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Control of C.I. Basic Violet 10 aggregation in aqueous solution by the use of poly(sodium 4-styrenesulfonate)

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ABSTRACT

The aggregation behavior of C.I. Basic Violet 10 in the presence of poly(sodium 4-styrenesulfonate) was modified, as a consequence of short-range interactions. In aqueous acidic media, the cationic dye forms hydrophobic ion pairs with polymeric benzene sulfonate groups which tend to aggregate in H-contacts, this tendency being readily influenced by the relative concentration of the macromolecule with respect to that of the dye. In the case of dilute aqueous dye solutions ($\leq 10^{-4}$ M), for which the probability of dye self-aggregation is small, C.I. Basic Violet 10 self-contacts are forced in the presence of a moderate excess of poly(sodium 4-styrenesulfonate). At dye concentrations $>10^{-4}$ M, for which the probability of dye self-aggregation increases, dye-dye contacts are minimized in the presence of a large excess of the polymer. Hence, the luminescence of dye solutions can be tuned insorar as, that of dilute dye solutions is quenched whilst that of concentrated dye solutions can be enhanced. This behavior was not observed for other polyelectrolytes such as poly(sodium vinylsulfonate), or the more hydrophobic poly(sodium 2-(*N*-acrylamido)-2-methyl-propanesulfonate).

1. Introduction

The interaction of rhodamines with colloidal particles, as micelles [1], vesicles [2], clays [3–5], and latex [6], has been investigated in the literature. The adsorption of these molecules to several solid materials has also been investigated [7,8]. By means of their interactions with these objects, the luminescent properties of the dyes may change, and some effects observed by emission and absorption UV–vis spectroscopy have been interpreted in terms of the self-aggregation of the dyes on the surface of these particles.

Interactions between low molecular-mass species (LMMS) and water-soluble polymers (WSP) have been extensively studied [9–16]. Polymers containing sulfonate groups behave as negatively charged strong polyelectrolytes, and undergo long-range electrostatic interactions with their counterions, which are generally described by the counterion condensation theory of Manning [9,10]. According to this, long-range electrostatic interactions produce non-site-specific territorial binding, and the counterions are able to move around the polyelectrolyte surface. However, in certain cases, experiments indicate the influence of short-range site-specific interactions. These short-range interactions may exceed in strength the long-range electrostatic interaction. In most cases, both modes of binding occur simultaneously where one mode is the dominant.

C.I. Basic Violet 10 is an interesting molecule with spectral-luminescent properties ascribed to its state of aggregation. Changes in its luminescence are due to self-contacts in sandwich H-type or head-to-tail J-type geometries, showing variable orders of aggregation (dimer, trimer, etc.). Recently, we have shown that C.I. Basic Violet 10 interacts with WSP containing aromatic rings such as poly(sodium 4-styrenesulfonate) (PSS) or poly(N-methacryloyl-5-aminosalicylic acid) [17–19]. Results by ^{1}H NMR spectroscopy indicated the existence of specific short-range π–π interactions between PSS and C.I. Basic Violet 10 [17–19], and a geometrical structure for the contact between C.I. Basic Violet 10 and PSS at pH 7 has been proposed [19].

Aromatic–aromatic interactions, such as π–π interactions, are one of the principal non-covalent forces governing molecular recognition and biomolecular structure [20–27]. These interactions have a short-range character, which implies that water molecules of the hydration sphere of the aromatic groups are released when these groups contact each other in aqueous solutions. Thus, the

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main forces driving these interactions are solvophobic, while site-specific interactions such as short-range electrostatic interactions, hydrogen bond formation, π–π interactions, or cation–π interactions also contribute to the free energy and define the geometry of the complexes [20,21]. They are important in the stabilization of DNA and its association with intercalators. They also play an important role in protein stabilization and protein functionality, as in enzymes [28–32], trans-membrane channels [33,34], etc. The dual relevance of these interactions motivates the development of synthetic systems whose structures and functionalities may be tuned by aromatic–aromatic interactions.

In this context, we will show in this paper that the luminescence of C.I. Basic Violet 10 solutions can be modulated in the presence of PSS. Diafiltration and emission and absorption UV–vis spectroscopic results on the interaction of these two species will be shown and compared with those obtained with other polyelectrolytes containing sulfonate groups such as poly(sodium vinylsulfonate) (PVS), or the more hydrophobic poly(sodium 2-(*N*-acrylamido)-2-methyl-propanesulfonate) (PAMPS).

2. Experimental

2.1. Reagents

Commercially available PSS (Aldrich, synthesized from the *para*-substituted monomer), PVS (Aldrich), PAMPS (Aldrich), and C.I. Basic Violet 10 (Sigma) were used to prepare solutions in deionized distilled water. The structures of C.I. Basic Violet 10 and the different polyelectrolytes are shown in Fig. 1, as well as the proposed geometry for the contact between PSS and C.I. Basic Violet 10 at pH 7 [19]. The pH was adjusted with minimum amounts of NaOH and HCl.

2.2. Equipment

The unit used for diafiltration studies consisted of a filtration cell (Amicon 8010, 10 mL capacity) with a magnetic stirrer, a regenerated cellulose membrane with a molecular-mass cut-off of 5000 Dalton (Ultracel PBCC, 25 mm diameter), a reservoir, a selector, and a pressure source. Distilled water was deionized in a Simplicity Millipore deionizer. The pH was controlled on Hanna pH211 and Horiba F-15 pH meters. UV–vis experiments were performed at 293 K in Jasco V-570 and in Heλios γ spectrophotometer. Fluorescence measurements were done in a Kontron SFM25 fluorescence spectrophotometer.

2.3. Procedures

Conventional procedures have been followed. Particular experimental conditions are provided in the figure captions.

