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Oscar E. Zimerman[a]; Juan J. Cosa[a]; Carlos M. Previtali[a]
[a] Departamento de Química y, Física Universidad Nacional de Río Cuarto, Río Cuarto, Argentina

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BINDING OF IONIC PYRENE DERIVATIVES TO POLYELECTROLYTES. A UV ABSORPTION AND FLUORESCENCE STUDY

OSCAR E. ZIMERMAN, JUAN J. COSA, and CARLOS M. PREVITALI*

Departamento de Química y Física
Universidad Nacional de Río Cuarto
5800 Río Cuarto, Argentina

ABSTRACT

The binding of pyrenesulfonic acid and pyrenebutyric acid to poly-(vinyl benzyl trimethylammonium) chloride was investigated by UV and fluorescence spectroscopy. It was found that the binding constant was 7.5×10^4 and $3.5 \times 10^4\ M^{-1}$, respectively. The addition of the polyelectrolyte quenches the fluorescence of the pyrene group, and at the same time the typical excimer emission appears. This emission originates in pre-formed ground state aggregates of the pyrene derivatives incorporated into the polyion domain. Similar effects were observed when anionic polyelectrolytes, poly(styrene sulfonic), and poly(vinyl sulfonic) acids were added to cationic pyrene derivatives. The binding constants depend on the length of the aliphatic sidechain of the derivatives.

INTRODUCTION

Much work has been concerned with the binding of small organic molecules, charged or uncharged, to polyelectrolytes. This is of particular interest because of the ability of polyelectrolytes to accelerate or retard the rates of thermal and photochemical reactions. Among the several experimental approaches to the study of the interactions between small molecules and polyions, UV-Vis absorption and emission spectroscopy has been widely used. This technique is especially suited for pyrene derivatives. In dilute solutions these compounds show a structured absorp-

tion spectrum in the near-UV and a strong fluorescence emission that is very sensitive to the environment of the pyrene moiety. This property has been widely used in order to investigate the properties of various organized systems using pyrene derivatives as fluorescent probes [1]. The fluorescence characteristics of pyrene are especially suited for the study of the structure and dynamics of polymer solutions [2]. For example, pyrene has been employed by Chen and Thomas as a fluorescent probe to study the structure of polymethacrylic acid as a function of pH [3] and by Quina and coworkers [4] to investigate the micellization of ionene polyelectrolytes. The aggregation of several copolymers was also studied using the fluorescence properties of pyrene [5]. The formation of hydrophobic domains in water-soluble block copolymers was demonstrated by the changes in the fine structure of pyrene fluorescence [6]. While unsubstituted pyrene is commonly employed for the study of the properties of polyelectrolyte solutions, the pyrene derivatives have received much less attention. Chu and Thomas employed pyrene and its derivatives in a study of hydrophobically modified polyelectrolytes [7]. Herkstroeter et al. [8] studied the association of ionic pyrene derivatives induced by polyelectrolytes of opposite charge. Association was manifested by the appearance of the excimer emission of the pyrene derivatives in the presence of the polyion. At the same time, changes in the absorption spectra were observed, which were not evaluated quantitatively. Becker et al. [9, 10] also observed the excimer emission of pyrene sulfonic acid in the presence of a cationic polyion. They ascribed this emission to ground state association of two or more pyrenes induced by the polyion. The association constants were determined by an analysis of the excimer emission as a function of the polyion concentration [9] or by fluorescence quenching experiments [10].

In previous work we employed pyrene [11] and ionic pyrene derivatives [12] to investigate the aggregation of low molecular weight poly(metha-allylsulfonate-vinyl acetate) copolymers. In the presence of a polyelectrolyte, both the absorption and fluorescence spectra of pyrene and its derivatives change. Since the most prominent of these changes are those in the fluorescence properties, the effect of the polyelectrolyte on the absorption characteristics received much less attention. In this work we report an investigation of the interaction of charged pyrene derivatives with synthetic polyelectrolytes using UV absorption and fluorescence spectroscopy. It will be shown that changes in the absorption spectra are very noticeable, and they allow the determination of binding parameters.

