

## STIMULI RESPONSIVE MICRO-COMPOSITES TAILORED BY ALTERNATE ADSORPTION OF WEAK POLYELECTROLYTES ON A MICROPOROUS MEMBRANE

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This study is focused on the surface modification of microporous polyacrylonitrile membrane properties, by alternate adsorption of oppositely charged weak polyelectrolytes. For multilayer construction, three polyanions, poly(sodium acrylate) and two copolymers of acrylic acid with maleic acid or with itaconic acid, as sodium salt, and chitosan as polycation, were used. The influences of the polyanion nature and of the double layer number on the properties of composite membranes were monitored by the amount of polymer adsorbed, the swelling degree in water, and by atomic force microscopy. The stimuli responsiveness of the composite membrane has been followed by the swelling degree as a function of pH and ionic strength.

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### 1. Introduction

The membranes surface, which plays an important role in the membrane performance, can be modified by different methods, usually classified into three groups: physical, chemical and bulk modifications [1,2]. Surface modification by physical methods is mainly based on ionic, H-bonds and hydrophobic interactions.

One of the most versatile and convenient physical method for surface modification is layer-by-layer self-assembly of oppositely charged polyelectrolytes [3-9]. The most substantial advantages of this technique are the simplicity of the deposition procedure, which allows the thin films construction on substrates with any shape not only planar, and a strict control of the average thickness and the nanoarchitecture of oppositely charged species layers [5-9]. Since attractive electrostatic interactions govern the formation of the polyelectrolyte multilayers, the thickness of the multilayer assembly depends mainly on the surface charge density, and the charge density of polyelectrolytes, which can be controlled by the pH and ionic strength of the deposition medium [8,10]. The formation of polyelectrolyte multilayer films by the layer-by-layer technique can provide materials with broad potential applications in the fields of surface modification, sensors, or separation membranes [7-9,11,12].

The aim of this study was to modify the surface properties of a microporous polyacrylonitrile (PAN) membrane, to control the swelling degree of the new composite materials. For this purpose, the membrane surface was modified by alternate deposition of three weak polyanions, poly(sodium acrylate) (PANa) and two copolymers of acrylic acid with maleic acid (PAAMNa) or with itaconic acid (PAAINa), and chitosan (CS) as weak polycation. The composite membranes have been characterized by swelling degree (SD) and atomic force microscopy (AFM), comparative with the starting membrane. The stimuli responsive behavior of the composite

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membrane was followed by the swelling degree as a function of environment pH and ionic strength.

## 2. Experimental

### 2.1. Materials

Asymmetrical PAN supporting membrane, characterized by an average pore diameter of 12 nm and an average thickness of about 60  $\mu\text{m}$ , having polyester fabric reinforcement, was previously treated with oxygen plasma (GKSS Research Center, Geesthacht, GmbH, Germany) [8].

PANa, PAAMNa and PAAINa were prepared according to ref [13]. The chemical structure and the molar mass of all polyanions are included in Table 1.

Table 1. Some characteristics of the polymers used in this study.

Polymer	Chemical structure	$M_w$ , g/mol
PANa		15900
PAAMNa		16900
PAAINa		17500

Fig. 1 shows the  $^1\text{H-NMR}$  spectra of polyanions involved in this study, recorded with Bruker NMR model Avance DRX 400 (400 MHz) spectrometer, in  $\text{D}_2\text{O}$  at room temperature. The codes of the protons assigned in  $^1\text{H-NMR}$  spectra correspond to the codes in the chemical structure of the corresponding polyanions (Table 1).

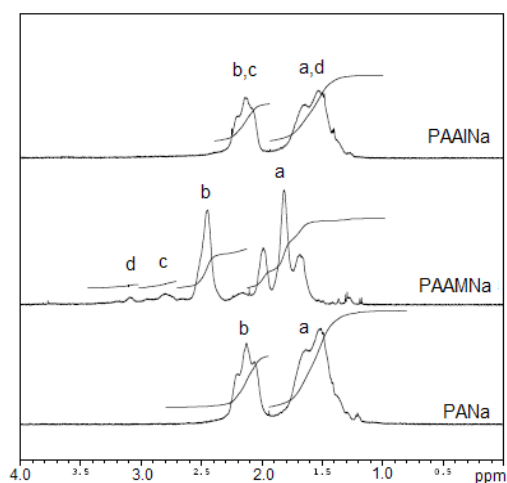


Fig. 1.  $^1\text{H-NMR}$  spectra of polyanions.

