Ion-Specific and Solvent Effects on PDADMA–PSS Complexation and Multilayer Formation

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Abstract: Among various parameters that influence the formation of polyelectrolyte complexes and multilayers, special emphasis should be placed on ion-specific and solvent effects. In our study, we systematically examined the above-mentioned effects on poly(diallyldimethylammonium chloride) (PDADMACl)-sodium poly(4-styrenesulfonate) (NaPSS) complexation in solution and at the surface by means of dynamic light scattering, ellipsometry and atomic force microscopy measurements. As solvents, we used water and water/ethanol mixture. The obtained results confirm the importance of ion-specific and solvent effects on complexes prepared in solution, as well as on multilayers built up on a silica surface. The experiments in mixed solvent solution showed that at a higher ethanol mole fraction, the decrease in monomer titrant to titrand ratio, at which the increase in the size of complexes is observed, takes place. The difference between chloride and bromide ions was more pronounced at a higher mole fraction of ethanol and in the case of positive complex formation, suggesting that the larger amount of bromide ions could be condensed to the polycation chain. These findings are in accordance with the results we obtained for polyelectrolyte multilayers and could be helpful for designing polyelectrolyte multilayers with tuned properties needed for various applications, primarily in the field of biomedicine.

Keywords: polyelectrolytes; polyelectrolyte complexes; polyelectrolyte multilayers; ion-specific effects; solvent effects

1. Introduction

Research on polyelectrolytes has long been of interest to colloidal and polymer chemists, both from fundamental and applicational points of view. Among other aspects, interfacial dynamics related to the metal oxide/polyelectrolyte solution interface attract substantial interest of researchers in various fields, such as the physical chemistry of macromolecules, biomedicine, biotechnology and various other technical sciences [1–3].

It is well known that just by mixing aqueous solutions of positively and negatively charged polyelectrolytes the products commonly known as polyelectrolyte complexes (PECs) or interpolyelectrolyte complexes are formed, predominantly due to the electrostatic attraction between the oppositely charged chains. Such reactions are usually considered to be entropically driven because of the rise in total entropy due to the release of counterions condensed to polyelectrolyte chains to the solution. Research on polyelectrolyte complexes began as early as the 1930s, when Bungenberg de Jong et al. [4] investigated the interactions between oppositely charged natural polyelectrolytes and noticed the formation of products known in the literature also as polyelectrolyte complex coacervates [5]. With the development of high-density synthetic polyelectrolytes, the formation of insoluble complexes was noticed by Michaels in the early 1960s [6], a property that soon became interesting to...
the pharmaceutical industry. The interpolyelectrolyte neutralization of various oppositely charged polyelectrolytes with a high charge density essentially proceeds, as suggested by Fuoss and Sadek in one of the first reported studies on that topic [7]. At lower molar ratios of titrant and titrand molecules, primary colloid complexes are being formed, bearing the charge of the titrand molecules which are present in excess. At higher molar ratios, oppositely charged secondary complexes of larger size are being formed, usually followed by the coalescence of primary and secondary complexes, which is observed as macroscopic phase separation, named flocculation. We showed earlier [8], on the example of complexation between poly(acrylate) (PA) and poly(allylammonium) (PAH) macroions, that at low polyelectrolyte concentrations and without added electrolyte strong overcharging of primary nanocomplexes occurs. On the contrary, the increase in polyelectrolyte concentration led to flocculation taking place near the equivalence (molar ratio of monomers). The nanocomplex charge reversal was also achieved in the high polyelectrolyte concentration regime by the abrupt instead of stepwise titrant addition.

Polyelectrolyte multilayers (PEMs) are, in fact, a specific example of a polyelectrolyte complex, wherein the complexes are prepared by alternating the deposition of polyions and polycations on a substrate, often a metal oxide surface. The most common way to prepare PEMs is by alternately dipping the surface in oppositely charged polyelectrolyte solutions [9]. However, other methods are also known, such as spin coating [10], spraying [11] or flowing the solution onto the substrate surface [12]. The mechanism of formation of multilayers could be interpreted as the binding of a polyelectrolyte to the surface of the opposite charge, whereby this polyelectrolyte binds in excess and there is the inversion of the charge on the surface (overcharging). With the excess charge of that polyelectrolyte on the surface, a polyelectrolyte of the opposite charge can be bound. Except electrostatics, other types of molecular interactions (e.g., hydrogen bonds) could be present during the formation of PECs and PEMs, especially when natural polyelectrolytes or polyelectrolytes of low charge density are used [2,13]. It is possible to prepare polyelectrolyte multilayers of different physicochemical and mechanical properties, depending on the preparation conditions—pH, ionic strength, type of salt [10,14,15]—which have a significant impact, while it seems that deposition time, polymer concentration and molar mass are less important parameters. Special emphasis should also be placed on the application of polyelectrolyte multilayers. In the literature, there are numerous examples of the application, e.g., in the field of membranes [16]. Moreover, there are many studies dealing with surface modifications using polyelectrolyte multilayers for obtaining surfaces with antibacterial [17,18], sensory [19], or biocompatible properties [20].