EXPERIMENTAL

Chemicals

Sodium poly(vinyl sulfonate) (PVS), molecular weight 5×10^5, was obtained from Hoechst (Frankfurt, West Germany); sodium poly(styrene sulfonate) (PSS), molecular weight 5×10^5, and poly(vinyl benzyl trimethylammonium) chloride (PVBTA), molecular weight 3×10^5, were from Dow Chemical Co. (Midland, Michigan, USA). They were recrystallized prior to use. Hexadimethrine bromide (Polybrene, PBR), obtained from Aldrich Chem. Co. (St. Louis, Missouri, USA), was used as received. 1-Pyrenebutyric acid (PBA), 1-pyrenesulfonic acid (PSA), 1-pyrene-methyltrimethylammonium iodide (PMTMA), (4-(1-pyrenyl)butyl) trimethylammonium bromide (PBTMA), and 1-pyrene-undecyltrimethylammonium

iodide (PUTMA) obtained from Molecular Probes (Eugene, Oregon, USA), were used as received. The concentration of the probes was in 1×10^{-5} M unless another value is stated. In the experiments with PBA, Tris buffer 1 mM, pH 8 was employed in order to make sure that the probe was in the negatively charged form. The polyelectrolyte concentration is expressed in normality units based on the molecular weight of the monomer.

Absorption and Fluorescence Measurements

UV absorption spectra were taken with a Hewlett-Packard 8452 diode array spectrophotometer. Difference spectra were determined by subtracting the spectra of the single components, previously stored in the computer, from the spectrum of the mixture. Fluorescence spectra were measured on an Aminco-Bowman spectrofluorimeter. The excitation wavelength was always such that the aromatic polyelectrolytes did not absorb any appreciable fraction of the excitation light. All measurements were carried out in air-equilibrated solutions at 25°C. The determinations of fluorescence lifetimes were carried out with a nitrogen laser (FWHM = 5 ns), a TRW 75A filter fluorimeter, and a digital oscilloscope that transmits the data to a PC for analysis and plotting.

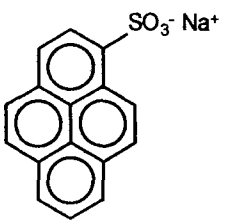
RESULTS

1-Anionic Pyrene Derivatives with Cationic Polyelectrolytes

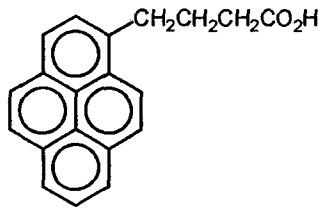
The effect of PVBTA and PBR on the absorption and emission properties of PBA and PSA was determined. The molecular structures of the polyelectrolytes and pyrene derivatives can be seen in Scheme 1. The effect of PVBTA on the absorption spectrum of PBA is shown in Fig. 1. In the absence of the polyelectrolyte, the spectrum presents two maxima at 326 and 342 nm. On addition of PVBTA, the spectrum shifts to the red, with the maxima now at 332 and 349 nm. Three isosbestic points in the spectra are an indication of two species in equilibrium. These two species are consider to be PBA anion in bulk water and PBA anion incorporated into the polymer domain. The bands in the presence of the polyion are broader, and an increase in the absorbance at wavelengths greater than 360 nm may indicate that other species probably coexist in the system. Similar but less pronounced spectral changes are observed when PVBTA is added to a 1×10^{-5} M solution of PSA.

The fluorescence of PSA and PBA in the 1×10^{-5} to 5×10^{-5} M concentration range in pure water shows the characteristic monomeric emission. However, the addition of small amounts of the cationic polyelectrolyte PVBTA causes the onset of the typical excimer emission, as can be observed in Fig. 2 for PBA. The ratio of excimer to monomer emission increases with the polyelectrolyte concentration and reaches a maximum at $\sim 2.5 \times 10^{-5}$ N for PSA and 4×10^{-5} N for PBA (Fig. 3). Then it decreases with a further increase in polymer concentration. At high PVBTA concentration the only emission bands are those of the monomeric species, but now shifted to the red by about 6 nm.

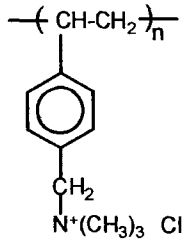
The excitation spectrum of PBA also presents changes in the presence of polyelectrolytes. When monitored at the maximum of monomer emission, 380 nm, the excitation spectrum is the same as in the absence of PVBTA. When monitored



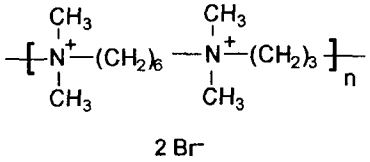
PSA



PBA



PVBTA



n = 11 ± 2

PBR

SCHEME 1.

at 480 nm, the wavelength corresponding to the maximum of the excimer spectrum, the excitation spectrum is red shifted by around 8 nm. From this it can be concluded that there are two distinct species emitting. One of them has the same excitation and emission spectrum as the probe in water in the absence of PVBTA. The presence of the other one is caused by the polyion, and it can be understood as being due to pyrene derivatives incorporated in the polymer domain. These pyrene derivatives can associate with each other due to their high local concentration. The addition of NaCl or urea to the probe–polyion solution decreases the excimer emission. In this case the NaCl decrease is accompanied by an increase of monomeric emission with the maximum wavelengths corresponding to the species in water. The effect of urea is shown in Fig. 4. It can be seen that urea reverts the emission spectrum to that of the monomeric form, but red shifted with respect to pure water. This is an indication that both electrostatic and hydrophobic effects are responsible for the interaction of the pyrene derivatives with the polyelectrolytes. Very similar observations on the emission behavior of a cationic pyrene derivative in the presence of negative polyions were made by Herkstroeter et al. [8].