The ratio between monomers in the copolymers structure was calculated from the protons relative intensity at 2.46 and 2.8 - 3.1 ppm for PAAMNa, and at 1.45 and 2.15 ppm for PAAINa.

CS was purchased from Heppe GmbH, Germany, as flakes, ash content less than 1%, and used without further purification. The viscometric average molar masses of CS sample,  $M_v = 470000$  g/mol, was estimated using the eq. (1) [14]:

$$[\eta] = 1.38 \times 10^{-4} M_v^{0.85} \quad (1)$$

The intrinsic viscosity of CS solution in the mixture of 0.3 M  $\text{CH}_3\text{COOH}$  and 0.2 M  $\text{CH}_3\text{COONa}$  (1:1, v/v) was measured with an Ubbelohde viscometer at  $25 \pm 0.1$  °C.

The CS deacetylation degree, of about 82.5 %, was determined from  $^1\text{H-NMR}$  spectra recorded on Bruker NMR model Avance DRX 400 (400 MHz) spectrometer. The CS sample was dissolved in  $\text{D}_2\text{O}$  and, to avoid the overlap between the signals of acetic acid and acetyl groups, some drops of HCl have been added to solubilize the polymer. The deacetylation degree was calculated as described before by Hiray et al. [15].

The CS solutions with a concentration of  $10^{-3}$  mol/L were obtained by solving the flakes in 1 vol.-% acetic acid solution and intensive stirring 48 h. Aqueous solutions of polyanions with concentrations of  $10^{-3}$  mol/L have been used in the multilayer construction.

## 2.2. Polyion multilayer buildup

Polyion adsorption on the membrane surface was carried out at room temperature in open Petri boxes with an immersion time of 20 min. After every polyion adsorption step, the membranes were rinsed three times each 1 min. with distilled water. The multilayer modified PAN membranes were kept usually under water and were not dried between the adsorption steps. The dry steps were necessary only to monitor the adsorbed polymer amount in dependence on the layer pair number.

## 2.3. Membrane characterization

The amount of polyions deposited after a certain number of adsorbed layer pairs,  $P$ , was determined with eq. (2):

$$P = (m_n - m_i) / m_i, \text{ g polymer/g membrane} \quad (2)$$

where  $m_n$  and  $m_i$  are the weights of the membrane after  $n$  adsorbed layer pairs and before adsorption, respectively. The value of  $m_n$  corresponds to the constant weight after the drying of the membrane in air (about tree days).

Equilibrium swelling of the membranes in water was investigated by monitoring the weight gain of the membrane immersed in an excess of a certain solvent, at ambient temperature, after 48 h, enough for the equilibrium swelling [8]. The SD values of the membranes were calculated using eq. (3):

$$SD = (m - m_0) / m_0, \text{ g solvent/g membrane} \quad (3)$$

where  $m_0$  and  $m$  are the weights of the dry and the swollen membranes, respectively. The mass of the wet membrane was obtained after the removal of the solvent in excess by wiping the membrane surface carefully.

The membrane surface was examined by means of a Nanoscope IIIa Dimension 3100 SPM (Digital Instruments Veeco Metrology Group, Woodbury, NY, USA), using a high resolution 'Golden' silicon NSG10/Au/50 cantilever with an Au conductive coating. The topographic images were obtained in tapping mode and were repeated on different areas of the same sample.

Potentiometric titration of the polyions was performed with the particle charge detector PCD 03 (Mütek, Germany), between pH 2 and 10, using 0.1 M NaOH and HCl, respectively.

### 3. Results and discussion

The carboxylic groups, generated on the surface of PAN microporous membrane as a consequence of the oxygen plasma treatment, have been transformed in  $\text{COO}^-$ , by the preliminary treatment with an aqueous solution of 1 wt.-%  $\text{NaHCO}_3$ . Therefore, the membrane can electrostatically interact with CS as the first adsorbed layer.

#### 3.1. Formation of polyelectrolyte multilayer films

The formation of polyelectrolyte multilayer films was first monitored by the variation of the polymer amount,  $P$ , adsorbed on the PAN membrane as a function of the number of polyion double layers and polyanion structure (Figure 2).