As stated above, in the studies of polyelectrolyte complexation and polyelectrolyte multilayer formation, special emphasis should be placed on ion-specific effects. Moreover, solvent effects on these processes should also be taken into account. Tirell and co-workers [21] recently found out that salt resistance could be weakened by switching the solvent to miscible ethylene glycol/water and ethanol/water, thus enabling the systematic introduction of more hydrophobic constituents.

Ion-specific effects on charged macromolecules' behavior were discovered in the case of aqueous protein solution, and the ordering of ions known as Hofmeister series was introduced [22]. Cations and anions were ordered due to their ability for altering the hydrogen bonding network of water, and thus were labeled as “water structure makers” or “water structure breakers”. However, there is mounting evidence that the first explanation of ion ordering has at least two problems. First, the effect of ions does not extend far beyond their first hydration layer. Moreover, the chemical details of the solutes are not considered [23]. Contemporary theoretical findings reveal that water structure is not central to Hofmeister effect and that this phenomenon needs to be understood by taking into account direct interactions between ions and macromolecules [24]. Such effects were also noticed in the case of various macromolecules, especially synthetic polyelectrolytes of high charge density. Often, anion-specific effects dominate over cation effects. Direct or inverse Hofmeister series is usually related to the size and hydration enthalpy of anions [25].
However, both effects (cation and anion) need to be additionally studied and, therefore, various theoretical models were introduced. Ion-specific effects are usually correlated with the degree of counterions condensed to the chain which influences its properties. Simple counterion condensation theories (e.g., cylindrical cell (CC) model) are usually valid at low concentrations of polymer or salt but could not explain the differences between fraction of condensed ions at moderate or high salt concentrations. Inclusion of not only ordinary electrostatics but also dispersion and hydration effects to ion–polyelectrolyte interaction significantly changes the predicted fraction of condensed counterions and might improve the interpretation of experimental results. For instance, molecular dynamics (MD) simulations showed higher fractions of condensed ions compared to the CC model, as well as the difference between Na\(^+\), K\(^+\) and Cs\(^+\), where the highest fraction was obtained for the smallest sodium cation \[26\]. Besides the condensation, the polyelectrolyte behavior is also influenced by its structure (geometry and fraction of polar/apolar groups), as well as by the type and properties of the solvent. With the aim of better understanding experimental results, various computer simulation methods were used for studying dynamic and structural properties of polyelectrolytes. These methods include coarse-grained and atomistic models in combination with molecular dynamics and Monte Carlo simulations. Atomistic MD simulations revealed that solvent significantly influences the fraction of dissociated/condensed ions altering charge screening effects and conformational behavior of the polyelectrolyte chain. Moreover, the presence of charged species, i.e., ions and polyelectrolytes, influences the structural properties of the solvent. These effects are more pronounced for small polar solvents, such as water. Usually, the effect of charged species on the solvent behavior is observed as change of the local dielectric constant in the vicinity of the charged species. So, for discussing ion-specific effects, not only direct interaction of ion and polyelectrolyte but also ion–solvent and polyelectrolyte–solvent interactions should be considered \[27\].

As well as for protic solvents, ions differ in their tendency for ion pair formation in aprotic solvents. Very recently, a conceptual density functional theory (DFT) was used for the detailed study of ion-specific effects of alkali and halide ions in various protic and aprotic solvents. Computed ion solvation energies revealed that corresponding cation–water interactions are stronger than anion–water interactions, which could explain the preferred occurrence of anion-specific effects in water. Further investigation showed that solvent affinities and occurrence of specific ion effects are mainly influenced by the chemical hardness and electronegativity differences between the ions and solvent molecules in their vicinity \[28\]. In order to explore the universality of the ion-specific effects in line with the Hofmeister and lyotropic series in water and pure non-aqueous solvents, and the consistency of effects in different experiments, Mazzini and Craig gave a very detailed summary of previous experimental investigations \[29\]. They showed that Hofmeister series, either forward or reverse, exist for both cations and anions in most of the investigated solvents. There is no evidence for correlation of ion-specific effects to the properties of the solvent. Interestingly, solvents behave more similarly with cations than anions, even though stronger specific effects are usually observed for the latter. In line with this article, the same authors wanted to extend “the law of matching water affinities” to many non-aqueous solvents \[30\]. This law is a powerful concept for predicting specific ion effects in many systems and it is connected to the interpretation of “volcano plots”. These plots usually show electrolyte solution properties versus difference in solvation energies between anion and cation. By using monovalent ions, they tested and proved the hypothesis that such plots are rather attributed to the characteristics of the ion (e.g., their size) and not the ion–solvent interaction. When compared to water, trends are the same in protic solvents for both cations and anions, but in aprotic solvents only for cations. This indicates that protic solvents are almost equally good for monovalent anions, with some exceptions, but aprotic solvents largely differentiate between the anions.