Details for diafiltration procedures can be found elsewhere [35–37]. The polyelectrolyte concentration has been chosen so that enough sensitivity is obtained by diafiltration at every pH. Briefly, solutions in twice-distilled water (10 mL) were prepared containing one or more of the following components: a WSP (polymeric molecular-mass fraction over 10,000 Dalton, 2.0×10^{-4} M and 10^{-3} M in monomeric units at pH 2 and 7, respectively) and C.I. Basic Violet 10 (1.0×10^{-4} M at pH 2 or 7). The solutions were placed into the diafiltration cell. The pH of the aqueous solution contained in the reservoir was adjusted to the same value as in the cell solution. The filtration runs were carried out over a regenerated cellulose membrane with a molecular-mass cut-off of 5000 Dalton under a total pressure of 3 bar, keeping constant the solution volume in the cell by creating a continuous flux of liquid through the cell solution from the reservoir (around 0.008 mL s^{-1}). Vigorous stirring is held in order to minimize concentration polarization and fouling. Filtration fractions (ranging between 6.0 and 8.0 mL) were collected and C.I. Basic Violet 10 concentrations analyzed by UV–vis spectroscopy. Calibration curves (absorbance = 107,842 [C.I. Basic Violet 10] at pH 2, and absorbance = 108,174 [C.I. Basic Violet 10] at pH 7) were obtained at 558 nm for pH 2, and 554 nm for pH 7, in a range of C.I. Basic Violet 10 concentrations between 1.0×10^{-6} and 1.0×10^{-5} M, with square linear regression factors of 1.00. Blank experiments were performed with the same procedure in the absence of the WSP. At least one replicate is done for every experiment.

The change in the pH caused by the interaction between C.I. Basic Violet 10 and PSS has been explored by mixing 20 mL of 10^{-4} M C.I. Basic Violet 10 solutions at different pHs with 100 μL of concentrated PSS in order to achieve a PSS final concentration of 2×10^{-3} M. In order to have absorbances in a range of 0.1–1.0, the optical path length was adjusted between 10^{-1} and 10^{-3} cm for solutions containing C.I. Basic Violet 10 at concentrations ranging between 10^{-4} and 10^{-2} M. When done, decomposition of spectra in Gaussians was performed with the Origin50 software. Fluorescence measurements were done under the following parameters: a voltage in the range 330–450 V was applied to control the light intensity of the high pressure Xenon arc lamp for C.I. Basic Violet 10 concentrations ranging between 10^{-6} and 10^{-2} M; the excitation wavelength was 530 nm; the bandwidth was 5.0 nm. For series of experiments where highly concentrated C.I. Basic Violet 10 solutions are observed, luminescence measurements have been

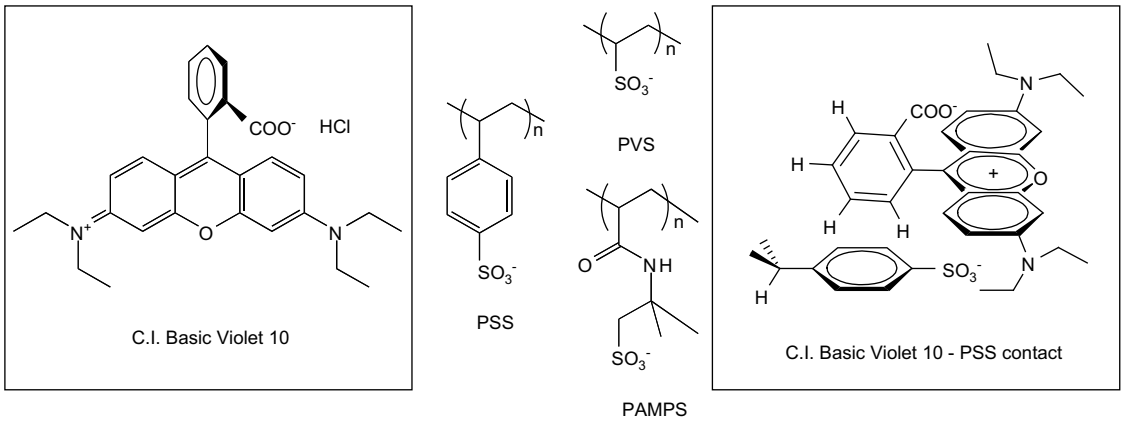


Fig. 1. Molecular structures of C.I. Basic Violet 10 and PSS, and proposed structure for their mutual contact at pH 7.

performed in the front-face mode by the use of a quartz vessel of triangular base, and the emitted light has been analyzed at the fluorescence maxima: 581 nm for C.I. Basic Violet 10 10^{-4} M, pH 2; 589 nm for C.I. Basic Violet 10 10^{-4} M, PSS 10^{-2} M, pH 2; 576 nm for C.I. Basic Violet 10 10^{-4} M, pH 7; 583 nm for C.I. Basic Violet 10 10^{-4} M, PSS 10^{-2} M, pH 7; 580 nm for C.I. Basic Violet 10 10^{-3} M, pH 2; 594 nm for C.I. Basic Violet 10 10^{-3} M, PSS 10^{-1} M, pH 2; 573 nm for C.I. Basic Violet 10 10^{-3} M, pH 7; 587 nm for C.I. Basic Violet 10 10^{-3} M, PSS 10^{-1} M, pH 7.