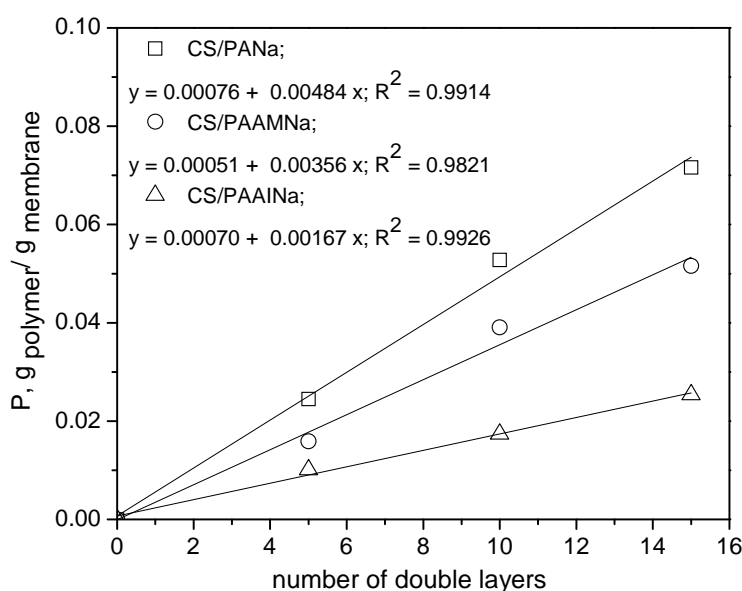


Fig. 2. Polymer amount,  $P$ , as a function of the number of double layers adsorbed on the PAN membrane.

As Figure 2 shows, an about linear increase of the adsorbed polymer with the increase of number of double layers took place, suggesting a regular increase of the multilayers. The influence of polyanion structure on the multilayer formation is very clear, the highest amount of polymer being adsorbed in the case of CS/PANa system and the lowest when PAAINa was used as weak polyanion, for the same number of double layers. PANa has the ionic groups located at regular intervals on the macromolecular backbone, with high ability to compensate the positive centers of CS. In the case of PAAMNa copolymer, which contains about 11.5% maleic acid, the chain flexibility decrease due to the ionic groups in *cis* position, with lower ability to compensate the ionic centers of the previously adsorbed layer. On the other hand, when the copolymer with about 15% itaconic acid (PAAINa) was used, the steric hindrance conducted to the lowest amount of polymer adsorbed on the surface of the PAN membrane.

The surface topography of the composite membranes was investigated using atomic force microscopy (AFM). Figure 3 shows the micrographs obtained on some composite membrane samples, with 15 double layers, and include the values of roughness mean square (RMS) and average height ( $h_a$ ), determined with Gwyddion 2.19 software.

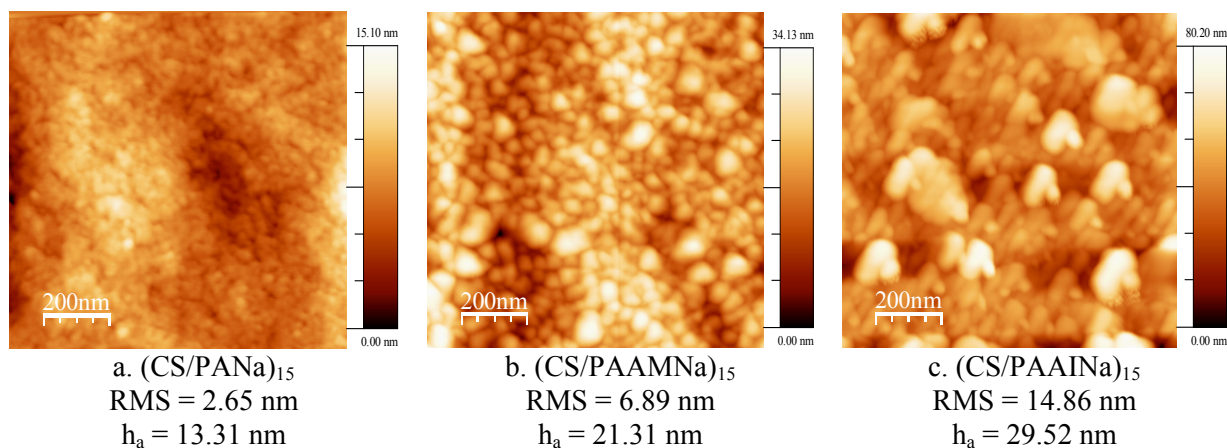


Fig. 3. Tapping mode height AFM images of (CS/polyanion)<sub>15</sub> modified membranes.

