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Surface Modification by Self-Assembled Polycation/Azo Dye Multilayers

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Summary: The formation and stability of some polycation/azo dye multilayers by the alternate adsorption of one polycation of integral type having 95 mol % of N,N-dimethyl-2-hydroxypropyleneammonium chloride repeat units (PCA_5) and four multicharged azo dyes: Crocein Scralet MOO (CSMOO), Ponceau SS (PSS), Direct Blue 1 (DB 1) and Direct Red 80 (DR 80) are discussed in this paper. The dyes were different either by the number of sulfonic groups (PSS, DB 1 and DR 80) or by their position (CSMOO and PSS). The multilayer growth, when PCA_5 was adsorbed from 0.2 M Na_2SO_4 aqueous solution, was followed by UV-Vis spectroscopy and by electrokinetic measurements. Solid state polycation/azo dye complexes were also prepared to get qualitative information on the charge compensation in the multilayers.

Introduction

The interaction between polyelectrolytes and dyes in dilute aqueous solutions has been intensively studied in recent years.[1-10] Many investigations were focused on the thermodynamic analysis of the binding isotherms,[1-5] but also on the practical aspects regarding the removal of the dyes from water,[10-12] the quantitative determination of polyelectrolytes in low concentrations,[6,7] improving the dyeability of fibres,[13] and so on. The use of the polydentate dyes as a component in order to buildup electrostatic self-assembled thin films is also of a great interest,[14-17] but the details regarding the influence of the dye structure on the architecture of this novel systems are still very few. The azo dyes are important as film forming materials, especially on inorganic surfaces (glass, quartz, silicon), resulting in thin films suitable as sensitive coatings to monitor different environments or as components for the electro-optical devices. The growth of some polycation/azo dye thin films using the polycation containing 95 mol % of N, N-dimethyl-2-hydroxypropyleneammonium chloride units in the backbone (PCA_5) and two azo dyes (Direct Blue 1, DB1, and Direct Red 80, DR80), in dependence on the counterion nature, has been already reported.[18,19] A regular increase of the absorbance, in dependence on the layer pair number, was found in the case of the (PCA_5/DR80)

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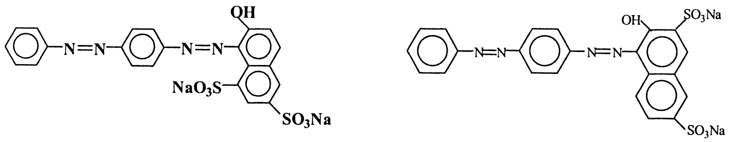
multilayers, even from the first layers, when PCA_5 has been adsorbed from Na_2SO_4 aqueous solution with different concentrations.[19] Consequently, for the study of the buildup and stability of the PCA_5/azo dye multilayers in dependence on the dye structure we used 0.2 M Na_2SO_4 aqueous solution for the polycation adsorption step. The dyes were thus selected: two azo dyes having the same basic structure of 3-hydroxy-4-[4-phenylazo]phenylazonaftalen and two sulfonic groups different by their position as following: 3-hydroxy-4-[4-phenylazo]phenylazo-5,7-naftalendisulfonic acid, disodium salt, Crocein Scarlet MOO (CSMOO) and 3-hydroxy-4-[4-phenylazo]phenylazo-2,7-naftalendisulfonic acid, disodium salt, Ponceau SS (PSS); DB1 with four sulfonic groups and DR80 with six sulfonic groups were also used in order to discuss the multilayer buildup in dependence on the dye structure.

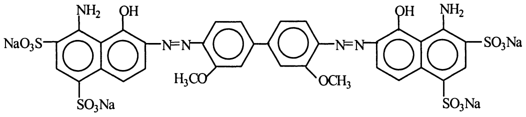
Experimental

Materials

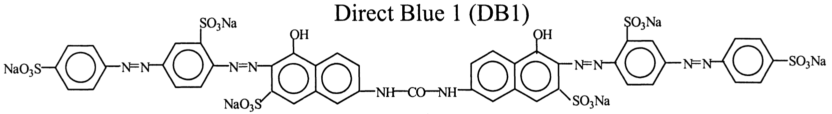
The molecular structures of the polydentate azo dyes and of the polycation used in this study are shown in Figure 1.