3. Results and discussion

3.1. C.I. Basic Violet 10 self-aggregation

Due to the presence of a positively charged xanthene group and a negatively charged carboxylic unit (see Fig. 1), C.I. Basic Violet 10 is zwitterionic at pH 7, and positively charged at pH 2. The pK_a of this dye has been described to be 3.2 at a concentration 10^{-5} M [17,38]. Both zwitterionic and cationic species show different UV–vis absorption spectra as can be seen in Fig. 2 for several C.I. Basic Violet 10 concentrations. It is generally accepted that at a C.I. Basic Violet 10 concentration up to 10^{-4} M the molecule is found in its monomeric state, showing its maximum of absorbance at 556 nm at pH 2 and 554 nm at pH 7 (Fig. 2, labels a and b). Increasing the C.I. Basic Violet 10 concentration from 10^{-4} M produces an increase of the bands at 524–522 nm (pH 2–7) relative to those at 556–554 nm (Fig. 2, labels c–d). This is accepted to be a consequence of the formation of dimers and higher-order aggregates of C.I. Basic Violet 10 in solution. The formation of these aggregates is normally accompanied by a decrease in the fluorescence of the dye due to H-contacts between the molecules [8].

3.2. Different binding in the presence of different polyelectrolytes

Diafiltration is a suitable technique to evaluate overall interactions between polyelectrolytes and LMMS such as metal ions or charged molecules, since it is a separation technique that discriminates the species by their size [35–37]. It allows calculating the apparent dissociation constants of the interaction between polyelectrolytes and specific counterions. The main magnitudes managed in diafiltration analyses are the filtration factor (F), defined as the ratio between the volume in the filtrate and the constant volume in the diafiltration cell, the concentration in the filtrate of the LMMS under study ($c_{\mathrm{LMMS}}^{\mathrm{filtrate}}$), the concentration of free LMMS in the cell solution ($c_{\mathrm{LMMS}}^{\mathrm{free}}$), the concentration of LMMS reversibly bound to the WSP ($c_{\mathrm{LMMS}}^{\mathrm{rev\text{-}bound}}$), the apparent dissociation constant ($K_{\mathrm{LMMS}}^{\mathrm{diss\text{-}WSP}}$), defined as the ratio $c_{\mathrm{LMMS}}^{\mathrm{free}}/c_{\mathrm{LMMS}}^{\mathrm{rev\text{-}bound}}$, the diafiltration parameters k^{m}, j, u, and v, and the polymer concentration in mole per liter of monomeric units (c_{P}). k^{m} and j parameters (the absolute value of the slope of the curve $\ln c_{\mathrm{LMMS}}^{\mathrm{filtrate}}$ versus F in the absence and in the presence of the WSP, respectively) are related with the strength of the interaction, while v and u are related with the amounts of LMMS reversibly or irreversibly bound to the polymer, respectively. By irreversibly bound we consider molecules bound in processes that may be reversible with an apparent dissociation constant that tend to zero at the conditions of the experiment.

Diafiltration experiments have been done to evaluate the interaction between C.I. Basic Violet 10 and PSS, PVS, and PAMPS at pH 2 and 7 and the results are shown in Fig. 3a and b, respectively, and Table 1. At pH 2, C.I. Basic Violet 10 is positively charged, so long-range electrostatic interactions should take place between the WSP and the dye. However, the strong ionic strength associated with such a low pH may screen the long-range electrostatic interactions. This is believed to be the main force concerning the interaction between PVS and C.I. Basic Violet 10, so that a negligible binding is found for this polymer, as shown by the filtration rates similar to blank experiments (Fig. 3a) and the corresponding high apparent dissociation constant (see Table 1). On the contrary, the interaction with PAMPS or PSS is not negligible. This may be due to the high hydrophobicity of these polymers. The lack of linearity in the case of PAMPS does not allow analytical interpretation of the results. In the case of PSS, the low value of the parameter j is related to practically quantitative binding. On the other hand, at pH 7, at which C.I. Basic Violet 10 is zwitterionic and thus long-range electrostatic interactions are avoided, PVS and PAMPS do not bind C.I. Basic Violet 10, while PSS shows a significant binding ability, and the corresponding $K_{\text{C.I. Basic Violet 10}}^{\mathrm{diss\text{-}PSS}}$ was found to be 0.50 ± 0.05.

The existence of interaction between C.I. Basic Violet 10 and PSS at pH 7 has been reported before. With the aid of ^{1}H NMR spectroscopy it has been determined that aromatic–aromatic interactions take place between the macromolecule and the dye (see Fig. 1) [18,19]. This kind of interaction has a short-range character, a fact that may determine the behavior of the system by means of

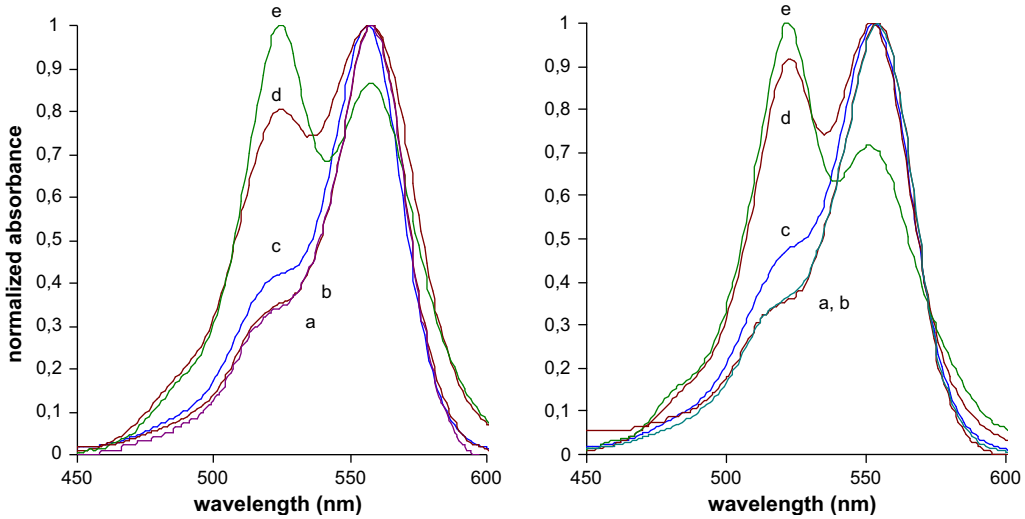


Fig. 2. Normalized UV–vis spectra at pH 2 (left) and 7 (right) of (a) C.I. Basic Violet 10 10^{-6} M; (b) C.I. Basic Violet 10 10^{-5} M; (c) C.I. Basic Violet 10 10^{-4} M; (d) C.I. Basic Violet 10 10^{-3} M; (e) C.I. Basic Violet 10 10^{-2} M.

