymer repetitive unit) and of a widely used surfactant such as CTAB.

Finally, using the molecular rotor as a probe, the results obtained for the polyvinylpyridinium and polyvinylimidazolium salts and their surfactants repetitive unit models allow the study of the influence of heterocycle chemical nature (imidazole and pyridine) on the aggregation way.

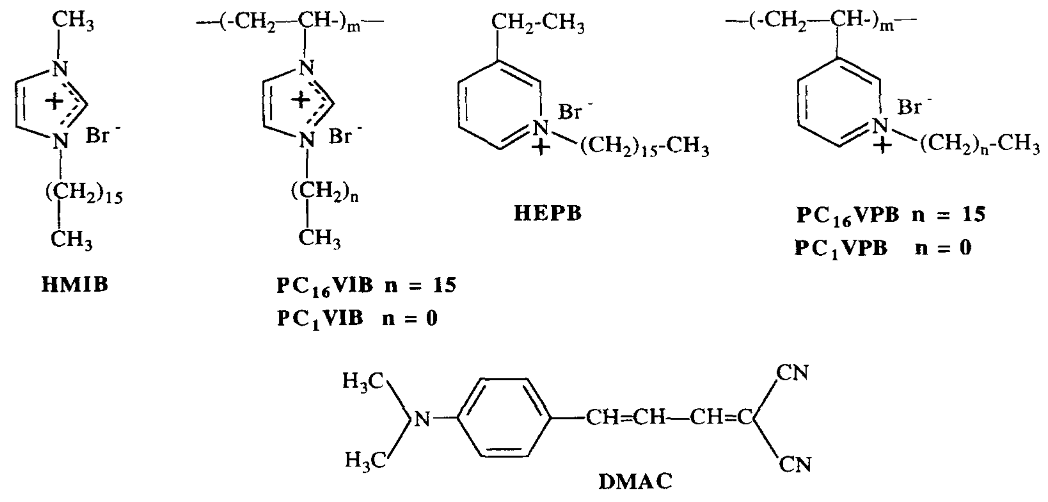
Experimental part

Materials

The synthesis of the homopolymers PC_1VIB, PC_1VPB, $PC_{16}VIB$, $PC_{16}VPB$ and their models HMIB and HEPB have been described elsewhere (see Scheme 1) [4, 6]. The rotor 1,1-dicyano-(4′-dimethylaminophenyl)-1,3-butadiene (DMAC) was synthesized according to a Knoevenagel's reaction between 4-(N,N-dimethylamino) cinnamaldehyde and malononitrile with an 84% yield after recrystallization from ethyl acetate (m.p. = 147 °C; literature 146–148 °C [7]). Commercial cetyltrimethylammonium bromide (CTAB) from Fluka was purified according to the method reported by Duynstee and Grunwald [8]. Pyrene was purchased from the Community Bureau of Reference (N° 177).

Methods

Absorption spectra were recorded on a Perkin Elmer (Lambda 2) UV/vis spectrophotometer. Fluorescence emission spectra were recorded on a Spex fluorolog-2 spectrometer equipped with a thermostatically controlled cell at 30 °C for CTAB, imidazolium derivatives PC_1VIB, $PC_{16}VIB$ and HMIB. At fixed concentration of pyrene (1.33×10^{-6} M in the final solution) no excimer band was observed. All the samples were excited at 332 nm and the emission spectra of pyrene shows vibronic peaks at $\lambda_1 = 371$–373 nm (intensity I_1) and $\lambda_3 = 382$–384 nm (intensity I_3), with a slit width = 0.5 mm ($\Delta\lambda_{1/2} = 2$ nm). Stock solutions were prepared by dissolution of the polymer or the surfactant in an aqueous mixture (ethanol/1-propanol/water, 1/3/96, v/v/v). For DMAC



Scheme 1 Chemical structures of the surfactants, amphiphilic polymers and the molecular rotor used in this work

(2.6×10^{-6} M), spectra were recorded in the range 500–600 nm (slit width 1.5 mm; $\Delta\lambda_{1/2} = 6$ nm) and the excitation wavelength ($\lambda_{ex} = 490$ nm) generates in all solvents only one single fluorescence peak, the position of which is medium-dependent.