The influence of the polyanion structure on the composite membrane surface morphology is clearly reflected in AFM images showed in Figure 3. Thus, the most uniform layers have been observed when PANa was used, low values of RMS (2.65 nm) and h<sub>a</sub> (13.31 nm) being obtained in this case (Figure 3a), showing a uniform compensation of complementary ionic sites. When the copolymers PAAMNa and PAAINa were used (Figures 3b and 3c), the surface morphology became fluffy and less uniform layers have been adsorbed, reflected in the significant increase of RMS and h<sub>a</sub> values, sustaining thus the results in Figure 2.

### 3.2. Swelling equilibrium in water

The SD value of the starting PAN microporous membrane in water was 0.7831 g<sub>H2O</sub>/g<sub>membrane</sub>. The treatment with NaHCO<sub>3</sub> conducted to an increase of SD at 0.8362 g<sub>H2O</sub>/g<sub>membrane</sub>, as a consequence of higher hydrophilic character of COO<sup>-</sup> groups. Figure 4 shows the SD variation of PAN composite membrane prepared by layer-by-layer self-assembly, as a function of the number of double layers adsorbed from aqueous solutions.

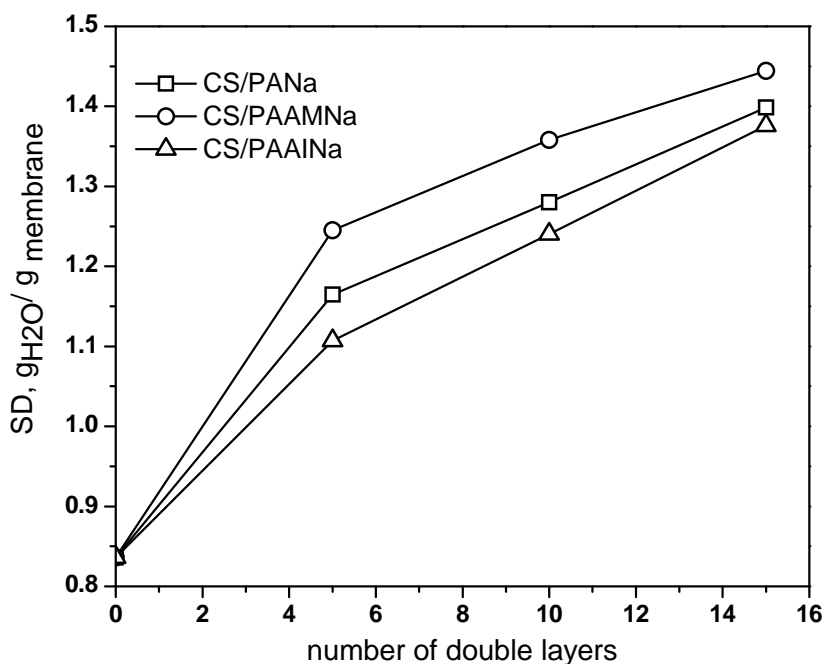


Fig. 4. Swelling degree, SD, in water as a function of the number of double layers adsorbed on the PAN membrane.

Fig. 4 shows that SD values had a similar behavior for the three composite membranes, increasing with the increase of adsorbed layers number. The highest SD values were obtained in the case of PAAMNa based multilayers, comparative with composite membrane constructed with PANa, irrespective of the number of double layers. The numerous ionic cross-links between layers, in the case of PANa based multilayers, led to smaller water adsorption capacity, comparative with PAAMNa based multilayers. However, the lowest SD values were obtained for the films formed with PAAINa, probably due of the highest hydrophobicity of this polyanion, induced by the presence of the itaconic acid.

### 3.3. Stimuli responsiveness as a function of environment

The polyions used in this study are weak polyelectrolytes, their ionization degree being dependent on the solution pH. Figure 5 shows the potentiometric titration curves obtained for CS, PANa and PAAINa.