In order to analyze the effect of the organic structure and size of the polyelectrolyte chain, the effect of PBR on the emission of the negative pyrene derivatives

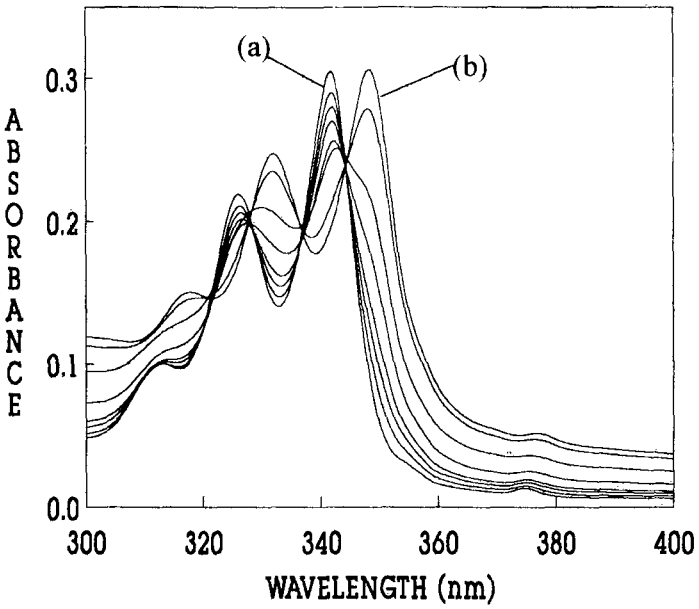
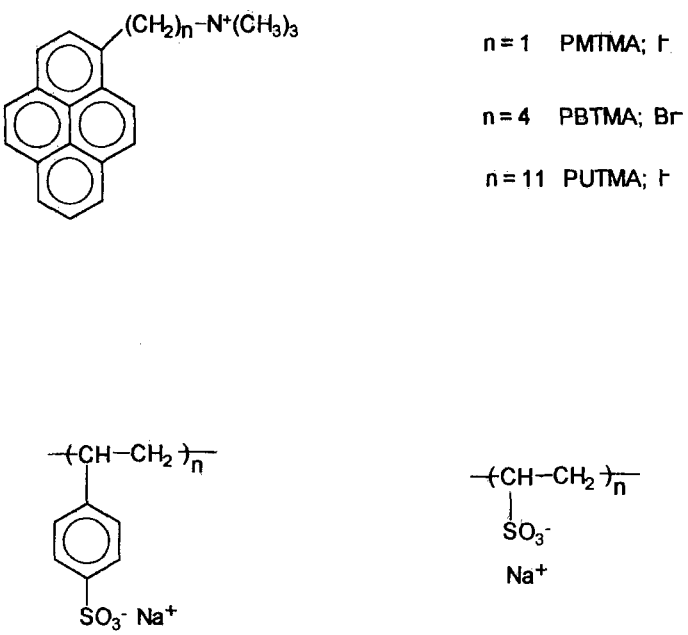


FIG. 1. Absorption spectra of PBA 8×10^{-6} M in water, buffer Tris, pH 8, curve (a); and in the presence of PVBTA 8.3×10^{-5} N, curve (b). The intermediate curves correspond to PVBTA concentrations of 1.0, 2.1, 3.1, 5.2, 6.2, and 7.2×10^{-5} N.



SCHEME 2.