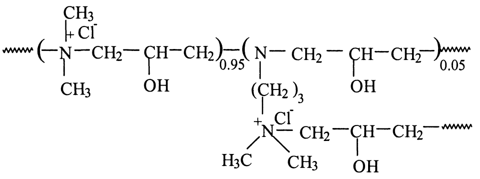
Crocein Scarlet MOO (CSMOO) Ponceau SS (PSS)



Direct Blue 1 (DB1)



Direct Red 80 (DR80)



PCA_5

Figure 1. Chemical structures of the dyes and of the polycation.

Crocein Scarlet M00 (CSM00), Ponceau SS (PSS), Direct Blue 1 (DB1) and Direct Red 80 (DR80) were purchased from Aldrich. Polycation (PCA_5) was synthesized by the condensation polymerization of epichlorohydrin with dimethylamine and N,N-dimethyl-1,3-diaminopropane according to the method presented in detail elsewhere.[20] Polycation was vacuum dried on P_2O_5, at room temperature and then characterized by elemental analyses and intrinsic viscosity in 1M NaCl aqueous solution, at 25° C. The ionic chlorine content (Cl_i) has been measured by potentiometric titration with 0.02 N $AgNO_3$ and the total chlorine content (Cl_t) was performed by combustion method (Schöniger technique). The viscometric measurements of the dilute solutions were carried out with an Ubbelohde viscometer with internal dilution at 25° C. Calcd.: N 10.49; Cl_i 25.26. Found: N 11.00; Cl_t 23.58; Cl_i 23.22. $[\eta]_{1MNaCl} = 0.46$ dL/g.

All solutions were prepared at room temperature one day before their using. A stock solution of the PCA_5 with a concentration of 10 mM was prepared first. The polycation concentration was determined by the polyelectrolyte titration using a Mütek PCD-Titrator. To obtain polycation in 0.2 M Na_2SO_4 aqueous solution, the corresponding amount of salt was added to the polycation aqueous solution already prepared. The salt concentration was 20 times higher than the polycation concentration and therefore we can assume that a whole ion exchange of the initial counterion (Cl^-) with the new counterion (SO_4^{2-}) took place after about 24 h. Poly(sodium styrenesulfonate) (NaPSS) with a molecular weight of 70 000 g/mol and a concentration of 10 unit mM was used as an anionic component for the background preparation in combination with PCA_5. Dye solutions with a concentration of about 1 mM were used except the DB1 and DR80 which concentration was about 0.22 mM.

Solid state PCA_5/dye complex formation

To avoid stacking of the dye by the polycation, the dye solution was slowly dropped into the aqueous solution of PCA_5 with a concentration of 2 unit mM, under a very efficient magnetic stirring at room temperature (~ 293K), until the phase separation was achieved. The stirring continued about two hours to accomplish the PCA_5/dye complex formation. The polycation/dye complexes were separated from aqueous phase by filtration, washed several times with bidistilled water and finally with acetone to remove the excess of the dye. The PCA_5/dye complexes were dried for several days in vacuum over P_2O_5 at room temperature and then were ground to very small crystalline particles. The bulk composition for the polycation-dye complexes was determined by chlorine, nitrogen and sulfur analyses, using an Elementar Vario EL device.

Multilayer deposition

Glass substrates with the dimensions of 76x26x1 mm were used to follow the PCA_5/azo dye multilayers buildup by the UV-Vis spectroscopy and the electrokinetic measurements. The substrates were cleaned in hot chromic acid at 80^0 C for 2 h, in an ultrasonic bath, just prior to the adsorption process and then washed with copious amounts of Millipore Milli-Q water. The adsorptions were carried out at room temperature in open glass beakers of 100 mL, for 20 min. After every deposited layer, the substrates were rinsed with Millipore water three times each 1 min. The substrates were not dried between the adsorption steps.

UV-Vis spectroscopy

The UV-Vis spectroscopic measurements of the PCA_5/azo dye multilayers were performed with a Perkin Elmer Lambda 800 device, on the dry slides.

Electrokinetic measurements

The electrokinetic measurements were performed using an Electrokinetic Analyser (EKA) (Anton Paar KG, Graz, Austria), by measuring the streaming potential between two electrodes. Two glass substrates were tightly mounted between the two Ag/AgCl electrodes in the measuring cell. A 10^{-3} M aqueous solution of KCl was used as a test solution for all the measurements. The zeta potential (ζ) was calculated from the streaming potential determined in dependence on the pressure difference and from the specific conductivity of the solution according to the following Equation:[21,22]

$$\zeta = (\eta/\varepsilon_0\varepsilon_r) \times (\Delta U/\Delta p) \times \kappa$$

where: ζ is the zeta potential; ΔU - the streaming potential; Δp - pressure; κ - conductivity; η - dynamic viscosity of the test liquid; ε_r - relative permitivity of the solution and ε_o – dielectric constant.