Solvents used for UV-visible absorption and fluorescence studies were of spectral grade and were purified before use by distillation. Their water contents do not exceed 0.1% (weight).

Results and discussion

In aqueous solution, the cationic amphiphilic polymers form a microphase structure, the association properties of which are comparable to those of micelles of conventional surfactants. According to the polymer structure, and particularly, in the absence of long chain pyridinium units which would be responsible for a probe quenching phenomenon (e.g. pyrene), the formation of hydrophobic microdomains in polyvinylimidazolium salts can be detected in aqueous media with both pyrene and molecular rotors as fluorescence probes.

Establishment of a polarity scale for DMAC rotor and pyrene

As shown in Fig. 1, the fluorescence wavelength of the molecular rotor DMAC depends on solvent polarity. In all solvents, polar or not, only one single band is observed for DMAC. In a polar solvent (e.g. water), the fluorescence maximum is red shifted by about 50 nm with reference to toluene. The use of solvents of different polarities allowed us to establish a DMAC rotor polarity scale [5]. By plotting the fluorescence emission wavelength [$\lambda_{f\,max}$] of DMAC vs. empirical polarity parameters $E_T(30)$ (intramolecular charge transfer band of the pyridinium-N-phenolbetaine) defined by Dimroth and Reichardt [9], two distinct correlations were deduced according to aprotic $\underline{1}$ and protic $\underline{2}$ (see Fig. 2).

Keeping in mind the idea of a comparison study with pyrene, the variation of the I_1/I_3 ratio [I_1 = intensity of the (0.0) peak at 372 nm; I_3 = intensity of the (0.2) peak at 382 nm] was measured for pyrene in various solvents. Indeed, pyrene as a polarity probe has been widely used [3, 4, 10]. This ratio, which has been proved to correlate with solvent polarity, is equal to about 0.6 in hydrocarbons, 1.2 in ethanol and 1.9 in neat water, as measured with our spectrofluorimeter (note that they are in good agreement with the reported values by Dong and Winnik [11], in spite of a different apparatus function). The plot of the I_1/I_3 ratio as a function of the $E_T(30)$ values for several solvents is shown in Fig. 3 (some Dong and Winnik's values are also plotted). Two correlations were also obtained: intensities I_1/I_3 ratio values are linearly correlated with $E_T(30)$, $\underline{1}$ for aprotic and $\underline{2}$ for protic solvents.

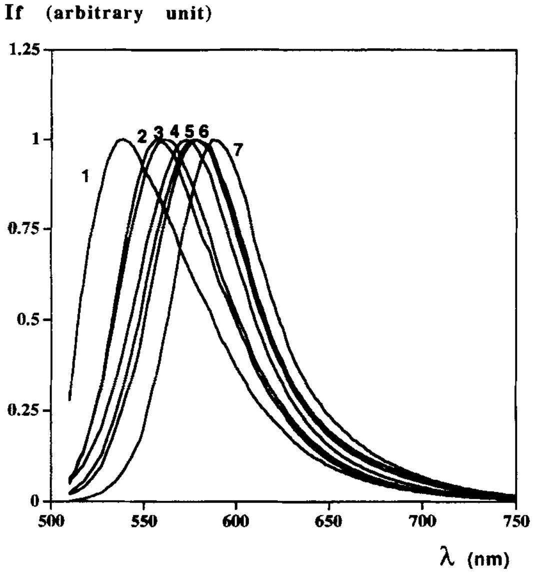


Fig. 1 Steady-state fluorescence spectra for DMAC recorded in various solvents at $\lambda_{ex} = 490$ nm. 1) toluene, 2) chloroform, 3) ethylacetate, 4) 2-butanol, 5) ethanol, 6) methanol, 7) water

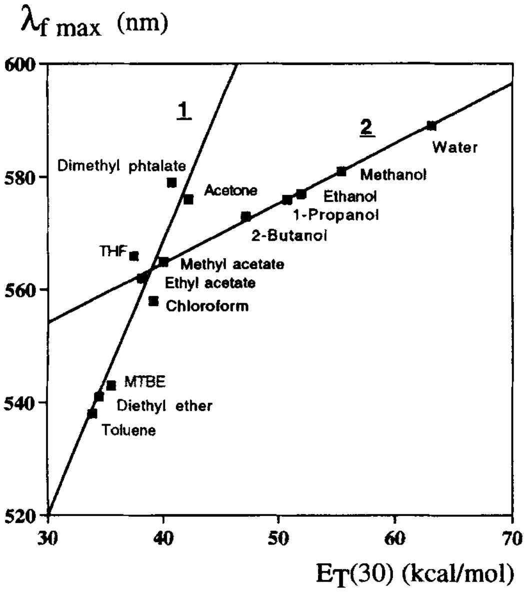


Fig. 2 Plot of $\lambda_{f\,max}$ values for DMAC vs $E_T(30)$ values. $\underline{1}$ aprotic solvents, $\underline{2}$ protic solvents

Polarity studies

Now, let us deal with systems capable of self-organizing in aqueous media and, more particularly, with cationic amphiphilic polymers ($PC_{16}VIB$) and conventional cationic surfactant (HMIB and CTAB) forming hydrophobic microdomains and micelles respectively. The surrounding polarity in each case can be detected by both types of fluorescence probes, pyrene and molecular rotor DMAC.

Pyrene as a polarity probe

Figure 4 illustrates the dependence of the ratio I_1/I_3 for pyrene as a function of the polymer or the surfactant concentration (medium: ethanol/1-propanol/water, 1/3/96, v/v/v). In the case of the homopolymer $PC_{16}VIB$, the decrease of the I_1/I_3 ratio occurs in a rather broad range of concentrations and the beginning of the detection of the microdomains formation was observed at the threshold concentration of the monomer units C_m: $C_m(PC_{16}VIB) = 1.7\ 10^{-5}$ mol/l (see Table 1). As expected, no variation was observed for the homopolymer PC_1VIB which is fully quaternized by methyl groups. In this latter case, the polarity sensed by the probe is that measured for the solvent medium itself (close to the polarity of water, $I_1/I_3 = 1.83$). For conventional surfactants such as HMIB and more particularly for CTAB, the transition is sharper and appears at a higher concentration than for the C_{16} homopolymer: CMC (HMIB) $= 4.5\ 10^{-4}$ mol/l,

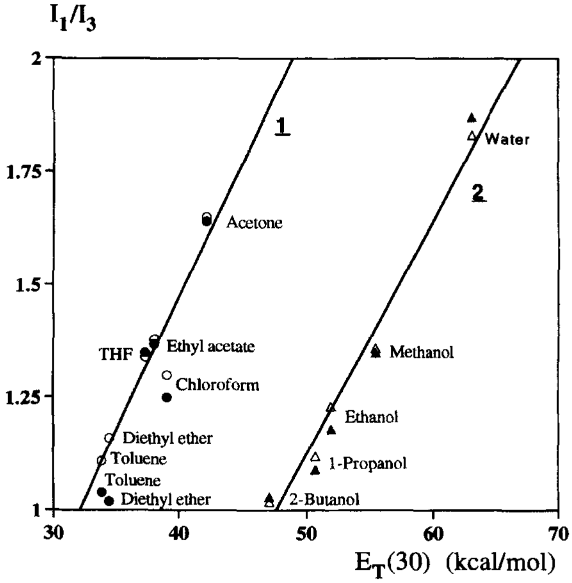


Fig. 3 Plot of I_1/I_3 ratio values vs $E_T(30)$ values. 1 aprotic solvents, ○ this work; ● Dong and Winnik [11] 2 protic solvents, △ this work, ▲ Dong and Winnik [11]