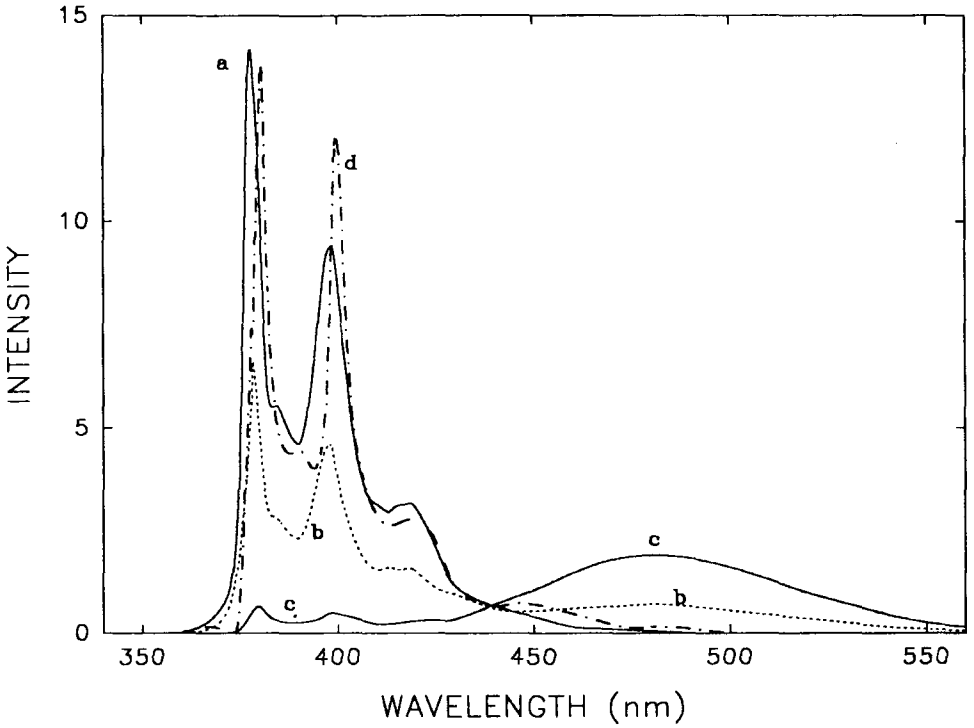


FIG. 2. Fluorescence spectra of PBA 1×10^{-5} M, buffer Tris, pH 8, in the absence (a) and in the presence of PVBTA 2×10^{-5} N (b), 3×10^{-5} N (c), and 8.2×10^{-4} N (d).

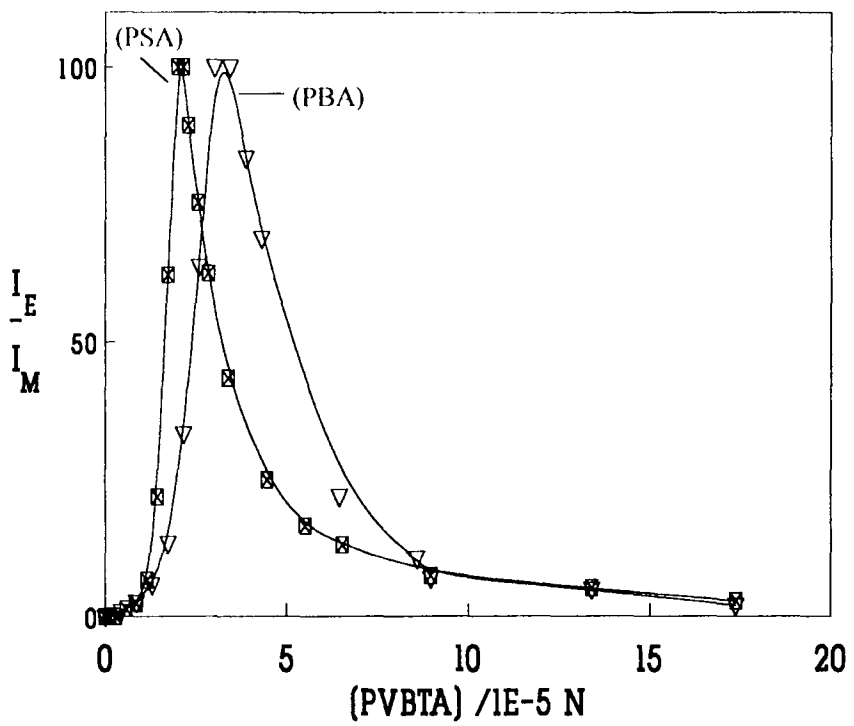


FIG. 3. Excimer (I_E = 480 nm) to monomer (I_M = 380 nm) fluorescence intensity ratio as a function of PVBTA concentration for PBA (▽) and PSA (⊠).