The previously mentioned computer simulations were used not only for the investigation of solvent and ion distribution around charged macromolecules, but also for inves-
tigations concerning polyelectrolyte complexes and multilayers. For instance, Qiao et al. used MD simulations of PSS and PDADMA polyelectrolyte mixtures at various NaCl concentrations and tried to relate properties of PECs and PEMs. [31] They found that at salt concentrations up to 1 mol dm$^{-3}$, intrinsic (polyion-polyion) charge compensation dominates over extrinsic (ion-polyion), but with a significant decrease in intrinsic charge compensation and PEC swelling by salt addition. Interaction energy calculations showed the opposite effect, i.e., preference of the extrinsic charge compensation over intrinsic, so they concluded that it does not play a central role in the ion pair formation. Furthermore, they investigated water distribution and hydration mechanisms. Water was found to be homogenously distributed and strongly bound inside the system. The PDADMA–Cl pair showed just slightly stronger hydration behavior than the PSS–Na pair, so they could not relate the experimentally observed asymmetric behavior and swelling–shrinking switch during the PEM buildup to the hydration, and concluded that the presence of the substrate plays a significant role. Finally, they found that dielectric constant in polyelectrolyte mixtures is one order of magnitude lower than in bulk water. Later on, Qiao et al. made the first MD simulation on the formation of the PSS–PDADMA bilayer resolved in atomistic detail [32]. They investigated the influence of the model substrate charge density on polyelectrolyte adsorption. The results indicated that a certain surface charge density is needed to achieve linear growth of PEMs. They noticed a strong tendency to the intrinsic charge compensation in the inner part, which changes to extrinsic charge compensation in the outer part of the bilayer. However, when extrapolating results from the bilayer to multilayer case, they should be taken with care. The same authors performed an MD investigation of static and dynamic properties of interfacial water interacting with bilayer adsorbed on hydroxylated substrate [33]. They observed qualitative changes in the dynamic properties of water (e.g., lateral diffusion) in the proximity of the bilayer, compared to the bare substrate. Static properties of water were similarly influenced. High polarization of water molecules was found farther from the adsorbed bilayer than expected. According to that, they identified three regions with different structural properties of water: the space between the substrate and the first layer, the adsorption region of the bilayer and the region next to the bilayer where no polyelectrolytes are present. In the first two regions, solvent properties were strongly affected by the presence of a bilayer and its mobility was notably decreased. Other authors used MD simulations to study microscopic structural changes of PDADMA–PSS complexes at high salt concentration ($c$(NaCl) = 2.5 mol dm$^{-3}$) when they changed from native to a more compacted form, which is analogous to ultracentrifugation experiments (densification of the system) [34]. Compaction of the system increases the coordination number of both polyelectrolytes (each monomer is on average coordinated by two oppositely charged monomers) and slows down the local rearrangements, thus stabilizing the system. They also focused on water content in compacted complexes obtaining 50–60% of water, where the fraction of hydration water was 25%, which was in agreement with experimental data. Another important investigation in the field of PEC formation is the polyelectrolyte-specific influence of hydration and temperature on water diffusion in hydrated complexes. For that purpose, Batys et al. studied two PEC systems: PAH (poly(allylamine hydrochloride)-PSS and PDADMA-PAA (poly(acrylic acid)) [35]. The results showed that hydrogen bonding between polyion and water molecules has an enormous influence on the water mobility. They observed one order of magnitude difference in the average water diffusion coefficient between PAH–PSS and PDADMA–PAA complexes at the same water fraction. Additionally, PAA–water hydrogen bonds were significantly less sensitive to temperature than PSS–water. The observed differences resulted from the various interactions strengths between polyions and polyion–water molecules, which are connected with the resulting structure of the PECs. In the case of PAH–PSS complexes, interaction between polyions dominates, and in the case of PDADMA–PAA strong interactions between PAA and water molecules compete with interpolyelectrolyte interaction, causing PEC swelling. The MD simulation differences between PDADMA–PAA
and PAH-PSS complexes were confirmed by experimental results obtained by differential scanning calorimetry.