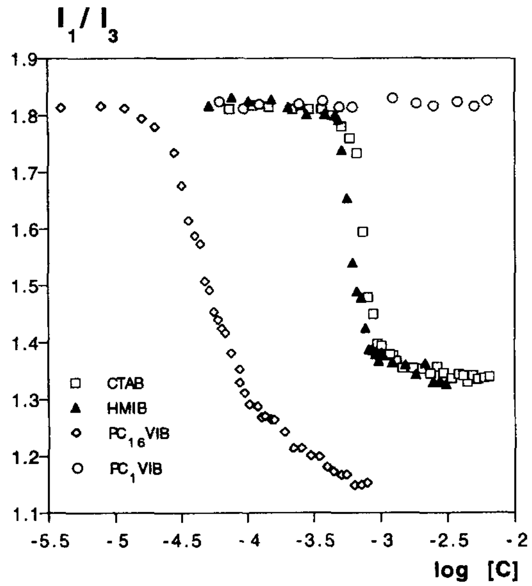


Fig. 4 Variations of I_1/I_3 with the concentration of polymers $PC_{16}VIB$, PC_1VIB and surfactants HMIB, CTAB (logarithmic scale). $T = 30\,^{\circ}C$, medium: ethanol/1-propanol/water, 1/3/96, v/v/v

Table 1 Data obtained from the use of the two fluorescent probes (DMAC and pyrene)

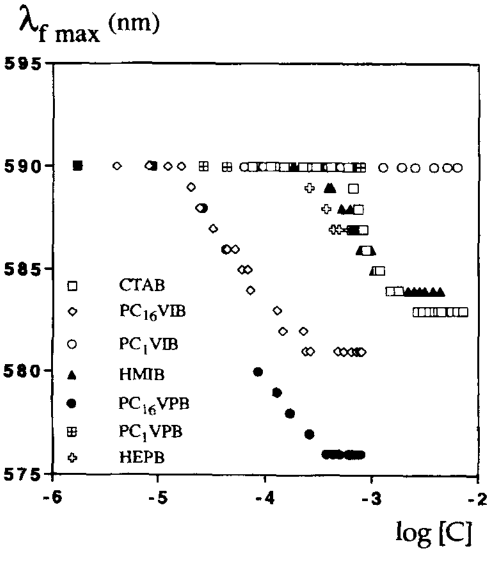
	DMAC					Pyrene		
	Polarity			Cohesion		Polarity		
Polymer or surfactant	$\lambda_{f\,max}$ (nm)	$\Delta\lambda_{f\,max}$ (nm)	CMC or C_m (mol/l)	Φ_f/Φ_{f_0}	CMC or C_m (mol/l)	I_1/I_3	$\Delta(I_1/I_3)$	CMC or C_m (mol/l)
$PC_{16}VIB$	581	9	$1.6\ 10^{-5}$	3.8	$1.65\ 10^{-5}$	1.15	0.66	$1.7\ 10^{-5}$
HMIB	584	6	$4\ 10^{-4}$	3.8	$4.3\ 10^{-4}$	1.33	0.51	$4.5\ 10^{-4}$
$PC_{16}VPB$	576	14	$2.3\ 10^{-5}$	4.6	$2.5\ 10^{-5}$	No possible measurement due to quenching phenomena		
HEPB	587	3	$3.9\ 10^{-4}$	2.8	$3\ 10^{-4}$			
CTAB	583	7	$6.3\ 10^{-4}$	3.9	$6.3\ 10^{-4}$	1.34	0.47	$5\ 10^{-4}$

CMC(CTAB) = 5×10^{-4} mol/l. Thus, the CTAB value is slightly lower than that given in the literature: CMC(CTAB) = $8.7\,10^{-4}$ mol/l [12]. It has to be noted that the final polarities (at the plateau) detected by pyrene in the micelle microenvironment for these two surfactants are almost identical ($I_1/I_3 \approx 1.33$), while for the homopolymer $PC_{16}VIB$, I_1/I_3 is leveled out at 1.15. This result indicates that the pyrene probe detects the same polarity microenvironment for the two surfactants, their only structural chemical difference being the polar head. Therefore, the most plausible explanation is that the pyrene probe location is in the neighborhood of the hydrophobic tails of HMIB or CTAB micelles. From the polarity scale (Fig. 3), the polymer microdomains polarity is comparable to that of the protic organic solvent, ethanol, while the micelles are more polar (e.g. methanol). This observation might be due to a faster dynamic exchange of detergent molecules between aggregates and bulk water for micelles than for polymer microdomains [13].