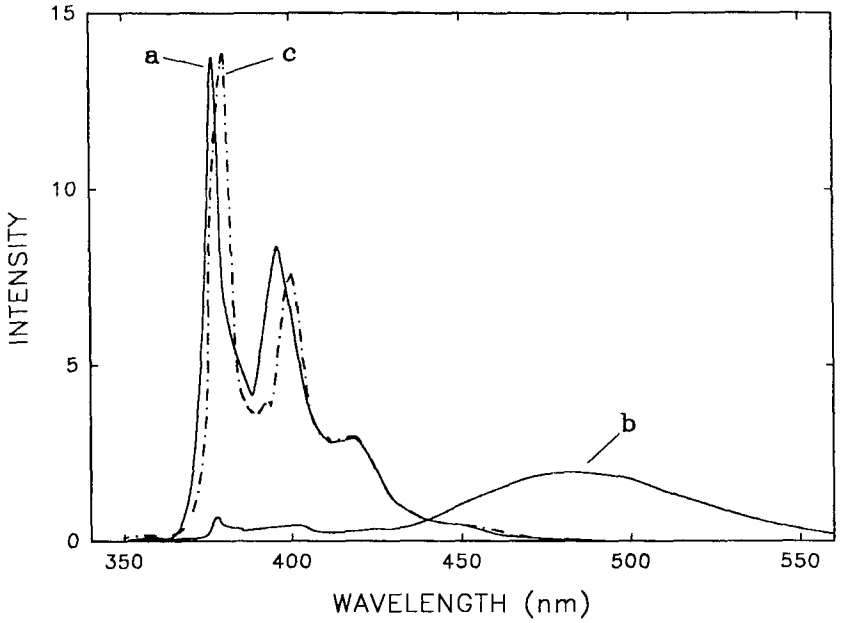


FIG. 4. Effect of added urea on the fluorescence spectrum of PBA 1×10^{-5} M. (a) Emission in water, buffer Tris, pH 8. (b) Emission in the presence of PVBTA 2×10^{-5} N. (c) Emission in the presence of PVBTA 2×10^{-5} N and urea 0.14 M.

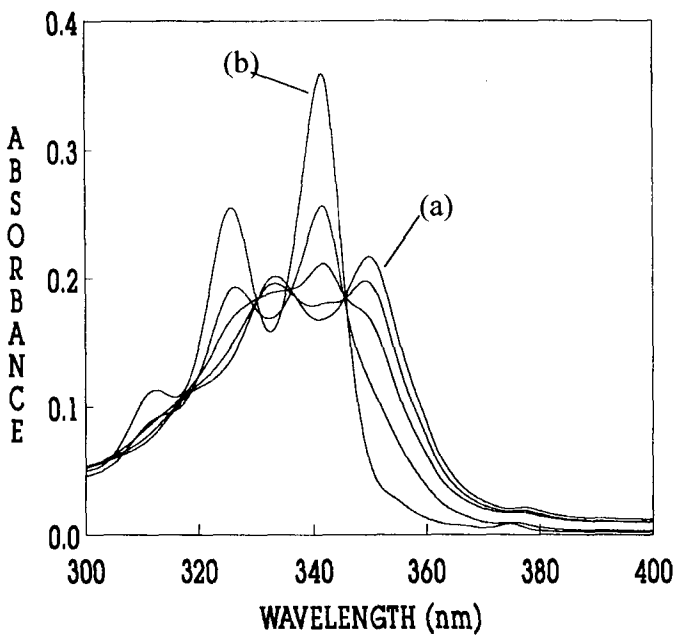


FIG. 5. Absorption spectrum of PBTMA 1×10^{-5} M in water, curve (b); and in the presence of PSS 2.7×10^{-5} N, curve (a). The intermediate curves correspond to PSS concentrations 0.7, 1.3, and 2.0×10^{-5} N.

TABLE 1. Fluorescence Lifetimes of PBA and PSA–PVBTA Systems[a]

PBA			PSA		
[PVBTA]	τ_{380}	τ_{480}	[PVBTA]	τ_{380}	τ_{480}
0	94	–	0	59	–
2.7×10^{-5}	89	56	1.0×10^{-6}	55	41
3.3×10^{-4}	90	54	5.3×10^{-6}	57	43
6.6×10^{-4}	84	nd	1.3×10^{-5}	56	41
1.3×10^{-2}	83	nd	1.0×10^{-2}	106	nd

[a]Lifetimes in nanoseconds; air equilibrated solution; nd = emission too low for detection.

TABLE 2. Fluorescence Lifetimes of PBTMA–PSS and PBTMA–PVS Systems[a]

[PSS]	τ_{380}	τ_{480}	[PVS]	τ_{380}	τ_{480}
0	103	–	0	99	–
6.7×10^{-5}	101	70	2.0×10^{-4}	95	44
1.2×10^{-3}	108	71	1.3×10^{-3}	102	41
1.0×10^{-2}	138	nd	1.0×10^{-2}	103	43

[a]Lifetimes in nanoseconds; air equilibrated solution; nd = emission too low for detection.

TABLE 3. Fluorescence Lifetimes of PUTMA–PVS System[a]

[PVS]	τ_{380}	τ_{480}
0	90	–
3.3×10^{-5}	96	37
1.1×10^{-3}	nd	38
1.0×10^{-2}	nd	41

[a]Lifetimes in nanoseconds; air equilibrated solution; nd = emission too low for detection.