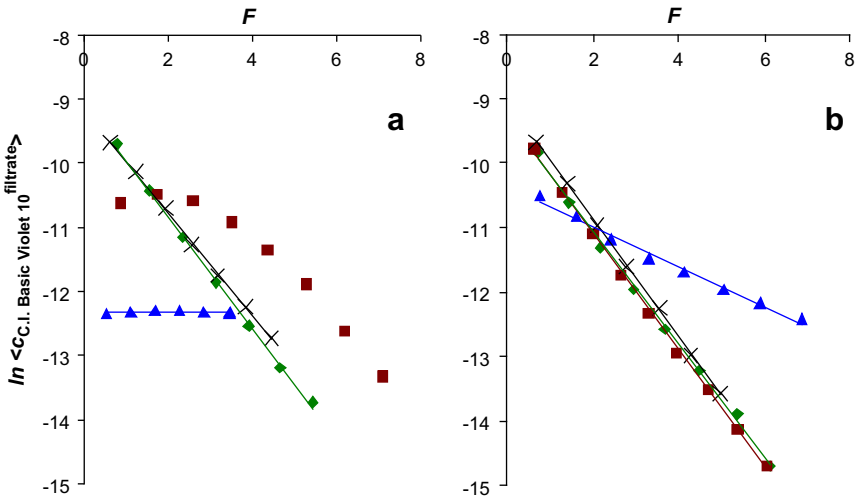


Fig. 3. Diafiltration profiles at pH 2 (left) and 7 (right) of C.I. Basic Violet 10 10^{-4} M in the absence of any polyelectrolyte (x); and in the presence of 2×10^{-4} M (pH 2) and 10^{-3} M (pH 7) of PVS (♦), PAMPS (■), and PSS (▲) (see Table 1 for linear adjustments).

the following hypothesis: when C.I. Basic Violet 10 interacts with PSS, site-specific binding occurs due to short-range interactions; when the cationic C.I. Basic Violet 10 is present (for example, at pH 2) ion pairs between C.I. Basic Violet 10 and the benzene sulfonate groups of the polymer are formed; these ion pairs are hydrophobic, so they may tend to aggregate.

Long-range interactions do not normally produce changes in the UV–vis spectra of the interacting molecules. Thus, in the presence of 100 times PVS and 100 times PAMPS, the absorption spectra of 10^{-5} M C.I. Basic Violet 10 solutions do not change from that of pristine C.I. Basic Violet 10 solutions at pH 2 or 7 (see Fig. 4). On the contrary, as short-range interactions take place with PSS, the C.I. Basic Violet 10 absorption spectrum shows the same profile as that of C.I. Basic Violet 10 monomer, but is shifted to lower energies, revealing the molecular interaction at both pHs. The shift of the absorbance band of xanthene dyes to lower energies is sometimes ascribed to formation of J-aggregates. However, the extent of the aggregation should be a function of the polymer to dye relative concentration, and should tend to decrease under a large excess of the polymer. Due to the large excess of PSS used, we interpret this shift as caused by the interaction of the C.I. Basic Violet 10 transition moment with those of the polymer (as a consequence of the short-range interaction as depicted in Fig. 1) and surrounding water.

3.3. Ion pair aggregation

3.3.1. Ion pair formation

Ion pairs are formed upon interaction of the cationic form of C.I. Basic Violet 10 and the benzene sulfonate groups of PSS, as a consequence of the short-range aromatic–aromatic interaction. It is important to verify if PSS binds both cationic and zwitterionic forms of C.I. Basic Violet 10, as depicted in Scheme 1.

The shift of the maximum of absorbance with the pH is useful to follow the acid–base equilibrium of the dye. It can be seen in Fig. 5, where the maxima of absorbance of 10^{-4} M C.I. Basic Violet 10 solutions in the absence and in the presence of 10^{-3} M PSS are plotted versus the pH, that its apparent pK_a is shifted from 3.2 to around 6 in the presence of the polymer. This reveals a higher affinity of the polymer to bind the cationic form of C.I. Basic Violet 10, provided that electrostatic interactions contribute to the overall interaction. The relatively high acidity of the carboxylic acid of C.I. Basic Violet 10 is justified by the stabilization effect produced by the positively charged xanthene group. As a consequence of the short-range interaction between C.I. Basic Violet 10 and PSS, the basicity of the carboxylate group increases. This can be caused by both the electrostatic stabilization of the electron deficient σ plane of the benzene carboxylic group of C.I. Basic Violet 10 by means of the interaction with the π electrons of the polymeric benzene ring, and the stabilization of the xanthene group of C.I. Basic Violet 10 by interaction with the sulfonate group of the polymer that should be placed next to it (see Fig. 1). A more hydrophobic environment may also contribute to the stabilization of the carboxylic form.