Molecular rotor DMAC as a polarity probe

Using the cinnamylidene molecular rotor DMAC as a polarity probe, the study was also performed on PC_1VIB, $PC_{16}VIB$, HMIB and CTAB (Fig. 5, note that previous results [5] for PC_1VPB, $PC_{16}VPB$, HEPB are figured). As expected, in the case of PC_1VIB, no variation is observed and the polarity detected by the rotor is identical to that of water ($\lambda_{f\,max} = 590$ mn). For the polysoap and the conventional surfactants, the plots of $\lambda_{f\,max}$ as a function of the concentration (polymer or surfactant) present an identical profile with that obtained with pyrene as the probe. The largest variation was also observed for the homopolymer ($\Delta\lambda_{f\,max} = 9$ nm) and the lowest one for HMIB ($\Delta\lambda_{f\,max} = 6$ nm). For this latter surfactant model, the $\lambda_{f\,max}$ variation for the rotor vs log[C] presents a clear break, identical to that obtained for the formation of CTAB micelles ($\Delta\lambda_{f\,max} = 7$ nm). One of the most interesting observation comes from HMIB and CTAB, for which, as compared to the study with pyrene, a slight difference for the microenvironment polarity is observed with the molecular rotor. From the final plateau values, which express the degree of polarity, the surfactant model HMIB leads to an organized assembly, the polarity of which is slightly higher than that of CTAB micelles.

Fig. 5 Fluorescent emission maximum of DMAC plotted against the polymers ($PC_{16}VIB$, PC_1VIB, $PC_{16}VPB$, PC_1VPB) and the surfactants (HMIB, CTAB, HEPB) concentration (logarithmic scale)



The variation of $\lambda_{f\,max}$ vs log[C], is characterized by an earlier and progressive transition for polymer $PC_{16}VIB$ as compared with the conventional surfactants. This behaviour reflects the gradual formation of hydrophobic microdomains, the polarity of which is lower than that of HMIB micelles. Referring to the behaviour of micelles, the organization of the polymer is such that the restriction of motion inhibits the penetration of water.

From each curve $\lambda_{f\,max}$ vs log[C], it is possible to determine C_m or CMC values which are reported in Table 1. They are in good agreement with the values using pyrene as the polarity probe.

Comparison of pyrene and molecular rotor DMAC as polarity probes

A better comparison can be visualized by gathering, for each type of compound (polymer $PC_{16}VIB$, surfactant HMIB and reference CTAB), the results stemming from the use of both, molecular rotor DMAC and pyrene.

Indeed, using the previous polarity scales (Figs. 2 and 3 for DMAC and pyrene respectively), a correspondence was established between the two responses for both pyrene ($\Delta(I_1/I_3) = 0.6$) and rotor DMAC ($\Delta\lambda_{f\,max} = 12$ nm) for a given polarity evolution, i.e., from water to ethanol through the empirical parameter $E_T(30)$. Thus, one can plot together the variations of the two parameters I_1/I_3 and $\lambda_{f\,max}$ as a function of log C (polymer or surfactant concentration).

The resulting curves (Figs. 6a, 6b and 6c) prove in terms of polarity for all compounds that the pyrene probe senses a more hydrophobic microenvironment than that detected with the molecular rotor (decrease of I_1/I_3 ratio is higher than $\Delta\lambda_{f\,max}$). This observation expresses the fact that pyrene is located more inside the hydrophobic microdomains whereas the rotor is more at the periphery (because of its polar functions).