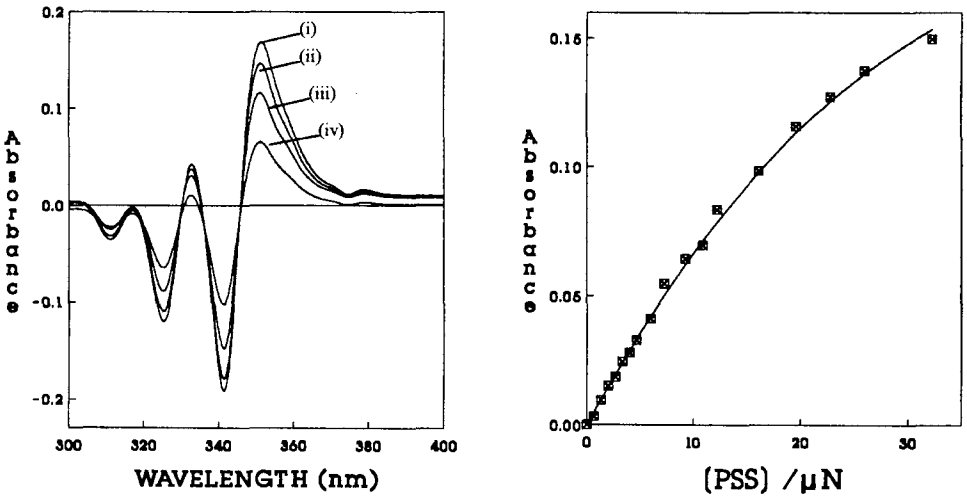


FIG. 6. (a) Difference absorption spectra of PBTMA-PSS. [PSS] = 0.7×10^{-5} (iv), 1.3×10^{-5} (iii), 2.0×10^{-5} (ii), and 2.7×10^{-5} N (i). (b) Intensity of the difference band at 355 nm vs PSS concentration. The curve is calculated with K and $\Delta\epsilon$ from Table 5.

TABLE 4. Equilibrium Constants and Extinction Coefficients of the Difference Band for the Association of PSA and PBA to PVBTA

	K, M^{-1}	$\Delta\epsilon$, $M^{-1} \cdot cm^{-1}$
PBA	3.5×10^4	17,000
PSA	7.5×10^4	23,000

TABLE 5. Equilibrium Constants and Extinction Coefficients of the Difference Band for the Association of Cationic Derivatives of Pyrene with PVS and PSS

	PVS		PSS	
	K, M^{-1}	$\Delta\epsilon$, $M^{-1} \cdot cm^{-1}$	K, M^{-1}	$\Delta\epsilon$, $M^{-1} \cdot cm^{-1}$
PMTMA	Not measured	Not measured	7.0×10^4	9,200
PBTMA	1.2×10^4	11,000	8.0×10^4	12,000
PUTMA	5.0×10^7	9,200	1.0×10^7	9,900

was investigated. PBR is an aliphatic polyion with a short chain. When PBR is added to a water solution of PSA or PBA (1×10^{-5}M), no excimer is observed. The only apparent change is a quenching of the monomer emission. This is probably due to the heavy atom effect of the bromide counterions of the polyelectrolyte. A similar effect is observed for CTAB (cetyltrimethylammonium bromide) micelles as compared with CTAC (cetyltrimethylammonium chloride) [13]. We think that the lack of induced excimer emission of PBR can be due to two effects. One can be the larger charge separation in this polyion. The PBA or PSA anions that are bound to the polymer chain are so far from each other that ground-state association is not possible. The other possible operating effect is that the association of pyrene ionic derivatives is not only an electrostatic effect, but the hydrophobicity of the polyelectrolytes domain also plays an important role, as was found for ionic indole derivatives [14]. The above-mentioned effect of added urea also confirms the hydrophobicity contribution to the association. PBR, due the aliphatic chain and lower molecular weight, will present fewer hydrophobic regions than PVBTA and therefore the pyrene will associate to a lesser extent with this polyelectrolyte.