A Fairbrother-Mastin programm was used for data evaluation.

Results and Discussion

The multilayer buildup by the alternate deposition of the PCA_5 and the azo dyes above mentioned was followed first by the UV-Vis spectroscopy. A $(PCA_5/NaPSS)_2$ precursor film was previously prepared, both polyions being adsorbed from aqueous solution. Figure 2 shows the UV-Vis spectra of the $(PCA_5/CSMOO)_n$ multilayers in dependence on the layer pair number. A batochromic shift of the characteristic maximum of the nonaggregated dye molecules from 510 nm at about 516 nm can be remarked which increased continuously with the increase of the $PCA_5/CSMOO$ layer pair number. The increase of the maximum at 350 nm is an evidence for a certain order of the dye molecules in the multilayer.

Figure 3 illustrates the changes of the $(PCA_5/PSS)_n$ multilayer UV-Vis spectra in dependence on the layer pair number. A red shift of the characteristic maximum of the nonaggregated dye molecules from 514 nm to about 530 nm and a shoulder at about 580 nm were evidenced in this case and both maxima regularly increased with the layer pair number.

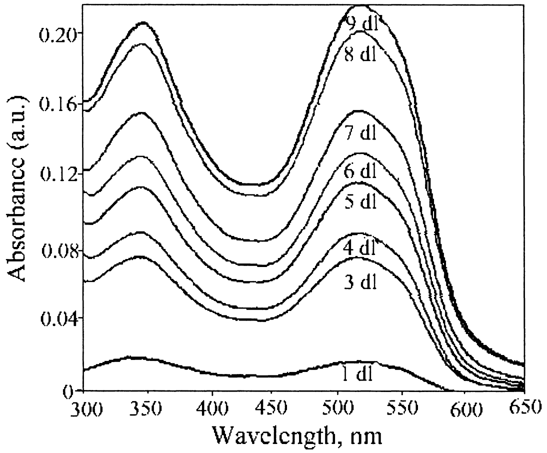


Figure 2. UV-Vis spectra of the $(PCA_5/CSMOO)_n$ multilayers in dependence on the layer pair number adsorbed on the glass substrates which had a $(PCA_5/NaPSS)_2$ precursor.

The differences between the UV-Vis spectra of the $(PCA_5/CSMOO)_n$ and $(PCA_5/PSS)_n$ multilayers revealed that a specific influence of the sulfonic groups position on the dye binding mechanism in the multilayer is possible, when PCA_5 was adsorbed as a compact layer (from 0.2 M Na_2SO_4 aqueous solution in all these experiments). Taking into account the continuous increase of the maximum at 350 nm, found in the $(PCA_5/CSMOO)_n$ multilayer UV-Vis spectra (Figure 2), we assume that an interdigitated interaction of the dye molecules in the multilayer takes place in the case of CSMOO.[23,24]

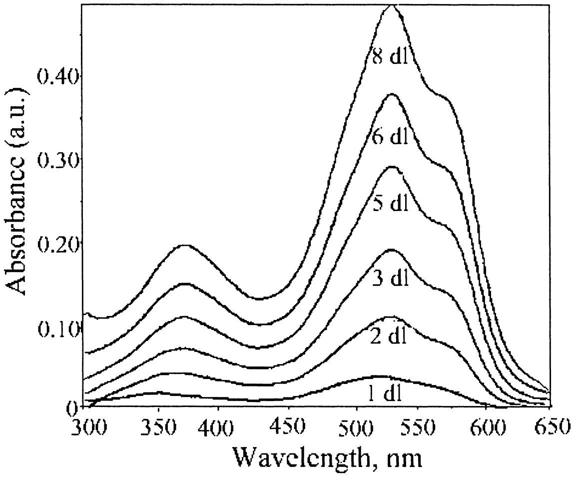


Figure 3. UV-Vis spectra of the $(PCA_5/PSS)_n$ multilayers in dependence on the layer pair number adsorbed on the glass substrates which had a $(PCA_5/NaPSS)_2$ precursor.