On the other hand, the zwitterionic form of C.I. Basic Violet 10 also interacts with PSS. We can demonstrate this fact by the following analysis: if upon mixing at pH 7 sufficiently concentrated C.I. Basic Violet 10 (in its zwitterionic form) and PSS solutions, all C.I. Basic Violet 10 molecules that bind to PSS protonate, there should be a significant increase in the pH, provided that diafiltration experiments show that PSS binds a significant amount of C.I. Basic Violet 10 at this pH (see Fig. 3 and Ref. [19]). Thus, upon

Table 1
Results for diafiltration of 10^{-4} M C.I. Basic Violet 10 solutions at pH 2 and 7 and different WSP.[a]

Experiment	c_P (M)	pH	v	u	j	k^m	$K^{diss\text{-}WSP}_{C.I.\ Basic\ Violet\ 10}$ [b]	Linear adjustments for the experimental data	R^2
C.I. Basic Violet 10-01	–	2	1.00	0.00	–	0.85	–	$y = -0.85x - 8.9$	1.00
C.I. Basic Violet 10-02	–	7	0.91	0.09	–	0.84	–	$y = -0.84x - 9.5$	1.00
PVS–C.I. Basic Violet 10-01	2×10^{-4}	2	0.90	0.10	0.87	–	$\rightarrow \infty$	$y = -0.87x - 9.1$	1.00
PAMPS–C.I. Basic Violet 10-01	2×10^{-4}	2	–	–	–	–	–	–	–
PSS–C.I. Basic Violet 10-01	2×10^{-4}	2	–	–	$\rightarrow 0$	–	$\rightarrow 0$	–	–
PVS–C.I. Basic Violet 10-02	1×10^{-3}	7	0.82	0.18	0.88	–	$\rightarrow \infty$	$y = -0.88x - 9.3$	1.00
PAMPS–C.I. Basic Violet 10-02	1×10^{-3}	7	0.88	0.12	0.91	–	$\rightarrow \infty$	$y = -0.91x - 9.3$	1.00
PSS–C.I. Basic Violet 10-02	1×10^{-3}	7	0.89	0.11	0.31	–	0.50 ± 0.05	$y = -0.31x - 10.4$	0.99

[a] For linear adjustments: $y = \ln <c^{filtrate}_{C.I.\ Basic\ Violet\ 10}>$; $x = F$; R^2 = linear regression factor.
[b] $K^{diss\text{-}WSP}_{C.I.\ Basic\ Violet\ 10}$ is calculated following $j/(1-j) \leq K^{diss\text{-}WSP}_{C.I.\ Basic\ Violet\ 10} \leq k^m j/(k^m - j)$.

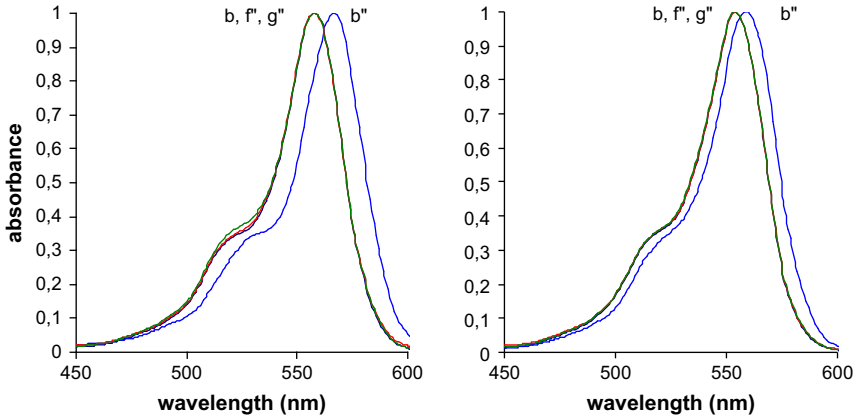


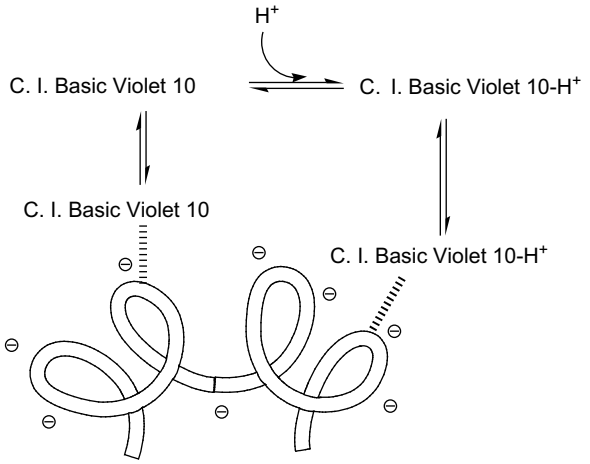
Fig. 4. Normalized UV–vis spectra at pH 2 (left) and 7 (right) of C.I. Basic Violet 10 10^{-5} M in the absence of any polyelectrolyte (b); and in the presence of 10^{-3} M of PSS (b″); PVS (f″); and PAMPS (g″).

mixing 10^{-4} M C.I. Basic Violet 10 solutions at different original pHs with negligible volumes of concentrated PSS (see Experimental section) a significant change in the pH is found between pH 3 and 5, indicating protonation of the dye as can be seen in Fig. 5. However, as the concentration of the zwitterionic form in solution increases, the increase in the pH upon mixing with PSS decreases, and at pH 7 no significant pH change is detected. The lack of change in the pH together with the diafiltration results indicates that the zwitterionic form binds the macromolecule.

Thus, ion pairs are formed between cationic C.I. Basic Violet 10 and benzene sulfonate groups of PSS at pHs under the apparent pK_a of C.I. Basic Violet 10 in the presence of the polymer. The flexibility of the polymer can produce that ion pairs, due to their hydrophobicity, aggregate with a definite geometry. This ion pair aggregation could eventually induce H-type contacts between stacked C.I. Basic Violet 10s. This would be noticed by an increase of the intensities of the bands at 524–522 nm (pH 2–7) relative to those at 556–554 nm, and by a consequent fluorescence quenching. So, these two observations can help us to verify the hypothesis stated before.

3.3.2. *Ion pair aggregation for diluted C.I. Basic Violet 10 solutions*

There must be a correlation between the tendency of the ion pairs to aggregate and the relative amount of benzene sulfonate groups with respect to C.I. Basic Violet 10. Moreover, the pH should influence the extent of ion pair aggregation, since for its formation C.I. Basic Violet 10 must be protonated.