1-Cationic Pyrene Derivatives with Anionic Polyelectrolytes

The effect of PSS and PVS on the absorption spectrum of PBTMA, PMTMA, and PUTMA was studied. The molecular structures of the polyelectrolytes and pyrene derivatives can be seen in Scheme 2. The polyelectrolyte effect observed for the systems PVBTA–PSA and PBA is also present in this case. The absorption spectrum of PBTMA as a function of PSS concentration is presented in Fig. 5. The polyelectrolyte produces a red shift and a loss of resolution in the spectrum. There are also several near-isosbestic points. This suggests the coexistence of two main species, one incorporated into the polymer domain and the other dissolved as a free species in water. Similar changes in the spectrum were observed for the system PBTMA–PVS and for PMTMA and PUTMA with both polyelectrolytes, PSS and PVS. The fluorescence excitation and emission spectra for all the cationic probes showed only monomeric emission in pure water; excimer emission is also present in the presence of the polymers. The intensities ratio $I_E I_M$ was determined as a function of the polyelectrolyte concentration. For PSS the changes resemble those observed in the case of anionic pyrene derivatives with added PVBTA (Fig. 3). On the other hand, for PVS the excimer emission remains present even at a polyion concentration as high as 0.01 N.

Dynamic fluorescence experiments were performed for PBA and PSA with PVBTA, for PBTMA with PSS and PVS, and for PUTMA with PVS. The fluorescence lifetimes are given in Tables 1–3. Both the monomer (380 nm) and excimer (480 nm) emission decay by first-order kinetics. The rise times at both wavelengths coincide within experimental error. When both bands are present in the emission spectrum, the fluorescence lifetimes measured at the wavelengths of monomer and excimer emission, τ_{380} and τ_{480}, respectively, are independent of the polyelectrolyte concentration.

DISCUSSION

The binding of arylmethyl-ammonium ions to polyelectrolytes was previously studied by Turro et al. for the case of naphthalene derivatives with PSS [15, 16]. They observed that the absorption spectrum is broader in the presence of the poly-

electrolyte. The shift in the absorption maxima observed in our case was not present in the case of the naphthalene derivatives. They proposed that the probe senses numerous slightly different environments. This results in a broadening of the absorption bands, but not in a shift of the absorption maxima. In our case the spectral shift and the presence of isosbestic points in nearly all cases suggest that we can analyze our results from the point of view of two species in equilibrium. One is the pyrene derivative in the bulk aqueous domain and the other is the derivative in the polyion domain. The fluorescence results are in agreement with this model. The emission spectral changes are better analyzed with the aid of the plots in Fig. 3. At low polymer concentration the probes incorporated into the polymer domain are close to each other and the emission is predominantly of the excimer type. As the polyion concentration increases, and the number of charged monomer units becomes much larger than the number of probe molecules, the pyrene derivatives bound to the polymer chain separate from each other and the excimer emission decreases (Fig. 3). At higher polymer concentration the excimer emission practically disappears, except for the case of PUTMA-PVS.

The fluorescence lifetime behavior in the presence of the polyelectrolytes reinforces this opinion. The lack of effect of the polyelectrolyte concentration on the monomer and excimer lifetimes (Tables 1-3) and the time profile of the excimer emission are an indication of a static mechanism for the quenching of the monomer fluorescence and for the origin of the excimer emission. This behavior is typical of the fluorescence of pre-formed ground-state aggregates [17]. If the excimer emission originates in a collisional process between excited and ground-state pyrene groups, then a rise time and a delay, with respect to the monomer emission decay, should be apparent in the time profile of the excimer emission [18]. Also, if this were the case, the monomer emission should not follow a first-order decay [18]. Therefore, the excimer emission does not arise from a dynamic process involving excited and ground-state monomeric species. Its origin must be the excitation of pre-formed dimers or higher aggregates of pyrene derivatives, and subsequent emission.

This model can be put in a simple quantitative basis by the equilibrium

$$D_w + P_w \rightleftharpoons D_p \tag{1}$$

Here D_w represents the pyrene derivative dissolved in the bulk aqueous domain, P_w the polyion binding sites, and D_p the derivative in the polymer domain. If it is assumed that all sites on the polyion are equivalent and independent, an equilibrium equation can be written as

$$K = \frac{[D_p]}{[D_w][P_w]} \tag{2}$$

The spectral changes caused by the presence of the polyelectrolyte can be quantitatively evaluated using this simple equilibrium. These changes are better treated when represented in the form of difference spectra determined as discussed in the Experimental Section. In Fig. 6(a) a typical difference spectrum is shown, while the absorbance difference at the maximum ΔA is plotted vs PSS concentration $[P_0]$ in Fig. 6(b).

The absorbance of the solution containing the pyrene derivative in the presence of the polyion can be written as

$$A = \epsilon_{D_P}[D_P] + \epsilon_{D_w}[D_w] + \epsilon_P[P_w] \quad (3)$$

where ϵ_x is the molar extinction coefficient of species x.

Using the total analytical concentration of the pyrene derivative $[D_0] = [D_w] + [D_p]$, and the total number of polyion binding sites (assumed to be the total analytical concentration of monomer units) $[P_0] = [P_w] + [D_p]$, the differential absorbance can then be written as

$$\Delta A = A - \epsilon_{D_w}[D_0] - \epsilon_P[P_0] = \Delta\epsilon[D_P] \quad (4)$$

with $\Delta\epsilon = \epsilon_{D_P} - \epsilon_{D_w} - \epsilon_P$.