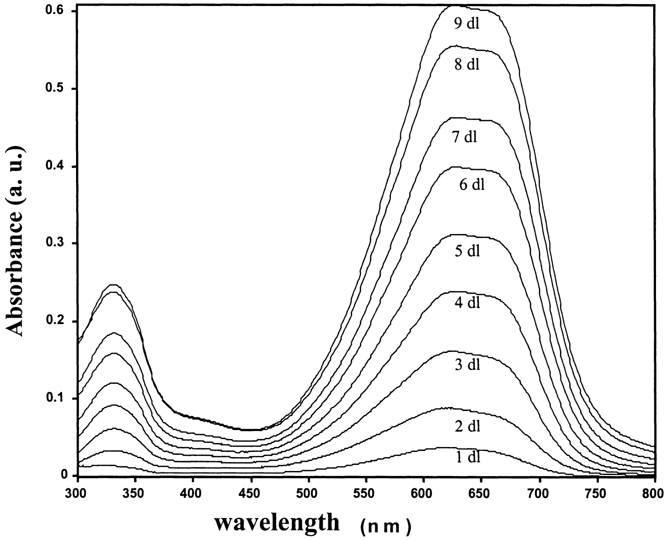


Figure 4. UV-Vis spectra of the $(PCA_5/DB1)_n$ multilayers in dependence on the layer pair number adsorbed on the glass substrates which had a $(PCA_5/NaPSS)_2$ precursor.

This is about a side-by-side interaction between the dye molecules which is usually accomopanied by maxima around 350 nm. Both sulfonic groups of the CSMOO could be involved in the interaction with the polycation layer, but a further dye amount could be adsorbed by the hydrophobic interactions between the non-polar part of the dye. In this way, the dye layer is able to interact with the next polycation layer by the electrostatic interactions. A so named J-aggregation (brick-stone aggregation) of the PSS molecules seems to take place in the $(PCA_5/PSS)_n$ multilayers, the red shift at 580 nm being an evidence for such an aggregation (Figure 3). A continuous increase of the characteristic maximum at 618 nm and a shoulder at about 680 nm were found in the UV-Vis spectra of the $(PCA_5/DB1)_n$ multilayers (Figure 4). The position of the maxima remained the same, irrespective of the layer pair number, and this shows that a regular increase of the multilayer thin film takes place also in this case. The characteristic maximum of the nonaggregated DR80 molecules, found at 520 nm in dilute aqueous solutions, was red shifted at 558 nm for the dye bound in the $(PCA_5/DR80)_n$ multilayers and a regular increase of the absorbance with the layer pair number was also observed. A J-aggregation of the dyes in the multilayers was suggested for both substantive dyes (DB1 and DR80) since only batochromic shifts of the characteristic maxima were found.

A competion between the water soluble polylectrolyte/dye complex and the dye bound in a polycation/dye multilayer it is possible,[17] as much as the dye is adsorbed also by other interactions than the electrostatic ones. To get further information on the dye binding in the PCA_5/azo dye multilayers the absorbance values at the characteristic wavelengths of the polycation/azo dye multilayers, after every adsorption step, were measured. The absorbance values at 516 nm for $(PCA_5/CSMOO)_n$ multilayers and at 527 nm for $(PCA_5/PSS)_n$ multilayers, respectively, after every adsorbed layer, were collected in Figure 5. As one can see, every polycation adsorption step was accompanied by the decrease of the absorbance in the case of CSMOO as a dye component, but no decrease was remarked in the case of PSS. This behavior shows that part of the adsorbed CSMOO molecules was removed in the polycation adsorption step, but no dye molecules left the substrate in the case of PSS. To explain the difference between these two azo dyes which have the same structure, only the sulfonic groups are in different positions, we suppose that only one sulfonic group of the PSS was bound on the polycation layer and the other one remained free and able to interact with a new polycation layer. On the other hand, in the case of CSMOO, both sulfonic groups could be involved in the interaction with the polycation layer and the excess of negative charges necessary for the adsorption of the next polycation layer is provided by the hydrophobic adsorption of further dye molecules. Part of the CSMOO molecules which were bound by hydrophobic interactions were removed during the adsorption of the next polycation layer.

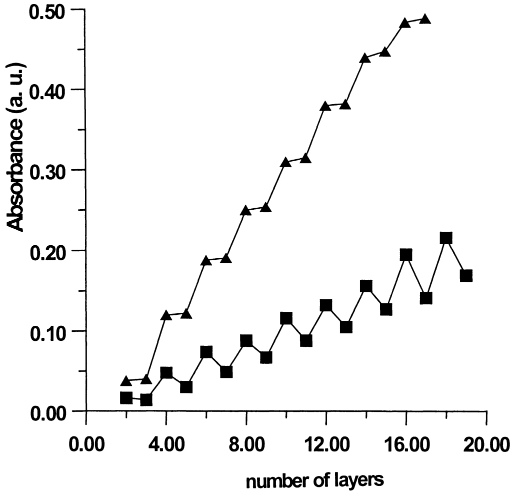


Figure 5. Absorbance at 516 nm of the $(PCA_5/CSMOO)_n$ multilayers (■) and at 527 nm of the $(PCA_5/PSS)_n$ multilayers (▲), respectively, in dependence on the number of layers adsorbed on the glass substrates which had a $(PCA_5/NaPSS)_2$ precursor.