Scheme 1.

Ion pair aggregation is induced in the presence of an excess of 10 times PSS at a C.I. Basic Violet 10 concentration 10^{-5} M and pH 2. This can be seen in Fig. 6 as an increase in the intensity of the band at around 524 nm relative to that at around 556 nm: the corresponding spectra (b, and b′ at pH 2) have been decomposed in two Gaussians, and the ratio band area centered at around 524 nm/band area centered at around 556 was found to be 1.21 and 1.59, respectively. This effect is not observed at pH 7, since the C.I. Basic Violet 10/PSS adducts are negatively charged and less probable to be formed at such diluted conditions (revealed by the small shift of the maximum of absorbance) due to the lack of the long-range electrostatic component in the overall interaction. On the contrary, no significant spectral variation is found in the presence of PVS or PAMPS at any pH.

However, in the presence of a large excess of PSS (100 times), H-contacts are minimized (see Fig. 4), and the intensity of the band at around 524–522 nm (pH 2–7) corresponds approximately to that of the C.I. Basic Violet 10 monomeric state. At these conditions, the C.I. Basic Violet 10 molecules should be far away from each other, distributed in the binding sites of the polyelectrolyte.

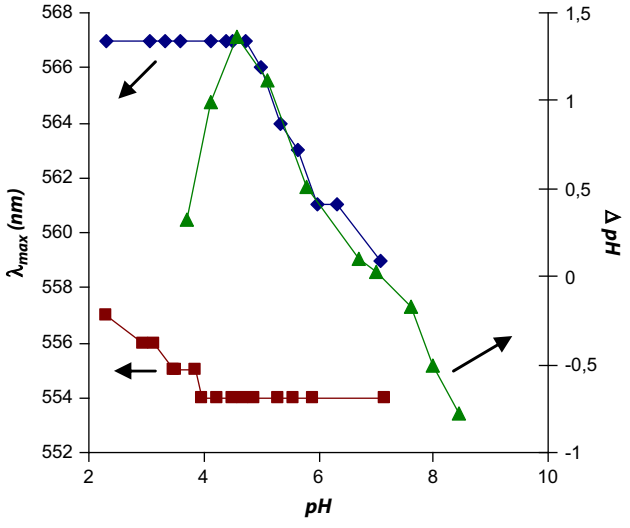


Fig. 5. Position of the maximum of absorbance of a 10^{-4} M C.I. Basic Violet 10 solution as a function of the pH: (■) in the absence of PSS (♦), in the presence of 10^{-3} M PSS; and increase in the pH upon mixing a 10^{-4} M C.I. Basic Violet 10 solution with 10^{-3} M PSS (▲).

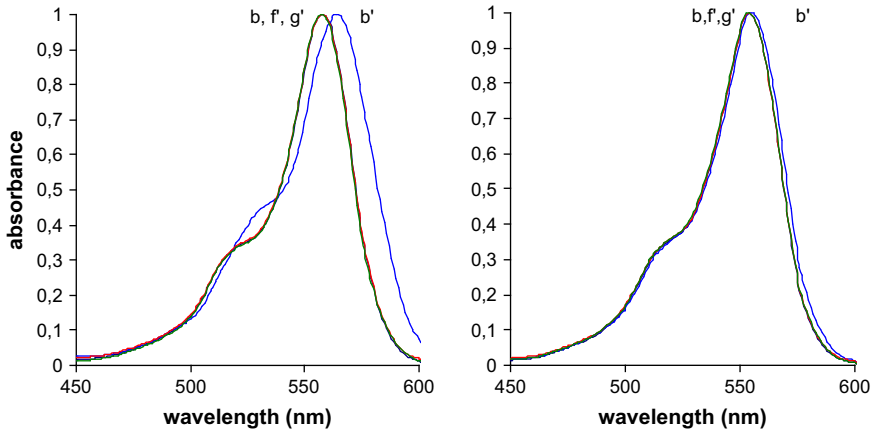


Fig. 6. Normalized UV–vis spectra at pH 2 (left) and 7 (right) of C.I. Basic Violet 10 10^{-5} M in the absence of any polyelectrolyte (b); and in the presence of 10^{-4} M of PSS (b′); PVS (f′); and PAMPS (g′).

The different probability to undergo H-contacts can be also followed observing the fluorescence quenching in C.I. Basic Violet 10 solutions. Corresponding to the shift in absorbance, the fluorescence band is also shifted to lower energies in the presence of excess PSS, while no shift is found for PVS or PAMPS (data not shown). The change in the fluorescence intensity as a function of the PSS/C.I. Basic Violet 10 ratio for different pHs can be seen in Fig. 7. The fluorescence quenching is optimal at PSS/C.I. Basic Violet 10 around 10 at acidic pHs. Smaller ratios will result in less binding and higher conformational restrictions, and higher ratios may result in a decrease in the probability of H-contacts between the ion pairs, since they should be far away from each other and surrounded by hydrophilic groups. On the contrary, no significant fluorescence intensity variation is found for PVS and PAMPS (data not shown) at any pH or for PSS at pH over 5.