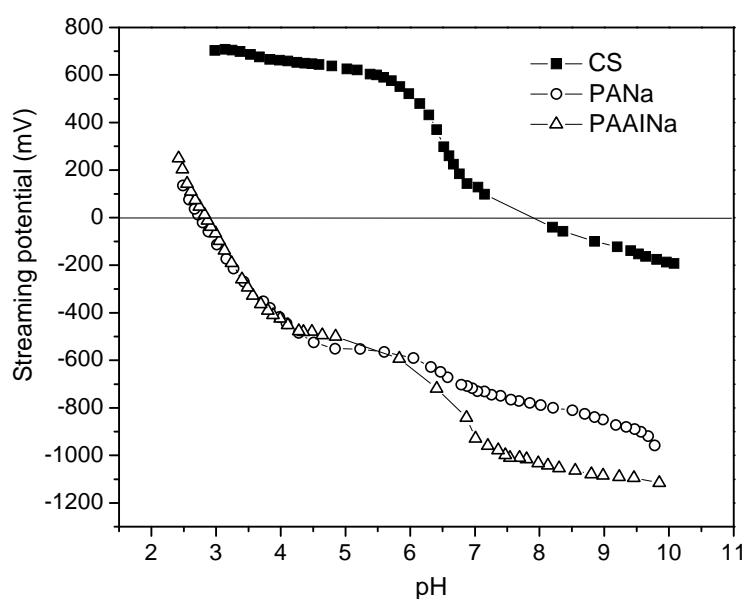


Fig. 5. Potentiometric titration curves.

As Figure 5 shows, the polyanions have a negative streaming potential at pH higher than 2.7 for PANa and 2.9 for PAAINa. At the same time, the two steps of ionization of PAAINa can be noticed, the complete ionization of carboxylic groups attached to this polyanion taking place at pH higher than 7. On the other hand, CS has a positive streaming potential at pH lower than eight, due to the protonation of its primary amino groups in the presence of hydronium ions.

The swelling degree of composite membranes modified with weak polyelectrolytes can be tuned by the characteristics of swelling medium. Figures 6 and 7 show the influence of environmental pH and ionic strength on the SD of composite membranes modified with ten double layers of polyions, respectively.

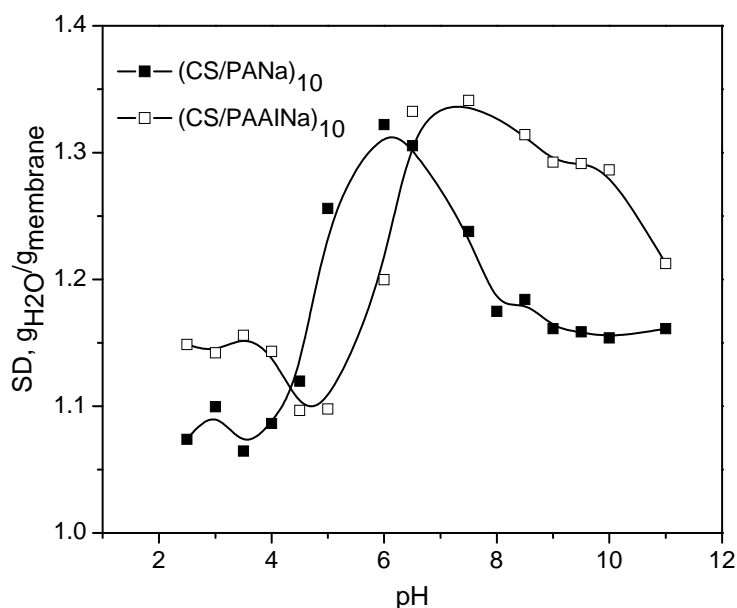


Fig. 6. The influence of pH on the swelling degree of composite films with ten double layers adsorbed on the PAN membrane.

As Figure 6 shows, the SD values significantly changed with the environmental pH, for both composite membranes. In the case of PANa based composite membrane the highest SD values have been obtained at pH 5 - 7, where both polyions are ionized (Figure 5). At pH < 5, CS is strongly ionized whereas the number of charges of PANa is small, and at pH > 7 the ionization degree of CS is very low and PANa is completely ionized. Thus, at pH < 5 and > 7 the degree of ionic cross-linking between layers was low. This may induce a partial destruction of multilayers, reflected in the decrease of SD. A different behavior has been noticed when PAAINa was used as weak polyanion. Thus, SD increased at pH > 5, the highest SD values being obtained on a large range of pH, located between 6 and 10. Even if at pH > 7 the ionic cross-links between layers were reduced, due to the very low ionization degree of CS, the higher resistance of this multilayer may be ascribed to the hydrophobic interactions and the numerous hydrogen bonds ( $>NH\cdots O=C<$ ) formed between layers.