In Eq. (3) it was assumed that the contribution of the polyion to the total absorbance is the same in the absence of the pyrene derivative. Introducing Eq. (4) in Eq. (2) and reordering, we obtain

$$\frac{1}{K} = [D_0][P_0]\frac{\Delta\epsilon}{\Delta A} - [P_0] - [D_0] + \frac{\Delta A}{\Delta\epsilon} \quad (5)$$

This equation is the basis of the Rose-Drago [19] method. From the experimental values of ΔA at different $[P_0]$, plots according to Eq. (5) were constructed. From these plots, approximate values of K and $\Delta\epsilon$ were determined. The final values of these parameters were obtained by a nonlinear least-squares adjustment of the plots of ΔA vs the polyelectrolyte concentration. The result of the application of this procedure can be seen as the full line in Fig. 6(b). The results for all the systems are summarized in Tables 4 and 5.

It can be seen in Table 4 that for the case of the cationic polyelectrolyte PVBTA, the binding constant and $\Delta\epsilon$ for both probes are very similar. The factor of 2 in the binding constants is in agreement with the position of the maxima in the plot of I_E/I_M. Figure 3 shows that for PSA the maximum in this ratio is reached at a lower concentration of polyelectrolyte. The similar extinction coefficients for the difference band $\Delta\epsilon$ can be taken as an indication that the pyrene groups are in a similar orientation or sensing a comparable environment when incorporated into the polyion. Becker et al. [9] studied the polyelectrolyte-induced excimer emission of PSA. The polyelectrolyte was of the tetraalkylammonium type, but it did not contain aromatic rings on the chain. They used a model with three equilibrium constants for fitting the excimer intensity vs polyion concentration plot. The three equilibrium constants correspond to the binding of the first, second, and third PSA ions to vicinal polyion sites. They obtained $7 \times 10^3\ M^{-1}$, $4 \times 10^4\ M^{-1}$ and $3 \times 10^4\ M^{-1}$, respectively, for these constants. These figures are very similar to our values in Table 4.

For the two anionic polyelectrolytes PVS and PSS, the binding constant increases with the hydrophobicity of the sidechain (see Table 5). This effect is especially noticeable in the binding constant of PUTMA which is three orders of magnitude higher than those for the probes with a shorter aliphatic chain. The extinction coefficients are very similar in all cases. This may indicate a comparable location of the probes in the polymer domain. However, for PUTMA-PVS and PBTMA-PVS systems the excimer emission remains even at a high polyelectrolyte concentration. The lifetimes of this emission are independent of the polymer concentration, as can be observed in Table 3. This lack of dilution effect can be understood by the formation of micelle-like structures in the polymer domain, induced by the surfac-

tant molecules. It is well known that surfactant molecules are strongly absorbed on polyions of opposite charge, and that the binding is highly cooperative [20]. From experimental determination of the enthalpy of binding of dodecyl- and cetylpyridinium cations to PSS, it was concluded that many small surfactant aggregates are formed in the polyion domain at a surfactant concentration much below the cmc [21]. This phenomenon has been observed for other surfactant–polyelectrolyte systems [22]. These structures, once formed, are not affected by the presence of other polymer chains [22]. If it is now assumed that the hydrophobic probes PBTMA and PUTMA form part of the hydrophobic centers like those described above, the lack of the dilution effect when the polyelectrolyte increases can be understood. Since the emission arises from molecules with an environment unaltered by the total polymer concentration, the excimer intensity and lifetime are not expected to change.

CONCLUSION

The results presented show that the anionic pyrene derivatives, PSA and PBA, strongly bind to the positive polyion PVTBA. This binding manifests as a new broad band in the emission spectrum of the pyrene derivative, similar to the typical excimer emission of pyrene. This emission arises in dimers or cluster of a higher number of pyrene groups formed in the polymer domain. In addition to electrostatic effects, hydrophobicity also contributes to the binding. This leads to changes in the absorption spectrum which allow for the determination of the binding constants. Similarly, the cationic pyrene derivatives PMTMA, PBTMA, and PUTMA interact with the negative polyions PSS and PVS. From the spectral changes, binding constants of the same order as those for the negative probe–positive polyion were observed, except for PUTMA. A very much higher constant was obtained for the latter. Also, excimer emission is present at a high concentration of the polyion. These results can be explained if it is assumed that derivatives with a long aliphatic chain induce the formation of micelle-like structures in the polymer domain.

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