Cohesion studies with the molecular rotor DMAC

Owing to the dependence of fluorescence quantum yield Φ_f with viscosity, molecular rotors can also be used as cohesion fluorescent probes [14–16]. Figure 7 shows the variation of the relative efficiency of the rotor Φ_f/Φ_{f_0} (where Φ_{f_0} represents the fluorescence quantum yield in water) as a function of log C (polymer or surfactant concentration) for PC_1VIB, $PC_{16}VIB$, HMIB and CTAB (note that previous results [5] for PC_1VPB, $PC_{16}VPB$, HEPB are also plotted).

As expected, no variation was observed for PC_1VIB. For $PC_{16}VIB$ and HMIB, the increase of the fluorescence quantum yield (four-fold) shows that the formation of hydrophobic microdomains or micelles is accompanied by an increase of the local order (the behaviour of each organized system will be discussed further in the next section).

From each curve Φ_f/Φ_{f_0} vs. log [C], it is also possible to determine C_m or CMC values which are gathered in

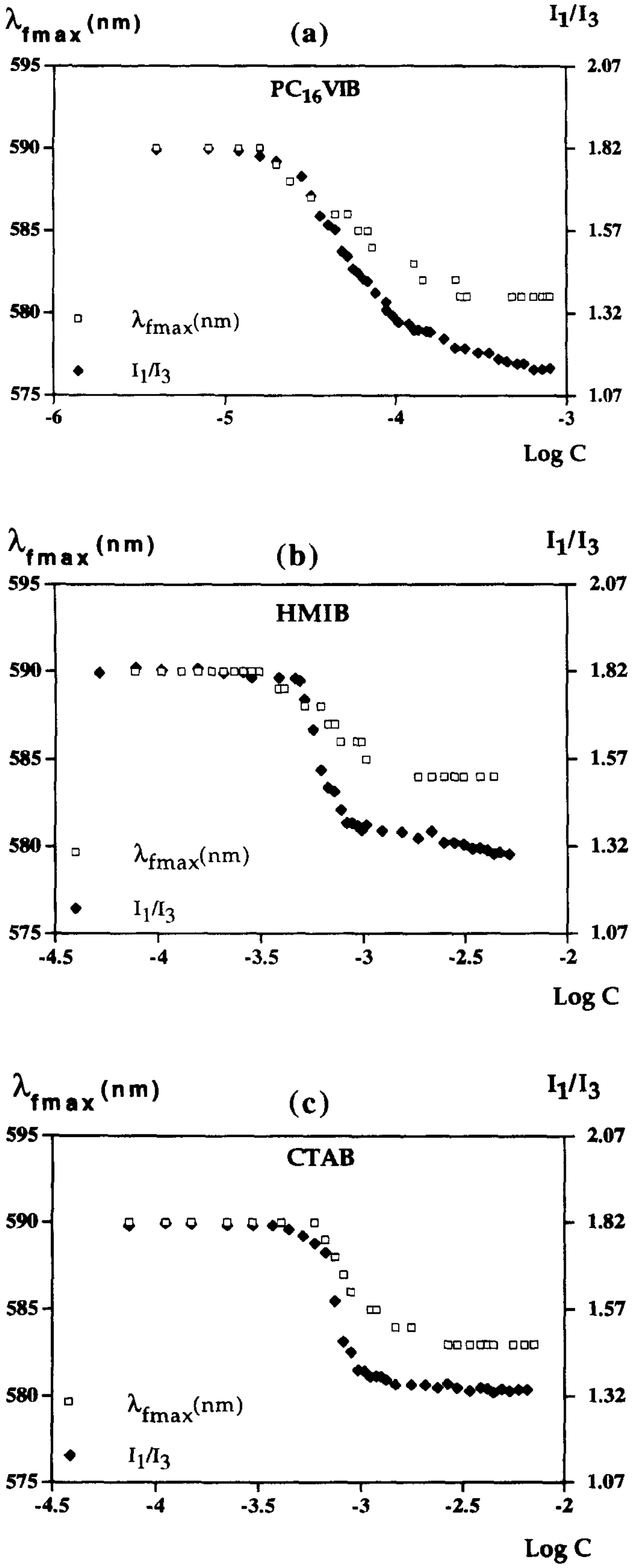


Fig. 6 Comparison (referring to the polarity scales) between the variations of $\lambda_{f_{max}}$ of the molecular rotor DMAC and the variations of I_1/I_3 ratio (pyrene) as a function of the concentration (polymer $PC_{16}VIB$ and surfactants HMIB, CTAB). a) $PC_{16}VIB$ b) HMIB c) CTAB