The aim of this paper is to investigate ion-specific effects in two different solvents on the formation and properties of complexes and multilayers formed by interactions of two model polyelectrolytes: poly(diallyldimethylammonium chloride) (PDADMACl) and sodium poly(4-styrenesulfonate), (NaPSS). The effects of salt type and concentration are commonly investigated in aqueous solution with this pair or other pairs of polyelectrolytes, predominantly on surfaces (PEMs) [10,36–44]. On the contrary, there is very little information about polyelectrolyte complexation [21,45,46] or multilayer formation [10,47] in organic or mixed aqueous/organic solvents. Such investigations are needed to elucidate to what extent the results obtained in solution can be used for the prediction of polyelectrolyte multilayer properties and vice versa [48].

2. Materials and Methods
2.1. Materials

Polyelectrolytes that were used are PDADMACl (poly(diallyldimethylammonium chloride), M_w < 100,000 g mol⁻¹, w = 35.5%) as a polycation, and NaPSS (sodium poly(4-styrenesulfonate), M_w ≈ 70,000 g mol⁻¹, degree of polymer functionalization, i.e., percent of charged monomer units, was f = 0.83) as a polyanion. Both polyelectrolytes were obtained from Sigma Aldrich (St. Louis, MO, USA). In addition, as salts (electrolytes), NaCl (Sigma Aldrich, St. Louis, MO, USA) and NaBr (Sigma Aldrich, St. Louis, MO, USA) were used. For mixed solvent preparation, ethanol absolute was used, also obtained from Sigma Aldrich.

Polyelectrolytes and salts were dissolved in water or in the appropriate water/ethanol mixture. Stock solutions were prepared (c = 0.1 mol dm⁻³) and later diluted to the desired concentrations needed for the certain experiment. Salt solutions were also prepared as stock solutions (c = 0.5 mol dm⁻³ or higher).

Water/ethanol mixtures were prepared using ethanol absolute and deionized water by weighing an appropriate amount of each solvent. Solvent content was calculated as a mole fraction of ethanol presented as x_E = 0.10 and x_E = 0.20. Higher mole fractions of ethanol could not be used due to the low NaPSS solubility.

For ellipsometry and AFM measurements, silicon wafers (5 cm × 1 cm and 1 cm × 1 cm, respectively) obtained from Wafernet Inc., San Jose, CA, USA, coated with thin layer of SiO₂ (15–20 Å) were used.

2.2. Methods
2.2.1. Dynamic Light Scattering

Dynamic light scattering (DLS) was used for determination of the hydrodynamic diameter of polyelectrolyte complexes. Measurements are performed by the instrument Brookhaven 90 Plus Particle Size Analyzer, Brookhaven Instruments Corporation, Brookhaven, NY, USA.

The principle of this method is to monitor scattered light radiation and its relaxation, which is described by the correlation function. Furthermore, using the correlation function, a diffusion coefficient could be obtained. Thus, using the Stokes–Einstein equation, the hydrodynamic diameter of spherical particles could be calculated.

\[ D_H = \frac{k_BT}{3\pi\eta D} \]  (1)

Experiments were performed at 25 °C, and angle of incident light was fixed at 90°. Viscosity and refraction index values for water–ethanol mixtures were found in literature [49,50].

2.2.2. Ellipsometry

Ellipsometry, which is an optical method based on elliptical polarization of electromagnetic waves, was applied for the measurements of the thickness of formed polyelectrolyte
multilayers. The measurements were performed using the instrument *Ellipsometer L116B-USB*, Gaertner Scientific Corporation, Skokie, IL, USA. Experiments were performed at room temperature, and the angle of incident and reflected light was fixed at 70°.

2.2.3. Atomic Force Microscopy

Atomic force microscopy (AFM) measurements were performed in a dynamic force mode (simultaneously acquiring topography, amplitude and phase images) using a Nanosurf FlexAFM under ambient conditions. AFM probes were obtained from AppNano (ACLA-SS with super sharp silicon tips of a nominal radius of curvature of 2 nm, with a nominal spring constant of 58 N/m and a nominal resonant frequency of 190 kHz). Images were subsequently processed with Gwyddion software [51].