The charge density and the resulting behavior of the weak polyelectrolytes in the multilayer assembly are influenced not only by the pH of the swelling medium, but also by the ionic strength. The presence of salts in the swelling solution can induce electrostatic screening of charges of the free functional groups, and can also influence the dynamics of the ionic bonds holding the layers together. Previous studies on the effect of salt on the swelling of polyelectrolyte multilayer thin films have shown that high salt concentration can lead to irreversible swelling and to the overall loss of material from the films [9,10,16]. To determine the effect of the ionic strength of the solution on the swelling of the (CS/PANa)<sub>10</sub> and (CS/PAAINa)<sub>10</sub> films, the NaCl concentration of the swelling medium was varied while the pH was maintained constant (pH = 5.5) (Figure 7).

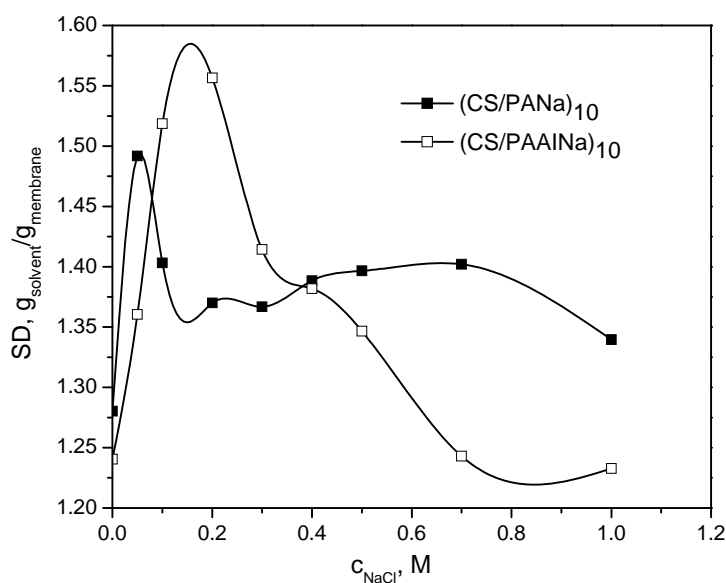


Fig. 7. Influence of the NaCl concentration on the swelling degree (SD) of composite films with ten double layers adsorbed on the PAN membrane.

The swelling profiles shown in Figure 7 indicate that the polyanions structure strongly influenced the swelling behavior in NaCl aqueous solution with concentrations from 0 to 1 M. Thus, when PANa was the weak polyanion, SD significantly increased at very low NaCl concentrations ( $< 0.05$  M), decreased at further increase of ionic strength up to 0.2 M NaCl, SD values being still higher than in the absence of NaCl, and remained almost constant up to 1 M NaCl. On the other hand, when the polyanion was PAAINa, SD increased up to 0.2 M NaCl, decreasing then with the increase of the NaCl concentration up to 0.7 M, reaching values lower than those obtained in the absence of NaCl. This suggests a partial delamination of the layers.

The increase of SD at low ionic strength may be explained by the increase of the concentration of small ions into the multilayer, leading to the increase of the osmotic pressure within the matrix, consequently resulting in a higher swelling degree. The bonds begin to break when the salt concentration increases, leading to the increase of the free volume available for the influx of water into the system. However, due to the dynamic nature of these bonds, the structural integrity of the films can withstand only a certain ionic strength, and after that the films begin to deconstruct and reversible swelling is no longer possible.

#### 4. Conclusions

This study followed the surface modification of a microporous PAN membrane by alternate adsorption of weak polyelectrolytes, which charge density varied as a function of environment pH. For this study, CS and three weak polyanions, PANa, PAAMNa and PAAINa have been used. The amount of the polymer adsorbed on the PAN membrane as a function of the number of polyion double layers and polyanion structure has been followed. The highest amount of polymers was adsorbed when PANa was used, the polyanion with the ionic groups located at regular intervals on the backbone, with high capacity to compensate the ionic sites of CS.

The SD values in water increased with the increase of polyion layer number and were influenced by the polyion structure, decreasing in the order PANa  $>$  PAAMNa  $>$  PAAINa. For PANa based composite membranes, the highest SD has been obtained in the domain of pH 5 – 7, and for PAAINa based composite membranes, SD had the highest values on a large pH domain, located between 6 and 10. The structure of polyanions influenced also the swelling behavior of the multilayers as a function of ionic strength. Thus, SD significantly increased at low NaCl concentrations ( $< 0.05$  M for PANa and 0.2 M for PAAINa).



This study shows the possibility to control and tune the swelling behavior of such multilayer assemblies by tuning the parameters which influence the hydration capacity of the films, this being an important characteristic for applications like controlled release, membrane filtration, and biomaterial coatings.

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