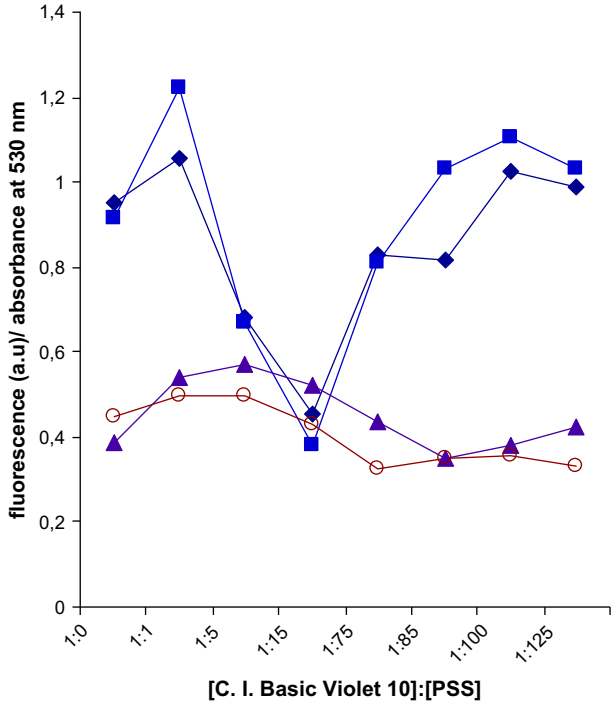


Fig. 7. Ratio fluorescence at 630 nm (a.u.)/absorbance at 530 nm of C.I. Basic Violet 10 2×10^{-6} M solutions in the presence of variable amounts of PSS at pH 2 (◆); 3 (■); 5 (▲); and 6 (○).

3.3.3. Ion pair aggregation for concentrated C.I. Basic Violet 10 solutions

As shown in Section 3.1, for C.I. Basic Violet 10 concentrations higher than 10^{-4} M the appearance of self-aggregates by means of H-contacts is produced and revealed by the corresponding fluorescence quenching and an increase of the bands at 524–522 nm (pH 2–7) relative to those at 556–554 nm (see Fig. 2).

However, PSS is able to disrupt the C.I. Basic Violet 10 self-aggregation tendency. It can be seen in Fig. 8 that in the presence of 100 times PSS, the corresponding absorption bands of C.I. Basic Violet 10 at concentrated C.I. Basic Violet 10 solutions are all equivalent and shifted to lower energies (566–560 nm, at pH 2 and 7, respectively) showing the formation of C.I. Basic Violet 10–PSS complexes. At this PSS/C.I. Basic Violet 10 ratio, C.I. Basic Violet 10 should be found in its monomeric form, so that the high excess of polymer is preventing C.I. Basic Violet 10 to self-aggregate. Thus, despite the high C.I. Basic Violet 10 concentration, the dyes are distributed in the polymer domain so that their aggregation is minimized.

This effect can be contrasted with the effects produced when the interaction has a predominant long-range nature: in the presence of 100 times PVS or PAMPS, at a C.I. Basic Violet 10 concentration of 10^{-3} M and pH 2, the systems undergo phase separation, showing a cooperative behavior in the binding of the dye. In the environment of the polyelectrolytes the local concentration of C.I. Basic Violet 10 increases and the dyes self-aggregate. These aggregates may behave as supramolecular polymers, and thus interpolymer complexes precipitate. The precipitates were filtered and the UV–vis spectra of the supernatants were measured showing C.I. Basic Violet 10 highly aggregated for these two polymer systems (see Fig. 9).

In the presence of 10 times PSS with respect to C.I. Basic Violet 10 (see Fig. 8), the shifting of the bands reveals interaction with PSS, and the intensity of the bands at around 524–522 nm (pH 2–7) relative to those at around 556–554 nm are higher than that of the monomeric C.I. Basic Violet 10 indicating the existence of H-contacts between the dyes. However, a lower absorption intensity is found at around 524–522 nm by comparison with the corresponding absorption of the aqueous C.I. Basic Violet 10 solutions at concentrations 10^{-2} and 10^{-3} M, which may indicate a different aggregation state: in the presence of PSS, low-order aggregates such as dimers may be formed, while higher-order aggregates may be found for the free dye at such high concentrations.

It is also noted that the probability of H-contacts at pH 7 is not zero, a fact that can be explained by the self-aggregation of C.I. Basic

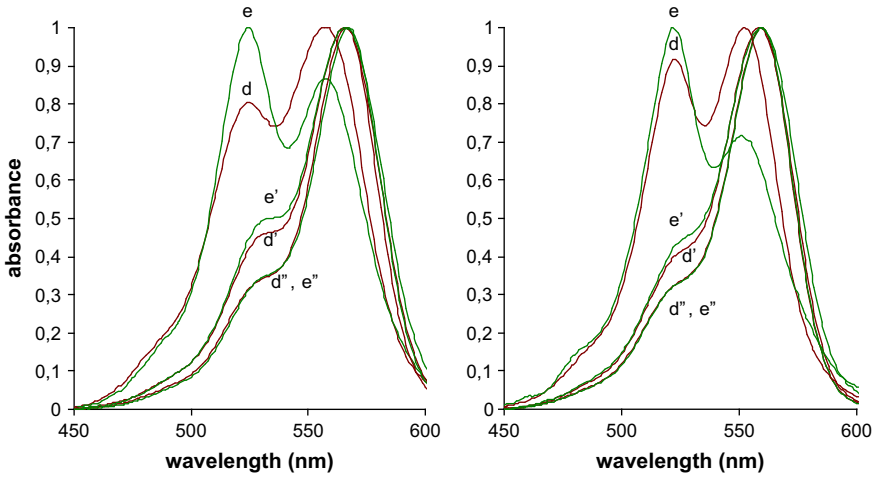


Fig. 8. Normalized UV–vis spectra at pH 2 (left) and 7 (right) of C.I. Basic Violet 10 10^{-3} M (d, d′, d″) and C.I. Basic Violet 10 10^{-2} M (e, e′, e″), in the absence of PSS (d, e), in the presence of 10 times PSS (d′, e′), and in the presence of 100 times PSS (d″, e″).

Violet 10 in any of their states at this high concentration: free, stacked zwitterionic C.I. Basic Violet 10 on PSS, or stacked cationic C.I. Basic Violet 10 on PSS.