3. Results and Discussion

3.1. PDADMA–PSS Complexation in A Mixed Solvent

Study of the formation of PDADMA–PSS polyelectrolyte complexes in mixed solvent solutions was the first step in our study. For that purpose, the results were obtained using dynamic light scattering, and the experiments with and without the addition of salt were carried out. The formation of complexes was followed using titration experiments, which were performed by the stepwise addition of polycation solution to the solution of polyanions and vice versa. Increase in the molar ratio of monomers with each addition of the titrant was 0.1. Polyelectrolytes were dissolved in the water/ethanol mixture as described above. All measurements were performed at 25°C.

During titration, polyelectrolyte complexes are being formed, and with the increase in the molar ratio of monomers, suspensions usually become more turbid, and eventually a sudden increase in hydrodynamic diameter occurs at certain specific ratios. This sudden increase usually coincides with the phase separation and formation of precipitate, the process known as flocculation.

3.1.1. PDADMA–PSS Complexation in Water/Ethanol Mixture at \(x_E = 0.10\)

The results obtained by the addition of polycation (PDADMA) to polyanion (PSS) solution (Figure 1) and vice versa (Figure 2), both prepared in water/ethanol mixture (\(x_E = 0.10\)), show that colloid complexes are formed by the stepwise titrant to titrand addition.

![Figure 1](image.png)

*Figure 1.* Mean effective hydrodynamic diameter of complexes formed during titration PDADMA → PSS in water/ethanol mixture at \(x_E = 0.10\) presented on a log scale, \(c_{\text{PDADMA}} = 0.02\) mol dm\(^{-3}\), \(c_{\text{PSS}} = 0.002\) mol dm\(^{-3}\), \(\vartheta = 25.0\) °C.
Figure 2. Mean effective hydrodynamic diameter of complexes formed during titration PSS → PDADMA in the water/ethanol mixture at $x_E = 0.10$ presented on a log scale, $c(\text{PSS}) = 0.02 \text{ mol dm}^{-3}$, $c(\text{PDADMA}) = 0.002 \text{ mol dm}^{-3}$, $\theta = 25.0 \degree \text{C}$.

In the case of negative complex formation, i.e., polycation to polyanion addition, colloid particles with a hydrodynamic diameter around 200 nm were formed at a lower monomer ratio of polyelectrolytes, while at the higher molar ratio (around unity) an abrupt increase in size occurred. In the presence of salt, the hydrodynamic diameter of formed complexes increased at a lower monomer ratio than with no salt added. At the same time, the difference between ratio in the presence of NaCl and NaBr was not observed. Here, we can assume that the difference between results of neutralization obtained in solution with and without added salt is primarily due to the increased condensation of counterions to the polyelectrolyte chains in the case of added salt and screening their surface charge. However, additional effects, such as Debye screening length, should not be underestimated. As there is no significant difference in the results between two salts, we can conclude that the type of anion (in the case of chloride and bromide ions) does not affect the ratio at which the increase in hydrodynamic diameter could be observed, at least in the examined concentration range. This is in accordance with previous aqueous solution-based results in the case of the PAH–PSS pair [52,53]. No anion- or cation-specific effect was observed in the case of negative complex formation. Additionally, to the type and concentration of counter ions, the solvent content could also be an important factor which influences the condensation of already present counterions to the polyelectrolyte chains.

In the case when titration was performed in the opposite direction (i.e., polyanion to polycation addition) (Figure 2), the corresponding titrant to titrand ratio, where an abrupt increase in size was observed, was lower when NaCl or NaBr was added to polyelectrolyte solution. More importantly, there was a significant difference between two salts, so we can state that in the case of positive complex formation, a counteranion effect is present. As bromides influence the corresponding ratio more, they are getting more condensed to the polycation chains than chloride anions. This is also in accordance with previous reported results in aqueous solution [52].

Here, the large increase in size which was observed in the presence of salts was not observed in the salt-free case. In that case, after the critical ratio, the size remains more or less constant. Such a difference could be explained by the mechanism of polyelectrolyte complex formation. The macroscopic phase separation was not observed for the salt-free case. According to the Fuoss and Sadek sequence of events, we were able to observe
secondary complex formation, but not flocculation. In other cases, secondary complex formation is not so obvious because it is almost immediately followed by flocculation (very large increase in size).