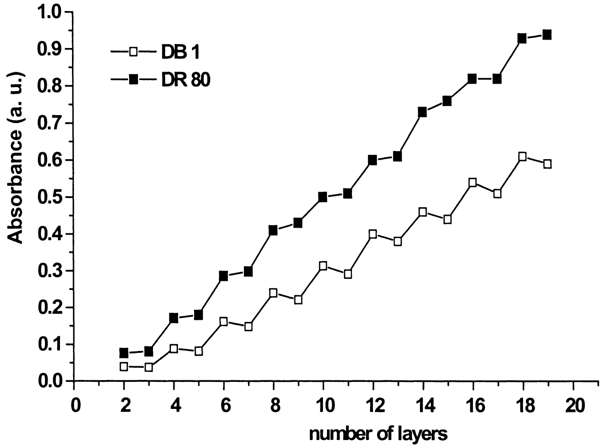


Figure 6. Absorbance at 558 nm of the $(PCA_5/DR80)_n$ multilayers and at 620 nm of the $(PCA_5/DB1)_n$ multilayers, respectively, in dependence on the number of layers adsorbed on the glass substrates which had a $(PCA_5/NaPSS)_2$ precursor.

A very good stability of the adsorbed dye layer was remarked in the case of the substantive azo dyes when every layer was measured (Figure 6). The high stability of the PCA_5/azo dye multilayers for the last two azo dyes show that only part of the sulfonic groups interact with the polycation layer and enough free negative charges remain to interact with the next polycation layer.

The electrokinetic measurements can give information on the surface charge and on the stability of the polycation/azo dye multilayers in dependence on the dye structure. In Figure 7 we collected the values of the ζ potential in dependence on pH for the $(PCA_5/\text{azo dye})_5$ multilayers when the polycation was adsorbed from 0.2 M Na_2SO_4 aqueous solution, on the glass substrates and the dye was the last layer adsorbed.

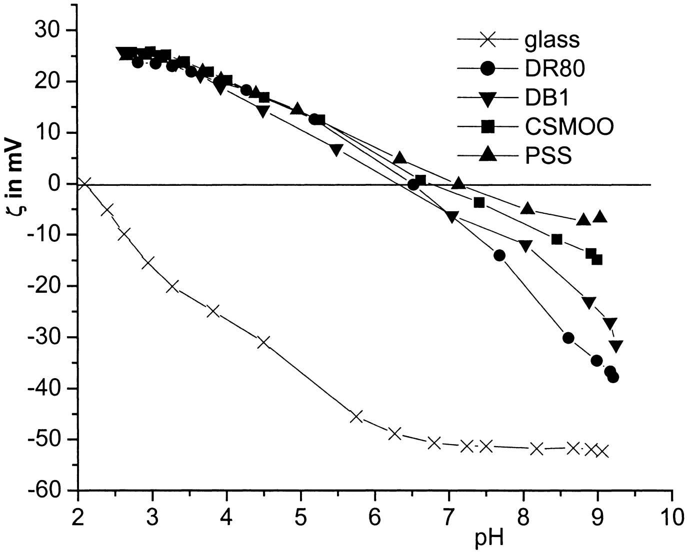


Figure 7. ζ potential in dependence on pH for the assembly $(PCA_5/NaPSS)_2$ + $(PCA_5/\text{azo dye})_5$ when PCA_5 was adsorbed from 0.2 M Na_2SO_4 aqueous solution.

As can be seen, a higher number of sulfonic groups of the dye led to a more negative surface after the dye adsorption, ζ potential values in the basic range being in the following order: $\zeta_{DR80}<\zeta_{DB1}<<\zeta_{CSMOO}<\zeta_{PSS}$. A higher compensation of the positive charges of the substrate led also to a lower pH value corresponding to the isoelectric point (pH_{IEP}). Thus, the electrokinetic measurements confirm the dye binding mechanism in the PCA_5/azo dye multilayer proposed on the basis of the UV-Vis measurements, the ζ potential values being lower in the case of the CSMOO as the last layer adsorbed than in the case of PSS. This behavior shows that a higher density of sulfonic groups is present on the film surface with CSMOO as the last layer adsorbed.