3.4. Luminescence modulation

The systems behave similarly at any C.I. Basic Violet 10 concentration in the presence of PSS at pH 2: under a moderate excess of PSS (10 times), the C.I. Basic Violet 10 bound to PSS undergoes H-contacts, but under a large excess of the polymer (100 times), the probability of H-contacts decreases. This has immediate consequences in the solution luminescence that are directly appreciable to the eye: solutions containing an excess of 10 times PSS in relation to C.I. Basic Violet 10 present very low luminescence, while solutions containing an excess of 100 times PSS are luminescent. The emitting light of concentrated C.I. Basic Violet 10 solutions in the presence and in the absence of 100 times PSS, irradiated at 530 nm, is analyzed by the front-face mode in Fig. 10. It can be seen that at these concentrated regimes, at which the probability to undergo self-association for C.I. Basic Violet 10 is high, the luminescence of the solutions is enhanced, since C.I. Basic Violet 10 self-aggregation is minimized. On the contrary, at a diluted regime, at which the probability to undergo self-association for C.I. Basic Violet 10 is low, the luminescence of the solution can be quenched by the addition of 10 times PSS, as can be seen in Fig. 7.

Similar tendencies are found at pH 7: although short-range aromatic–aromatic interactions are held with the polymer, the absence of long-range electrostatic interactions with the zwitterionic form of C.I. Basic Violet 10 produces less binding, so the increase in the fluorescence in the concentrated regime is less noticeable (see Fig. 10). The absence of ion pair formation at this pH due to the zwitterionic nature of the dye prevents aggregation and fluorescence quenching is not observed for very diluted C.I. Basic Violet 10 solutions (see Fig. 7).

The luminescence enhancement of highly concentrated C.I. Basic Violet 10 solutions cannot be obtained with PVS or PAMPS. Thus, the possibility of luminescence modulation of C.I. Basic Violet 10 aqueous solutions by means of aromatic–aromatic interaction with PSS may be useful for C.I. Basic Violet 10 applications.

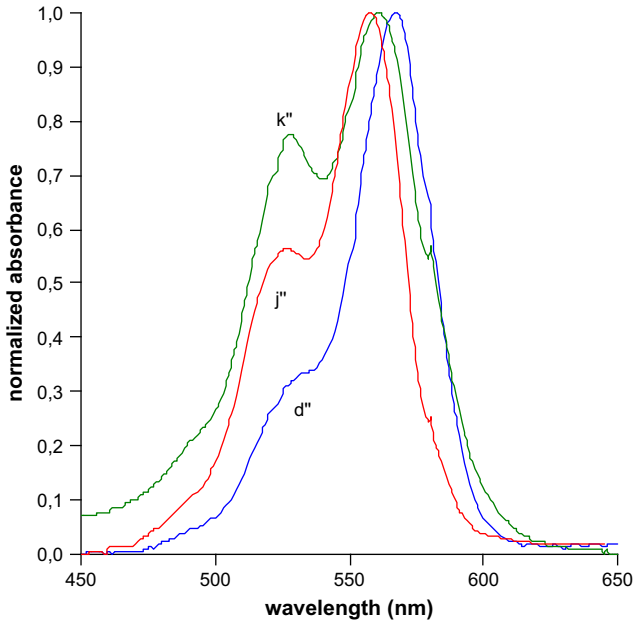


Fig. 9. Normalized UV–vis spectra at pH 2 of 10^{-3} M C.I. Basic Violet 10 filtered solutions in the presence of (d″) 10^{-1} M PSS; (j″) 10^{-1} M PVS; (k″) 10^{-1} M PAMPS.

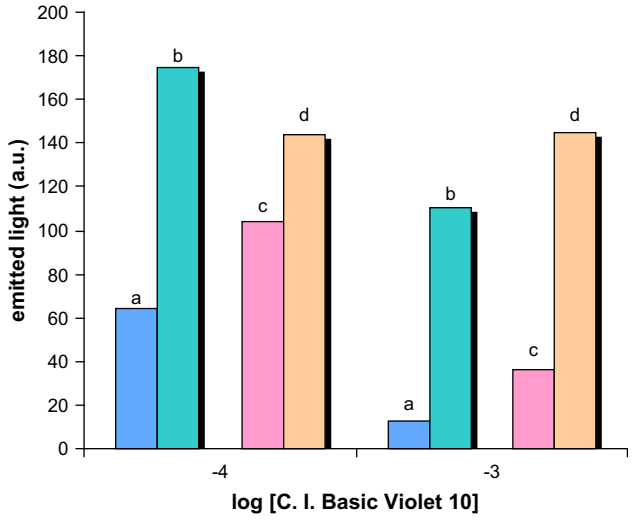


Fig. 10. Intensity of light emitted at pH 2 (a, b) and 7 (c, d) as a function of C.I. Basic Violet 10 concentration in the absence of PSS (a, c), and in the presence of 100 times PSS (b, d).

4. Conclusions

The aggregation of C.I. Basic Violet 10 in the presence of the polyanion containing aromatic groups poly(sodium 4-styrenesulfonate) (PSS) has been investigated. C.I. Basic Violet 10–C.I. Basic Violet 10 H-contacts are probable in water at C.I. Basic Violet 10 concentrations higher than 10^{-4} M. As a consequence of short-range interactions with PSS at pH 2, the positively charged C.I. Basic Violet 10 forms highly hydrophobic ion pairs with the benzene sulfonate groups that tend to aggregate in an H-type binding. The extent of this tendency is related to the relative concentration of the dye with respect to the macromolecule so that H-contacts can be enhanced at conditions at which they are not probable (diluted C.I. Basic Violet 10 solutions, moderate excess of PSS) or avoided at conditions at which they are probable (concentrated C.I. Basic Violet 10 solutions, large excess of PSS). Thus, the luminescent properties of C.I. Basic Violet 10 solutions can be modulated by aromatic–aromatic interactions with PSS.

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