3.1.2. PDADMA–PSS Complexation in Water/Ethanol Mixture at $x_E = 0.20$

One of the questions that arise for the above-mentioned results is if the increase in the ethanol content in the water/ethanol mixture would influence the ion-specific effects. The results obtained by DLS for the titration of polyanion (PSS) with polycation (PDADMA) in water/ethanol mixture at $x_E = 0.20$ are presented in the Figure 3. There is a difference between the ratio at which the size of a negatively charged complex abruptly increases in salt-free solution compared to the case when salt is present. Moreover, the increase in hydrodynamic diameter in the presence of salt is not so obvious because it rises in small steps, and the exact ratio could not be obtained. Similar to the results at lower ethanol content, the ion-specific effect in the case of chloride and bromide ions could not be observed.

![Figure 3](image)

**Figure 3.** Mean effective hydrodynamic diameter of complexes formed during titration PDADMA $\rightarrow$ PSS in the water/ethanol mixture at $x_E = 0.20$ presented on a log scale, $c$(PDADMA) = 0.02 mol dm$^{-3}$, $c$(PSS) = 0.002 mol dm$^{-3}$; $\theta = 25.0$ °C.

The results obtained for the titration of PDADMA with PSS in water/ethanol mixture at $x_E = 0.20$ (Figure 4), i.e., for positive complex formation, are also similar to those at lower ethanol content (Figure 2). There is a difference between results in salt-free solution and in solution where salt is present. Moreover, a significant difference between the types of ions could be observed, i.e., the presence of an ion-specific effect. The ratio at which a large increase in size could be observed decreases in the presence of salts compared to the salt-free solution. This decrease is more pronounced at higher ethanol content and in the presence of NaBr.

As can be seen from Figures 1–4, solvent effect is also important for the outcome of interpolyelectrolyte neutralization in solution. An increase in ethanol mole fraction in mixed solvents leads to the decrease in monomer titrant to titrand ratio, at which a large increase in size and/or flocculation could be observed. Used solvent has a lower dielectric constant compared with pure water, so, as stated earlier, it also affects condensation, and probably the fraction of directly bound counterions to the polymer chain. This is accordance with the conclusion made by Smiatek [27] that both solvent and ion species play the crucial role in the behavior of a polyelectrolyte chain.
3.2. PDADMA–PSS Multilayer Formation in A Mixed Solvent

In the following stage of our study, PDADMA/PSS multilayers were prepared by the layer-by-layer (LbL) method on silicon wafers with thin layers of spontaneously formed oxide film. Polyelectrolyte solutions (both PDADMA and PSS) were prepared in water/ethanol mixture at $x_E = 0.10$. Multilayer formation started with a PDADMA layer due to the negatively charged SiO$_2$ surface in solutions with pH $> 4$. Multilayers consisted of eight layers. After the deposition of each layer, the total thickness of formed multilayer was measured by means of ellipsometry. In addition, between each deposition step, one wafer was rinsed with deionized water, and the other one with the mixed solvent. Concentration of both polyelectrolytes was $1 \times 10^{-2}$ mol dm$^{-3}$. As a solvent in this experiment, we used a water/ethanol mixture of $x_E = 0.10$. Used salts were NaCl and NaBr in the concentration of 0.1 mol dm$^{-3}$.

From the results presented in Figure 5, the increase in thickness with each deposited layer of prepared multilayers could be observed. Furthermore, the difference between multilayer’s formation in 0.1 mol dm$^{-3}$ NaCl after rinsing with water compared with mixed solvent rinsing can be observed after the 4th layer. Multilayers that were rinsed with solvent between each deposition step were thicker than those rinsed with water. A similar rinsing effect can be observed in the case of NaBr solution (Figure 6). This difference in thickness obtained with two rinsing protocols could be explained by the exchange of the solvent in the multilayer. As the solvent polarity affects condensation and conformation of polyelectrolyte chains, larger thickness increments could be expected for PEMs prepared from the mixed solvent of lower polarity (polyelectrolyte chains tend to obtain more globular conformation). In both used preparation methods, PEMs formed in NaBr solution are significantly thicker than those formed in NaCl solution. In addition, the standard error of average thickness value is larger in the case of bromide, indicating higher surface roughness. This could be due to the more pronounced condensation of bromide anions to the polycation chain, which is in accord with the herein presented results in solution.
Figure 5. Thickness of PDADMA/PSS multilayer formed in water/ethanol mixture at $x_E = 0.10$ in the presence of 0.1 mol dm$^{-3}$ NaCl, $c$(PDADMA) = $c$(PSS) = 0.01 mol dm$^{-3}$; $n$—number of layers.

Figure 6. Thickness of PDADMA/PSS multilayer formed in water/ethanol mixture at $x_E = 0.10$ in the presence of 0.1 mol dm$^{-3}$ NaBr, $c$(PDADMA) = $c$(PSS) = 0.01 mol dm$^{-3}$; $n$—number of layers.