The stability of the $(PCA_5/\text{azo dye})_5$ nanoarchitectures under the streaming potential measurement conditions, in dependence on the dye structure, was checked by the UV-Vis spectroscopy measurements after the ζ potential measurement. Small differences were found in the case of PSS, DB1 and DR80 as the last layer adsorbed and also when the PCA_5 was the topmost layer. These results revealed that the interaction between these dyes and the polycation layer is not disturbed under the streaming potential measurement conditions (streaming pressure of 150 mbar, over 4h). A different behavior was observed in the case of the $(PCA_5/CSMOO)_5$ assemblies when the dye was the last layer adsorbed. Very small differences between the absorbance values at 516 nm, before and after the electrokinetic measurement were evidenced. On the other hand, the maximum at 350 nm was about completely diminished after the streaming potential measurement. That is the interdigitated aggregation of the CSMOO molecules, which were adsorbed in a certain order by hydrophobic interactions, was disturbed under the streaming potential measurement conditions.

Solid state PCA_5/azo dye complexes

Elemental analysis of the PCA_5/azo dye complexes in the solid state can give qualitative information at least on charge compensation in the multilayer. The polycation-azo dye complex formation takes place according to the following equation:

$$PC^{n+} + n/mxD^{m-} \rightarrow PCxn/mD + nNaCl \qquad (1)$$

Molecular weight (MW) of the theoretical repeat unit of the polycation-dye complex was calculated starting from the assumption that only stoichiometric complexes were formed. In this case, MW of the complex repeat unit was calculated by the following relationship:

$$MW_{\text{complex repeat unit}} = MW_{\text{dye}} + mxM_{\text{repeat unit of PCA5}} - mxM_{\text{NaCl}} \qquad (2)$$

where m is the number of sulfonic groups of the dye.

Elemental analyses calculated for the PCA_5/dye complexes, taking into account the structures of the polycation and the dyes presented in Figure 1, were collected in Table 1. Table 2 contains the elemental analyses found for the PCA_5/azo dye complexes in the solid state. A good agreement between the theoretical and the experimental values of the elemental analyses was found for these complexes.

Table 1. Elemental analyses calculated for the possible PCA_5/Azo-dye complexes.

Polycation/dye complex	M_W of the dye / g/mol	PCA_5/dye molar ratio for the theoretical structure	M_W of the PCA_5/dye complex repeat unit / (g/mol)	Cl / %	N / %	S / %	S/N
PCA_5/CSMOO	556.50	2.0	720.25	0	11.66	8.86	0.76
PCA_5/PSS	556.50	2.0	720.25	0	11.66	8.86	0.76
PCA_5/DB1	992.82	4.0	1320.82	0	10.60	9.69	0.914
PCA_5/DR80	1373.1	6.0	1865.1	0	12.01	10.29	0.856

Table 2. Elemental analyses found for the PCA_5/Dye complexes in the solid state in dependence on the dye structure.

PCA_5/dye Complex	PCA_5/dye molar ratio to the phase separation	Cl / %	N / %	S / %	S/N
PCA_5/CSMOO	2.2	<0.50	10.65	8.14	0.764
PCA_5/PSS	1.9	<0.50	11.05	8.68	0.785
PCA_5/DB1	4.01	<0.50	10.02	9.57	0.955
PCA_5/DR80	5.9	<0.5	11.38	9.35	0.821

The very low content of the small counterions in the PCA_5/azo dye complexes is an evidence for their stoichiometry and for a good compensation of charges. The elemental analysis values, found in the case of PCA_5/CSMOO complex, which were close to those corresponding to the stoichiometric complexes, showed that the excess of the dye has been removed by cleaning of the complexes with an organic solvent (acetone) (Experimental part).

Conclusions

In the present study on the influence of the dye structure on the polycation/azo dye multilayer construction we have shown that there is a clear influence not only of the sulfonic groups number, but also of their position. The interdigitated aggregation proposed for the CSMOO adsorption, has been supported by both the UV-Vis spectroscopy and the streaming potential measurements. The dye binding mainly by the electrostatic interactions and a J-aggregation of PSS, DB1 and DR80, when PCA_5 was adsorbed from 0.2 M Na_2SO_4 aqueous solution, were supported by the red shifted characteristic maxima of these dyes and by their high stability under the streaming potential measurements conditions.

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