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Mechanisms of adsorption of an azo-polyelectrolyte onto layer-by-layer films

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Abstract

The mechanisms which lead to the adsorption of the azopolyelectrolyte poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzene sulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) layer adsorbed onto layer-by-layer films were investigated by monitoring the adsorbed amount per unit of area as a function of time. The adsorption kinetics curves were obtained as a function of adsorption variables as PAZO concentration and drying process. The PAZO adsorption kinetics data was shown to be described by two processes, one with smaller adsorption characteristic time, of the order of seconds, which was attributed to a nucleation mechanism and a second process, with adsorption characteristic times of the order of tenth of minutes, associated to diffusion. During the first process, PAZO molecules rapidly adsorb onto the substrate surface creating an electrostatic barrier that makes difficult the adsorption of more PAZO molecules. However, positive counterions are allowed to be adsorbed and as they are the potential barrier is lowered, allowing more PAZO molecules to be adsorbed. This last mechanism is accounting for the second adsorption process. The adsorption processes are not seen to be influenced by the layer drying and only contribute for the changes in the values of adsorption parameters, i.e., adsorption characteristic times and corresponding adsorbed amounts. These parameters were related with the available number of adsorption sites which are dependent of the presence of both water and counterions adsorbed on the last adsorbed layer.

Keywords: Layer-by-layer; Adsorption; Polyelectrolyte; Water network; Azo-polyelectrolyte; PAZO

1. Introduction

The main interest to study the formation of PAZO layer is due to its photoisomerization capabilities about the N=N bond which makes it suitable for multipurpose device applications as holographic image storage, optical switching, optical computation, reversible optical storage, optical relief refractive and index gratings, digital video recorders, photosensitive artificial membranes and eventually molecular-machines [1]. The adsorption kinetics of polyelectrolytes onto solid surfaces, obtained by measuring the adsorbed amount with time, has been investigated for several decades by adsorbing them onto solid substrates, usually silica spheres, that where initially immersed in an aqueous solution and the polyelectrolyte injected afterwards while the solution is being stirred. Consequently, the polyelectrolyte adsorption kinetics has a characteristic time which is dependent of the polyelectrolyte diffusion process in the solvent and of the polyelectrolyte interactions with the substrate, assuming that the polyelectrolyte concentration, pH and ionic strength and other factors as temperature and pressure are held constant during adsorption. With the advent of the layer-by-layer (LbL) technique [2–4], which consists of sequential adsorption cationic and anionic polyelectrolytes from aqueous solutions onto solid substrates, with the adsorption taking place at a planar substrate during a determined period of time. Both, the experimental procedure and, consequently, the adsorption kinetics are different. Although the adsorption process is expected to be also driven by electrostatic forces, different adsorption characteristic times are expected, since the solid planar substrate is immersed rapidly in the polyelectrolyte solution, allowing that the polyelectrolyte molecules are instantaneously in contact with substrate. Moreover, since during the production of LbL films the polyelectrolyte layers are often dried after adsorption other mechanisms should be involved. In fact, experimental results of adsorption kinetics dependence on the layer drying process, obtained for polyanilines and poly(*p*-phenylene vinylene) (PPV) precursor [5,6], revealed that polyelectrolyte adsorption onto itself is allowed which is odd in what is expected to be

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an electrostatic driven process. Different kinetics curves were also obtained for the case of polyanilines and poly(*p*-phenylene vinylene) precursor [5,6], where it was shown that the number of immersions and the drying of the film influences the film growth kinetics. This behaviour was associated with the polyelectrolyte hydrogen bonding capabilities. However, this could not be the reason for the adsorption of all polyelectrolytes. Consequently, the experimental procedure used to obtain the true kinetics curves must be well controlled when using the LbL technique namely for taking into account the adsorption processes dependence on the surface where adsorption is taking place. As suggested [7,8], the kinetics curves should be obtained by doing only one immersion per layer using different adsorption periods of times, being the kinetics curves the adsorbed amount per layer as a function of immersion time. This was the procedure adopted in this work, to investigate the mechanisms involved on the adsorption kinetics of a PAZO layer, a high degree of charge polyelectrolyte [9], onto already deposited PAH/PAZO LbL films during different periods of time, under different adsorption conditions as solution concentration and drying process. In this article, the mechanisms involved in the adsorption of one PAZO layer onto PAH/PAZO LbL films are discussed which explain the two processes, nucleation and diffusion, which are occurring during the PAZO adsorption.