In order to study the morphology and roughness of PDADMA/PSS multilayers formed in water/ethanol mixture, atomic force microscopy measurements were performed on multilayers (total seven layers) with polycation (PDADMA) as a terminating layer. The reasons for this are the larger differences expected in the morphology and surface roughness of PEMs finished with a polycation layer prepared in the presence of different counteranions, due to the counteranion effect observed in solution (only in the case of positive polyelectrolyte complexes, i.e., excess of polycation).

From the topography images presented in Figure 7, one could observe a slight difference in the morphology of two PEMs prepared from different salt solutions. The structure of PEM prepared from NaBr solution is more granular-like with higher surface roughness.
Figure 7. 1 × 1 µm² AFM topography and 3D surface images of Si-[PDADMA/PSS]₃-PDADMA multilayer prepared in 0.1 mol dm⁻³ NaCl (a,b) and NaBr (c,d) in water/ethanol mixture, xₑ = 0.10, as well as corresponding profiles across the lines (e) denoted in topography images.

RMS value of surface roughness (Rₛ) was determined from AFM measurements as image roughness:

\[ R_q = \sqrt{\frac{1}{N} \sum_{j=1}^{N} r_j^2} \]  

(2)
The presented values are the average values calculated from images taken at several different positions on the sample. In the case of NaCl, surface roughness is estimated to be $R_q = 1.26 \pm 0.01 \text{ nm}$, while in the case of NaBr, $R_q = 1.90 \pm 0.05 \text{ nm}$. As expected, bromide anions caused rougher multilayer surface. This is in agreement with the difference in the counteranion affinity of PDADMA observed in solution experiments when positive polyelectrolyte complexes were formed, i.e., when polyanion was added to polycation solution (Figures 2 and 4).

3.3. PDADMA–PSS Multilayer Formation in Water

In the next phase of the presented study, influence of anions and salt concentrations on PDADMA/PSS multilayer formation in water was investigated. For comparison, the same salts were used as in the case of mixed solvents—sodium chloride and sodium bromide. The influence of ionic strength on multilayer growth in water was explored by preparing the multilayers in the presence of sodium chloride solutions of various concentrations. Figure 8 shows that higher ionic strength causes the increase in multilayer thickness. Moreover, in the first few steps of multilayer growth, it can be described as linear, while later on as exponential. Following experiments with sodium chloride, the same were investigated in the presence of sodium bromide.

![Figure 8. Thickness of PDADMA/PSS multilayer formed in water in the presence of NaCl, $c$(PDADMA) = $c$(PSS) = 0.01 mol dm$^{-3}$; $n$—number of layers.](image)

As shown in Figure 8, in the presence of NaCl, the increase in ionic strength caused the systematical increase in multilayer growth. On the other hand, the results presented in Figure 9 obtained in the presence of NaBr, lead to different results. In that case, the increase in multilayer thickness could be observed for the ionic strength up to $I_c = 0.5 \text{ mol dm}^{-3}$. Possible reasoning for such a result is previously observed multilayer “swelling” in the presence of high bromide concentrations. Larger concentrations are known to be used to remove multilayers from the surface at which they were adsorbed [38]. Another possible reason is the very expressed interaction of counterions with polyelectrolytes at a given NaBr concentration. Such an interaction causes them to transfer to a more stable, condensed form where the number of possible interactions is reduced, making them unavailable for multilayer formation.
Figure 9. Thickness of PDADMA/PSS multilayer formed in water in the presence of NaBr, $c$(PDADMA) = $c$(PSS) = 0.01 mol dm$^{-3}$; $n$—number of layers.

Figure 10 shows multilayer growth in the presence of both NaCl and NaBr at different ionic strength values. At the lowest ionic strength, there are almost no differences among levels of multilayer growth in the presence of different anions. On the other hand, at medium ionic strength, multilayer formed in the presence of bromide ions is significantly thicker. The same was expected (considering the Hofmeister effect) for the highest ionic strength, where the results showed a different trend. The thickest layer was formed in the presence of sodium chloride. All these findings are in agreement with solution-based results, i.e., PDADMA–PSS complexation in water where ion-specific effects were observed already at 0.1 mol dm$^{-3}$ sodium salt concentration, but were more pronounced at higher salt concentrations. Critical salt concentration where positive complexes (excess of PDADMA) aggregate was significantly lower in the case of bromide than in the case of chloride, indicating more pronounced bromide condensation to the polycation chain [48].

Figure 10. Three-dimensional graph of PDADMA–PSS multilayer growth in water at different salt types (sodium chloride—green bars, sodium bromide—brown bars) at different ionic strengths; $n$—number of layers in multilayer, $d$—thickness of multilayer.
In order to examine surface morphology and roughness, the same type of multilayer as in the case of mixed solvent (seven layers, polycation as a terminating layer) was built up from aqueous NaCl and NaBr solution and studied using AFM. Since the largest difference in ellipsometrically obtained thickness between these two salts was observed in 0.5 mol dm$^{-3}$ solutions, multilayers for AFM measurements were prepared from the solution with higher salt content than in the case of the mixed solvent.

As in the case of the mixed solvent, a different morphology and surface roughness was observed in the case of PEM prepared from NaCl and NaBr solution (Figure 11). In the case of NaCl, surface roughness has a value of $R_q = 1.08 \pm 0.07$ nm, while in the case of NaBr, $R_q = 1.35 \pm 0.07$ nm.

![AFM images of Si-[PDADMA/PSS]$_3$-PDADMA multilayer](image_url)

Figure 11. 1 × 1 µm$^2$ AFM topography and 3D surface images of Si-[PDADMA/PSS]$_3$-PDADMA multilayer prepared in 0.5 mol dm$^{-3}$ NaCl (a,b) and in 0.5 mol dm$^{-3}$ NaBr in aqueous solution (c,d) as well as corresponding profiles across the lines (e) denoted in topography images.

By comparison of multilayers prepared from different solvents, we can observe that the difference between surface roughness in NaCl and NaBr is more pronounced in the case of mixed solvent, which leads to the conclusion that stronger condensation of bromide than of chloride anion is additionally influenced by changing the polarity of solvent. By decreasing the dielectric constant of solvent, more bromide anions come closer to the polyelectrolyte chain, i.e., there are probably more directly bound anions than in water.

Additionally, the ellipsometrically obtained thickness of PEMs prepared from mixed solvent in the presence of 0.1 mol dm$^{-3}$ NaCl and NaBr (Figures 5 and 6—mixed solvent rinsed) was higher than the thickness of PEMs prepared from an aqueous solution of the same ionic strength (Figures 8 and 9—black squares). Dubas and Schlenoff [10] have also...
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4. Conclusions

The results obtained in the presented study for the PDADMA/PSS system show an ion-specific effect and solvent influence on complexes prepared in solution as well as on multilayers formed on silica surface. In the case of the mixed solvent (water/ethanol mixture), a sudden increase in the size of colloid complexes was observed at a lower molar ratio of monomers when salt is added, compared to the ratio with no added salt. A more pronounced influence of salt was observed in the case when positive complexes were formed, i.e., during the titration of polycation with polyanion. Moreover, it was shown that the presence of bromide caused a larger shift of the corresponding ratio than the presence of chloride anion. The difference between chloride and bromide was more pronounced at a higher mole fraction of ethanol, suggesting a larger amount of directly bound (condensed) bromide to the polycation chain. These findings were in accordance with the results of PEM preparation. As expected, higher surface roughness (around 50%) was measured for PEM prepared in the presence of bromide than in the presence of chloride.

Multilayers prepared from aqueous solution were investigated in a wider range of salt concentrations than in the case of mixed solvent. This was due to the fact that the difference in the ellipsometrically obtained thickness of PEMs prepared in the presence of 0.1 mol dm\(^{-3}\) NaCl and NaBr was not so significant. It was shown that in the presence of chloride ions, thickness of the multilayer systematically increases by increasing the electrolyte concentration. The same does not hold for bromide ions. In that case, multilayer thickness increases up to the certain salt concentration (\(\approx 0.5\) mol dm\(^{-3}\)). For that reason, PEMs prepared in 0.5 mol dm\(^{-3}\) salt concentration were then used for investigation of the ion-specific effect on morphology and surface roughness. The same effect was noticed in the mixed solvent: surface roughness was higher (around 25%) in the case of bromide than in the case of chloride anion, but it was more pronounced in the case of mixed solvent, even though salt concentration was lower. The results obtained in our study lead to the conclusion that the design of the appropriate polyelectrolyte multilayer needed for optimized applications could be achieved by choosing the appropriate combination of ionic strength, salt type and solvent with lower dielectric constant. Moreover, the studies of corresponding polyelectrolyte complexes could be a valuable tool in obtaining polyelectrolyte multilayers with tuned properties (such as thickness and surface roughness), which are needed for their specific application, especially as possible antibacterial coatings.

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