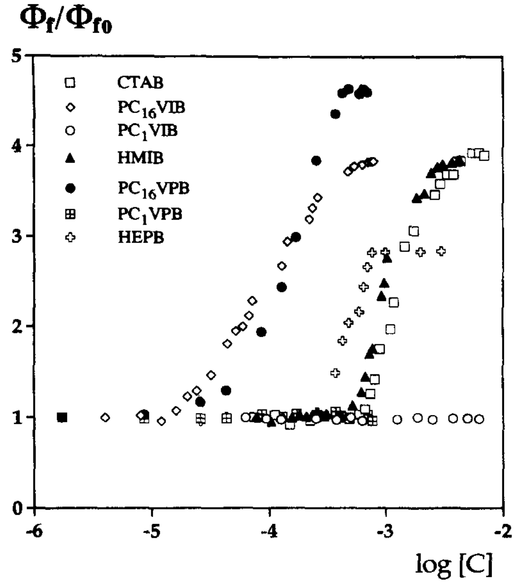


Fig. 7 Fluorescence quantum yield ratio Φ_f/Φ_{f_0} as a function of the polymers and surfactants concentration (logarithmic scale)

Table 1. They are in very good agreement with those determined using rotor-DMAC as the polarity probe.

Effect of the nature of polar heads of the amphiphilic cationic systems on their association behaviour by using the molecular rotor DMAC as polarity and cohesion probe

Homopolymers ($\mathrm{PC_{16}VIB}$ and $\mathrm{PC_{16}VPB}$), surfactant models (HMIB and HEPB) and CTAB bears the same pendent $\mathrm{C_{16}}$ chain linked to a different polar head (imidazolium ring for $\mathrm{PC_{16}VIB}$ and HMIB, pyridinium ring for $\mathrm{PC_{16}VPB}$ and HEPB and trimethylammmonium for CTAB). The aggregation way for these systems was studied by taking the molecular rotor DMAC as the fluorescent probe. The polarity and viscosity measurements are summarized in Figs. 5 and 7 respectively (this work and [5]).

For the two homopolymers, the main results can be compared as followed:

$$\Delta\lambda_{\mathrm{f\,max}}(\mathrm{PC_{16}VPB}) = 14\ \mathrm{nm} > \Delta\lambda_{\mathrm{f\,max}}(\mathrm{PC_{16}VIB}) = 9\ \mathrm{nm}$$

$$\Phi_{\mathrm{f}}/\Phi_{\mathrm{f0}}(\mathrm{PC_{16}VPB}) = 4.6 > \Phi_{\mathrm{f}}/\Phi_{\mathrm{f0}}(\mathrm{PC_{16}VIB}) = 3.8$$

The lower $\lambda_{\mathrm{f\,max}}$ value at the final plateau for $\mathrm{PC_{16}VPB}$ as compared with the $\mathrm{PC_{16}VIB}$ one (Fig. 5) indicates a less polar microenvironment for the pyridinium polymer than that of its imidazolium homologue, which might indicate for $\mathrm{PC_{16}VPB}$ a more compact structure. Indeed, a larger fluorescence quantum yield increase for the rotor is observed for $\mathrm{PC_{16}VPB}$ reflecting a higher restriction of motion (see Fig. 7). In this particular case, the observations related to the behaviour of the homopolymers in terms of polarity and microviscosity are going in the same way: the more rigid the microdomain structure, the less important is the polarity. However, it would be speculative to directly compare polarity and viscosity informations because they are not always going in the same way. Examples will be described further to argue this point.

For the two *surfactants HMIB and HEPB* and the *reference CTAB*, the main results can be compared as followed:

$$\Delta\lambda_{\mathrm{f\,max}}(\mathrm{CTAB}) = 7\ \mathrm{nm} \geq \Delta\lambda_{\mathrm{f\,max}}(\mathrm{HMIB}) = 6\ \mathrm{nm} > \Delta\lambda_{\mathrm{f\,max}}(\mathrm{HEPB}) = 3\ \mathrm{nm}$$

$$\Phi_{\mathrm{f}}/\Phi_{\mathrm{f0}}(\mathrm{CTAB}) \geq 3.9 \approx \Phi_{\mathrm{f}}/\Phi_{\mathrm{f0}}(\mathrm{HMIB}) = 3.8 > \Phi_{\mathrm{f}}/\Phi_{\mathrm{f0}}(\mathrm{HEPB}) = 2.8$$

The hydrophobicity degree, sensed by the rotor in the formed micelle, is in the following order: CTAB $\geq$ HMIB > HEPB (see Fig. 5) (trimethylammonium $\geq$ imidazolium ring > pyridinium ring). This order is also observed from the cohesion values (see Fig. 7) and it can be considered as a response to both electronic and steric factors.

It is also interesting to consider the information coming from both polarity and viscosity experiments to be able to compare polymers and micellar systems for each type of cationic head group:

- from *polarity data*: i) for the polymer microdomains, the pyridinium polymer is less polar than the imidazolium one, while it is the reverse for micelles; ii) the hydrophobicity is always higher for polymer microdomains than for micelles, and moreover a larger gap is observed for pyridinium ring ($\Delta\lambda = 11$ nm) than for imidazolium ring ($\Delta\lambda = 3$ nm),
- from *viscosity data*: i) for the polymer microdomains, the pyridinium polymer is more rigid than the imidazolium one (which is in agreement with the more hydrophobic medium detected by polarity sensing), while it is the reverse for micelles; ii) for the pyridinium ring, polymer microdomains are markedly more rigid than the model micelles (in agreement with the polarity sensing), while for the imidazolium ring, micelles are as rigid as the polymers microdomains, although the micelles are more polar than polymer microdomains. This latter observation argues our important previous remark which points out that there is not always a direct correlation between polarity and viscosity.

Finally, a comparison between the values of C_{m} and of CMC is possible in respect to the polar head nature (p and v denoting polarity and viscosity sensing respectively):

$$C_{\mathrm{m}}(\mathrm{PC_{16}VPB}) = 2.3_{\mathrm{p}}/2.5_{\mathrm{v}}\ 10^{-5}\ \mathrm{M} > C_{\mathrm{m}}(\mathrm{PC_{16}VIB}) = 1.6_{\mathrm{p}}/1.65_{\mathrm{v}}\ 10^{-5}\ \mathrm{M}$$

$$\mathrm{CMC(CTAB)} = 6.3\ 10^{-4}\ \mathrm{M} > \mathrm{CMC(HMIB)} = 4_{\mathrm{p}}/4.3_{\mathrm{v}}\ 10^{-4}\ \mathrm{M} > \mathrm{CMC(HEPB)} = 3.9_{\mathrm{p}}/3_{\mathrm{v}}\ 10^{-4}\ \mathrm{M}$$

The analysis of these orders regarding the nature of the head ring shows a reverse order for homopolymers microdomains by comparison with micelles. It is to be noted this difference was also observed before (see the preceedings comparisons).

Conclusion

As regards amphiphilic polymers and their models in aqueous solution, the aim of this work was to compare their association way using pyrene and a molecular rotor DMAC as fluorescent probes. We have been able first to establish a correspondence between the polarity scales on the basis of the variation of fluorescence emission features with solvents of different polarities and second to show that the results stemming from the use of each probe are going in the same way. However, due to their chemical nature, the two probes have different localization sites, which are expressed by low variations in their polarity response. Last, the main advantage of the molecular rotor over pyrene is its employment whatever the chemical nature of the studied system inducing or not a quenching phenomenon and especially that has been applied for the study and the comparison between polysoaps bearing either pyridinium or imidazolium rings.

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