2. Experimental

The poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) kinetics adsorption studies were performed adsorbing PAZO onto (poly(allylamine hydrochloride)(PAH)/PAZO)/PAH LbL films. For that, aqueous solutions of PAH (average $M_w = 50{,}000$–65,000 g/mol) with concentration of 10^{-2} M and solutions of PAZO with different concentrations in a buffer solution at pH 10 were prepared. The polyelectrolyte concentrations were based on the molecular weight repeat unit. Chemicals were obtained from Sigma–Aldrich and the polyelectrolytes molecular structures are shown in Fig. 1. The pure water with a resistivity of 18.2 MΩcm was supplied by a Millipore system (Milli-Q, Millipore GmbH). For pH 10 buffer solution, a 0.05 M sodium bicarbonate ($NaHCO_3$) aqueous solution and a 0.1 M sodium hydroxide (NaOH) solution were used in the proportion 500:107 (v/v) [10].

The films were directly deposited on BK7 optical glass substrates for the adsorption kinetics studies. The substrates were hydrophilized with a H_2SO_4/H_2O_2 (1:1) bath for 1 h, after which the glass and silicon slides were washed exhaustively with pure water [5].

Two types of films, dry and wet, were prepared. The dried films were obtained by immersing the substrate in the PAH solution during 3 min, washing it with water, drying it using a nitrogen flux, immersing it during a determined period of time in the PAZO solution, washing it with buffer solution and finally drying it with a nitrogen flux. This procedure gives rise to a bilayer film. Films with several bilayers were obtained by repeating this procedure. The wet samples were obtained immersing the substrate in the PAH solution during 3 min, washing with water, immersing the substrate in the PAZO solution during a determined period of time and washing with the buffer solution. This procedure was repeated during five times and finally, the samples were left to dry at room conditions.

The adsorbed amount of PAZO per unit of area was quantified by measuring the UV–vis absorbance spectra of PAZO solutions at different concentrations which were obtained dissolving the weighted PAZO polymer powder in the buffer solution at pH 10 and plotting the maximum absorbance at 360 nm, which is associated to the $\pi \rightarrow \pi^*$ azo-chromophore transition, versus the solution concentration. The obtained experimental points were fitted with a straight line and using the Beer–Lambert law, an extinction coefficient ($\varepsilon_{360\,\mathrm{nm}}$) of $4.30 \pm 0.07\ \mathrm{g^{-1}\,m^2}$ at 360 nm for PAZO was estimated. The amount of PAZO per unit of area (Γ) adsorbed onto a solid substrate is estimated using again the Beer–Lambert law:

$$\Gamma = \frac{\mathrm{Abs}_{360\,\mathrm{nm}}}{2\varepsilon_{360\,\mathrm{nm}}} \tag{1}$$

The UV–vis absorbance spectra of liquid and solid samples were measured using a Shimadzu UV-2101PC spectrophotometer.

3. Results and discussion

3.1. PAZO adsorption kinetics at pH 10 of dried samples

The adsorption kinetics of PAZO onto (PAH/PAZO)$_n$/PAH LbL films was obtained preparing PAH/PAZO LbL films with different PAZO adsorption times and maintaining the adsorption time of 3 min for the PAH. After each adsorption period, the samples were dried with a nitrogen flux and the absorbance spectra of LbL films having different number of bilayers were measured. The graph of Fig. 2 shows the spectra of (PAH/PAZO) LbL films with different number of bilayers obtained for PAZO adsorption time of 30 s. Plotting the maximum absorbance as a function of the number of bilayers for the LbL films prepared

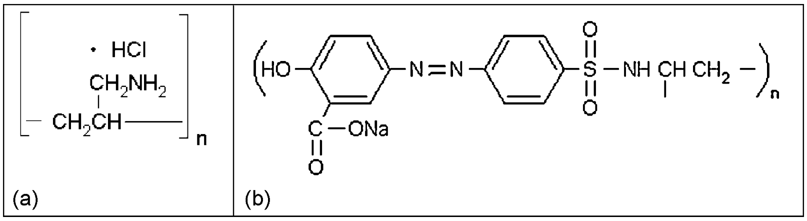

Fig. 1. Polyelectrolyte molecular structures: (a) poly(allylamine hydrochloride) (PAH) and (b) poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO).