Usage of Layer-by-Layer Method for Obtaining Polyelectrolyte Multilayer Films Containing Transition Metal Cations

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Abstract

The alternating layer-by-layer deposition of oppositely charged polyelectrolytes at solid substrates is an attractive technique for preparation of nanostructured surface coatings of controlled thickness. This paper reports the results of covalently binding of cobalt (II) and copper (II) ions within polyelectrolyte multilayers (PEMs). We have used polycation as polyethyleneimine (BPEI) and polyanion as poly(acrylic acid) (PAA) and the electrostatic layer-by-layer assembly technique to make uniform thin film coating on solid template with controllable thickness. Thermodynamic characteristics as stability constant, free Gibbs energy, enthalpy and entropy of complex forming processes of these polyelectrolytes with Co(II) and Cu(II) cations in solution were calculated by modified method of Bjerrum. The correlation between log β values and some of the fundamental properties of the metal ions are discussed. It was found that the ratio of Me:L in water solvent is 1:4 in the investigating systems Cu^{2+}:BPEI and Co^{2+}:BPEI and in the systems Co^{2+}:PAA and Co^{2+}:PAA - 1:2. PEMs were deposited onto silicon wafers, glass slides, or coated on silica oxide particles. Dipping solutions of different pH were used in order to find the optimum conditions for absorbing maximum amount of metal cations. These PEMs films are found to offer high capacity and selectivity for copper over cobalt in both acidic and alkaline media. Preliminary investigation have shown that metal containing PEMs has catalytic activity for oxidation of toluene with molecular in mild condition.

Introduction

Polyelectrolyte multilayers (PEMs) coatings created by alternate LbL adsorption of oppositely charged deposition of polycations and polyanions were first introduced by Decher [1]. An important property of this films to controllably interact with small ions of varied valency has been used to regulate polymer deposition within the films, as well as to construct novel types of PEM-based ion-selective membranes [2, 3], useful in water softening and seawater desalination. Multivalent ions were also used in LbL deposition as polymer ‘crosslinkers’ enabling construction of fluorescent coatings with metal ion sensing capabilities [4], or development of inorganic ion/polymer assemblies for tunable release of biological molecules [5].

Metal ions infiltrated within PEMs also can be used as precursors for synthesis for film-embedded metal or metal oxide nanoparticles useful in optical and electronic applications [6]. Recently, the latter approach has also been used to engineer catalytically active PEMs [7].

Catalyst-carrying PEM films share several common features with more traditional heterogeneous catalysts immobilized upon a range of insoluble supports [8], including the ease of catalyst separation, recovery and reuse. In the case when a catalyst presents a multivalent metal ion, immobilization of these ions at/within insoluble matrix through strong metal ion-polymer binding also prevents contamination of the product with trace amounts of metal cations [9]. In addition, earlier approaches to immobilization of metal complexes via covalent attachment to functionalized polymers demonstrated another advantage of polymer-bound metal catalysts, rooted

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in the unique microenvironment created for the reactants within the polymer support. In particular, improved catalyst stability within the polymer matrix and increased selectivity for intramolecular reactions has been reported [10].

The potential of PEMs in heterogeneous catalyst has been previously explored primarily with the focus on synthesis of zero-charge nobel metal nanoparticles, such as Pt, Pd, or Au, in order to produce large surface area of heterogeneous catalyst. One interesting approach has been proposed by Wang and Lee, who synthesized nanosized Pd within PEMs deposited at the magnetic nanoparticles, and tested these nanocomposite catalysts in the hydrogenation reaction of olefinic alchohols [7].

Here, we explore an alternative approach to constructing PEM-based catalytic coatings, which involves the use of transition metal ions, such as Co^{2+} and Cu^{2+}. We study interactions of transition metal salts with PEMs constructed using weak polyelectrolytes, and show that both the film assembly pH and fraction of permanent charge in the polymer chain are important for assembly of films with the highest capacity to absorb Co^{2+} and Cu^{2+}. Investigation of polymer-metal complex formation processes has special emphasis. In this work, we also have determined the stability constants and the polymer-metal complex compositions using potentiometric titration of polymer and polymer-metal salt mixtures using the modified Bjerrum's method developed for polymeric ligands. Their results do not have only theoretical for developing of polymer's coordination chemistry, but also have importance in application.

Experimental Part

Materials

Branched poly(ethyleneimine) (BPEI; M_w 65kDa), trizma hydrochloride, hydrochloric acid, sodium hydroxide, nitric acid, cobalt(II) chloride, copper (II) chloride were purchased from Sigma Aldrich. Acetic acid was from Fluka. Poly(acrylic acid) (PAA; M_w 450 kDa) was purchased from Scientific Polymer Product, Inc. Monodisperse silica particles with diameter of 4.0 ± 0.2 mm were purchased from Polysciences Inc. as 10% dispersions in water. All chemicals were used without any further purification. Millipore (Milli-Q system) filtered water with a resistivity 18.2 MΩ was used in all experiments. Silicon (110) wafers were prime grade, p-type with boron dopant, 525 ± 25 μm thick, with native oxide layer of ~ 2 nm thick, were bought from Cemat Silicon S.A.

Layer deposition

PEMs were deposited onto silicon wafers, glass slides, or coated on silica oxide particles. Silicon wafers and glass slides were pre-cleaned under a quartz UV lamp for at least 2 hours, soaked in concentrated sulfuric acid for 1 hour, and then carefully rinsed with Milli-Q water. Then, the silicon wafers and glass slides were immersed in 0.25 M NaOH solution for 10 min, rinsed with water, and dried under a flow of nitrogen. Preparation of multilayers at the surface of substrates was performed using 0.3 mg/mL of polyelectrolyte solutions at $pH > 6$ in 0.01M trizma buffer and at $pH < 6$ in 0.01M acetic buffer. Polycation and polyanion were allowed to sequentially adsorb 10 minutes at the surface. Each deposition step was followed by rinsing with buffer solution at the same pH value. The films were then stabilized by thermal crosslinking in an oven at 125°C for 1 h. Desired number of layers was deposited.

Incorporation of metal cations within the films

To load a metal cation, multilayers films were exposed to $CoCl_2$ or $CuCl_2$ solutions (0.05 mole/L in water at pH 5.0 for 10 h) to achieve complete absorption within the films. Loading was followed by rinsing with appropriate solvent.

Determination of metal amount in the films

The amount of metal ions in the PEMs films was quantified by ICP ISO analysis of solutions of samples treated with UV radiation and dissolved in 5% nitric acid solution. The solutions were then analyzed for Co(II) and Cu(II), using Varian Vista MPX inductively coupled plasma spectrophotometer with an optic emission detector (ICP-OES) and previously obtained calibration curves for Co^{2+} and Cu^{2+} ions at wavelength 231.16 nm and 324.75 nm respectively.

Instrumentation

Scanning electron microscopy (SEM) analysis were performed using a Zeiss Auriga Dual-Beam

FIB-SEM. Silicon wafers were glued to the SEM stage by conductive tape. Au-Pt alloy was sputtered onto the sample surfaces with RF-plasma chamber for 10 seconds. The applied voltage was varied from 1 to 3 kV. Atomic force microscopy (AFM) measurements were performed in air at room temperature using a NSCRIPTOR™ dip pen nanolithography system (Nanoink, USA) operating in AC (tapping) mode. Phase-modulated ellipsometry measurements of dry films were performed using a home-built, single-wavelength, phase-modulated ellipsometer at 65° of incidence. Optical properties of the substrates and oxide layer thickness were determined prior to polymer deposition. In measurements of dry film thickness, the refractive index was fixed at a value of 1.5.

Results and Discussion

Binding of multilayer components with Cu^{2+} and Co^{2+} ions

In order to create multilayer films capable to absorb catalytically active Cu^{2+} and Co^{2+} ions, we explored the use of several polyelectrolytes such as branched poly(ethyleneimine) (BPEI) and poly(acrylic acid) (PAA). The choice of polymers was largely dictated by the ability of their functional groups to form strong complexes with transition metal ions. Polymers of our choice - BPEI and PAA - contain amino and carboxyllic groups, which are able to form chelate complexes with transition metal ions, including Co^{2+} and Cu^{2+}. In the literature, it was shown that these metal cations form more stable complex compounds with polyligands compared to monomers [11]. Ratio of $k = [Me^{2+}]/[LP]$ (LP – ligand group of a polymer) was found by potentiometric titration technique. Potentiometric titration curves of polymer-metal systems in water medium are shown in Fig. 1. A value of k = 0.25 (corresponding to 1:4 metal-to-polymer ligand ratio) was found for binding of BPEI with both metal cations (Cu^{2+} and Co^{2+}). At the same time, both Cu^{2+} or Co^{2+} ions coordinated only 2 carboxylic groups of PAA. From known coordination numbers of Cu and Co (4 and 6 respectively), we conclude that coordination spheres of transition metal ions were saturated with polymer ligands in Cu^{2+}:BPEI complex. For binding of Co^{2+} with BPEI, as well as both metal ions with PAA, metal coordination spheres were not occupied exclusively by the polymers ligands, and probably additionally contained solvent and/or small counterions.

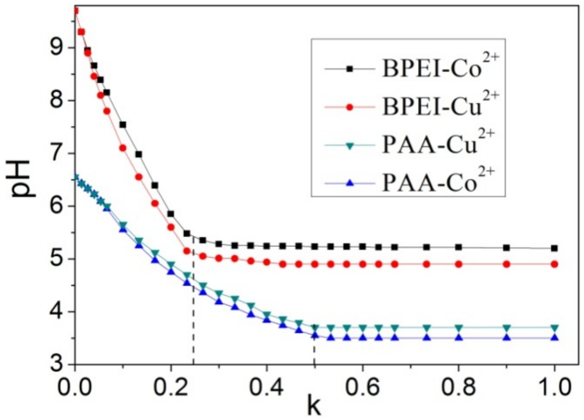

Fig. 1. Potentiometric titration curves of BPEI and PAA with salts $CuCl_2$ and $CoCl_2$ in water medium (*C(polymer)* = 0.01M; *$C(Me^{2+})$* = 0.01M; I = 0.1M; T = 298 K).

In this work, we have determined the stability constants and the polymer-metal complex compositions using potentiometric titration of polymer and polymer-metal salt mixtures using the modified Bjerrum's method developed for polymeric ligands by Gregor et al. [12]. Titration was performed in water at several temperatures (25°C, 35°C, 45°C) and ionic strengths (in 0.1, 0.5, and 1.0M $NaNO_3$ solutions). Stability constants were calculated on the base of competition of proton and metal cation for ligand. As it is seen from Fig. 2, stability constants β of polymer-metal complexes rise with increase of temperature in all systems. The most stable complexes can be obtained in the system BPEI-Cu^{2+}.

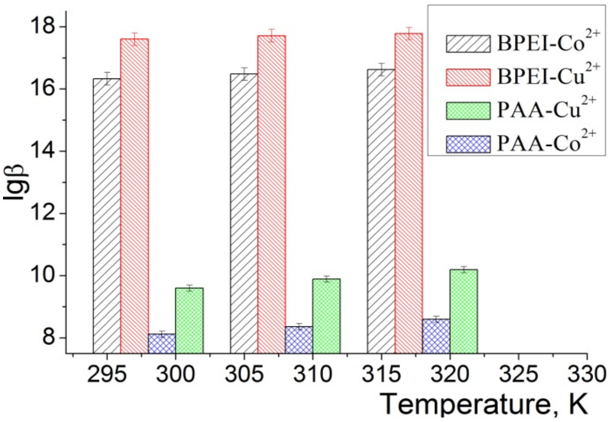

Fig. 2. Dependence of thermodynamic stability constants of polymer-metal complexes in the systems BPEI-Co^{2+}, BPEI-Cu^{2+}, PAA-Co^{2+} and PAA-Cu^{2+} on temperature.

Table 1 compares thermodynamic parameters as change in Gibbs free energy Δ_rG^0, change in enthalpy Δ_rH^0 and change in entropy Δ_rS^0 of the metal chelation with BPEI and PAA in water.

These parameters were calculated on the base of thermodynamic stability constants β^0 of polyelectrolyte complexes of Cu^{2+}, Co^{2+} ions. Thermodynamic stability constants were found by interpolation to zero the dependence of stability constant on ionic strength of solution $lg\beta = f(I)$.

Gibbs energy was calculated using isotherm equation of chemical reaction $\Delta G^0 = -RT\ln\beta^0$, where R – universal gas constant; T – temperature, K; β^0 – thermodynamic stability constant.

Table 1

Thermodynamic characteristics of Me^{2+}-polymer binding in water solution

System	$-\Delta_rG^0$, kJ/mole	Δ_rH^0, kJ/mole	Δ_rS^0, J/mole·K
Co^{2+}–BPEI (k=0.25)	93.01±1.51	24.28±0.35	393.59±6.67
Cu^{2+}–BPEI (k=0.25)	96.83±0.82	11.73±0.19	364.29±6.35
Co^{2+}-PAA (k=0.5)	45.59±0.48	42.13±0.82	294.36±3.92
Cu^{2+}-PAA (k=0.5)	54.68±1.36	52.12±0.72	358.40±7.13

The enthalpy of complex forming processes was found by differential van't-Hoff equation, which based on the dependence of stability constant on temperature: $\ln\frac{k_2}{k_1} = -\frac{\Delta H(T_2-T_1)}{RT_1T_2}$. The change of entropy was estimated from Gibbs-Helmholtz equation $\Delta G^0 = \Delta H^0 - T\Delta S^0$. Negative values of Δ_rG^0 for all types of Cu^{2+}: polymer and Co^{2+}: polymer complexes predict that binding should occur between transition metal salts and all three polymer types. Small positive values of Δ_rH^0 indicate that the formation of complexes is a weakly endothermic process, and positive changes in entropy drive the binding of metal ions to polymer ligands. The positive change in entropy probably results from breaking the solvation shell of ligand groups, as well as displacement of solvent molecules from the first coordination sphere of metal ions during metal ion-polymer binding. These results also predict that polyelectrolytes chelate Cu^{2+} stronger Co^{2+} in agreement with the Irwing-Williams series. The order of the stability constants is largely determined by electrostatic effects: the effective nuclear charge increases across the period and so the ligands are bound more strongly, but there is also the effect of the ligand field stabilization energy, LFSE. The $Co^{II}(d^7)$ and $Cu^{II}(d^9)$ complexes have extra stabilization which is proportional to the LFSE [13]. Another explanation: Crystal Field Theory is based on the idea that a purely electrostatic interaction exists between the central metal ion and the ligands. This suggests that the stability of the complexes should be related to the ionic potential; that is, the charge to radius ratio. In the Irving-Williams series, the trend is based on high-spin M(II) ions, so what needs to be considered is how the ionic radii vary across the d-block. Taken together, these data suggest that binding of Cu^{2+} and Co^{2+} is the weakest with PAA ligand, and the strongest chelation occurs in the Cu^{2+}–BPEI system. Using these results as a guideline, we were then seeking to explore binding of Cu^{2+} and Co^{2+} ions with PEM films which combine both polycation and polyanion components.

Construction of Metal Ion-absorbing PEMs

Figure 3. illustrates deposition of PEMs at planar substrates, and subsequent loaded of metal ions within the assemblies. Coordination of metal ions to amino groups of a polycation is shown as a process dominating the binding, as metal chelating strength of PAA segments was found to be significantly weaker. L in this case represents a low molecular compound, molecule of solvent or carboxylic groups of PAA.

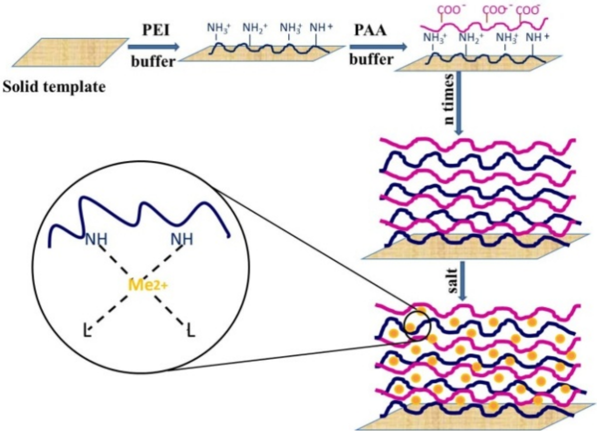

Fig. 3. Schematic representation of constructing BPEI/PAA films containing Me $^{2+}$ ions.

We aimed to construct LbL films with various amounts of polymer segments which are not participating in ionic pairing essential for film stability, but instead are included in unbound polymer ‘loops’ and therefore are available for chelating metal cations. Our strategy for film construction was first based on previous studies on assembly of weak polyelectrolytes, which showed that the film thickness, molecular organization and the amount of polymer adsorbed can be controlled by simple adjustments of the pH of the dipping solution [14]. Second, we also relied on prior studies on PEM assemblies of polyelectrolytes with different permanent charge densities, which reported thicker films for polymers with lower degrees of permanent charge [15].

Figure 4 (top panel) shows dry thicknesses of $(BPEI/PAA)_{50}$ films as a function of deposition pH. Film thicknesses were quantified by AFM by measuring the heights of steps cut in the film with a razor blade. During the deposition of BPEI/PAA films, both polymer solutions, as well as 0.01M trizma and acetic rinsing buffers were at the same pH value that was systematically varied between 5.0 to 9.5. In agreement with earlier findings by Rubner and co-workers for a similar type of weak polyelectrolyte multilayers [16], at neutral pH (region II) both of polyelectrolytes totally ionized and form highly ionically crosslinked film, with the smallest thickness. At pH lower than 6.0 and higher than 7.0 (regions I, III), thickness of $(BPEI/PAA)_{50}$ film increased as a result of neutralization of PAA (pKa 5.0) and BPEI ($pK_b \sim 8.8$) and the formation of low-charge-density “loops”. Top view and 3D AFM images (bottom panel) shows that uniform film was formed (Fig. 4 bottom panel). In all systems the thicknesses of PEMs grow linear as shown in Fig. 5.

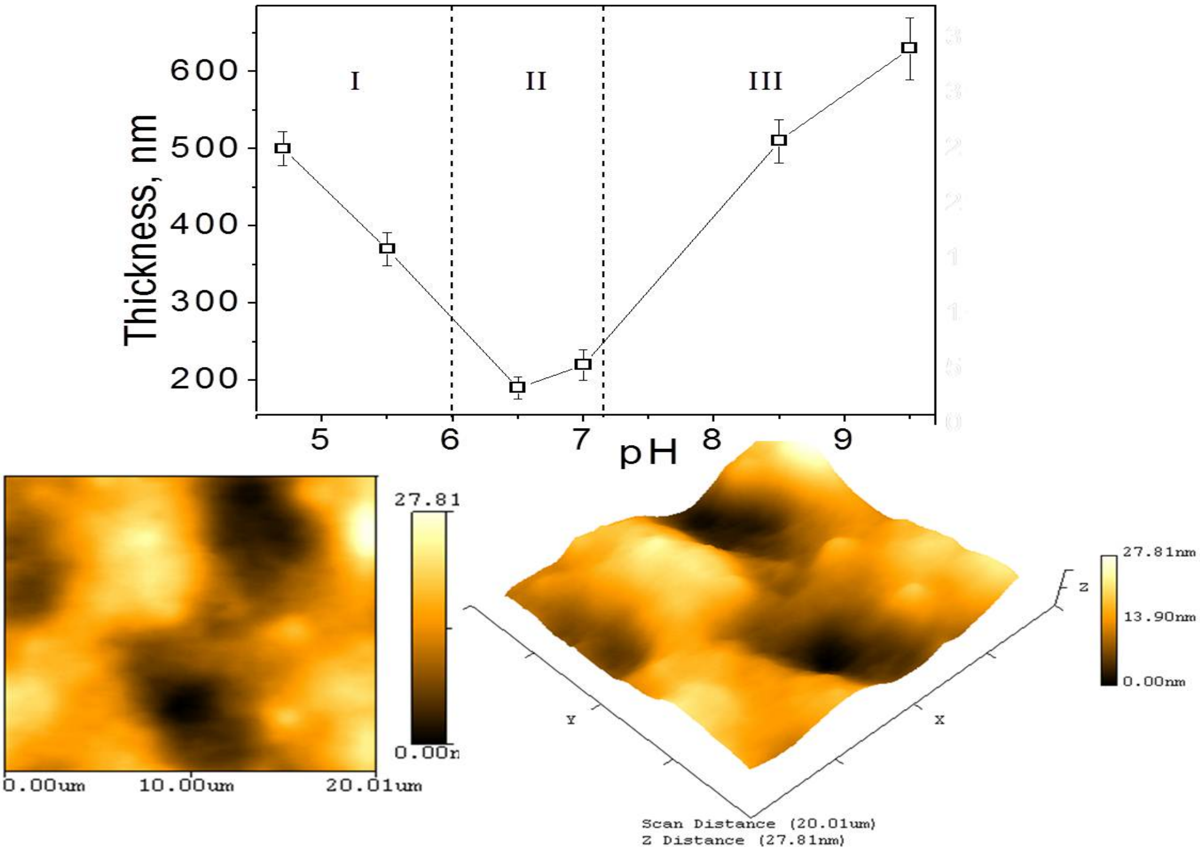

Fig. 4. Dependences of film thickness of $(BPEI/PAA)_{50}$ films on pH (top panel), and AFM images of $(BPEI/PAA)_{50}$ film deposited at pH 8.5 (bottom panel).

Binding of Me^{2+} within PEM Films

In this section we show how the amount of Cu^{2+} and Co^{2+} loaded within PEM systems can be controlled by PEM assembly conditions and type of assembled polyelectrolytes. Metal cations were allowed to absorb within BPEI/PAA multilayers were covalently crosslinked at 125°C for 1h (minimal time required for sufficient crosslinking), in order to stabilize the film.

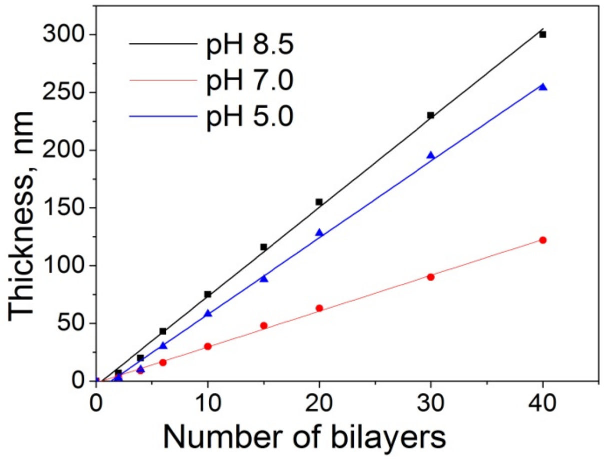

Fig. 5. Thicknesses of dry LbL films BPEI/PAA deposited at pH 8.5 (squares), pH 7.0 (triangles) and pH 5.0 (circles). Thicknesses were measured by elipsometry. All films were deposited from 0.3 mg/ml polymer solutions in 0.01M trizma and acetic buffer solutions.

Figure 6 schematically shows examples of multilayer systems used for metal ion loading. Cu^{2+} and Co^{2+} ions can be electrostatically bound within carboxylic, and/or involved into chelate complexes with amino groups of BPEI. Figure 6 shows the result of metal ion inclusion within the mutlilayers.

Overall, the amount of ions included followed the trend seen in the dependences of PEM film thicknesses on pH (see Fig. 4). However, the amount of Cu^{2+} and Co^{2+} included per film mass was significantly lower for BPEI/PAA systems assembled at low pH values than those for film constructed at basic pHs (Fig. 7). This result suggests that, as follows from studies of binding of metal cations with individual polyelectrolyte chains (Fig. 2), Cu^{2+} and Co^{2+} can bind with excess carboxylic groups of PAA contained within BPEI/PAA films assembled at pH 5.0, but binding constant of metal ions with PAA carboxylic groups is significantly lower than with amino groups of BPEI. With films assembled at basic pH values, PAA is fully ionized and not available for binding with Me^{2+}, as carboxylic groups of the polyacid participate in ionic pairing with polycations.

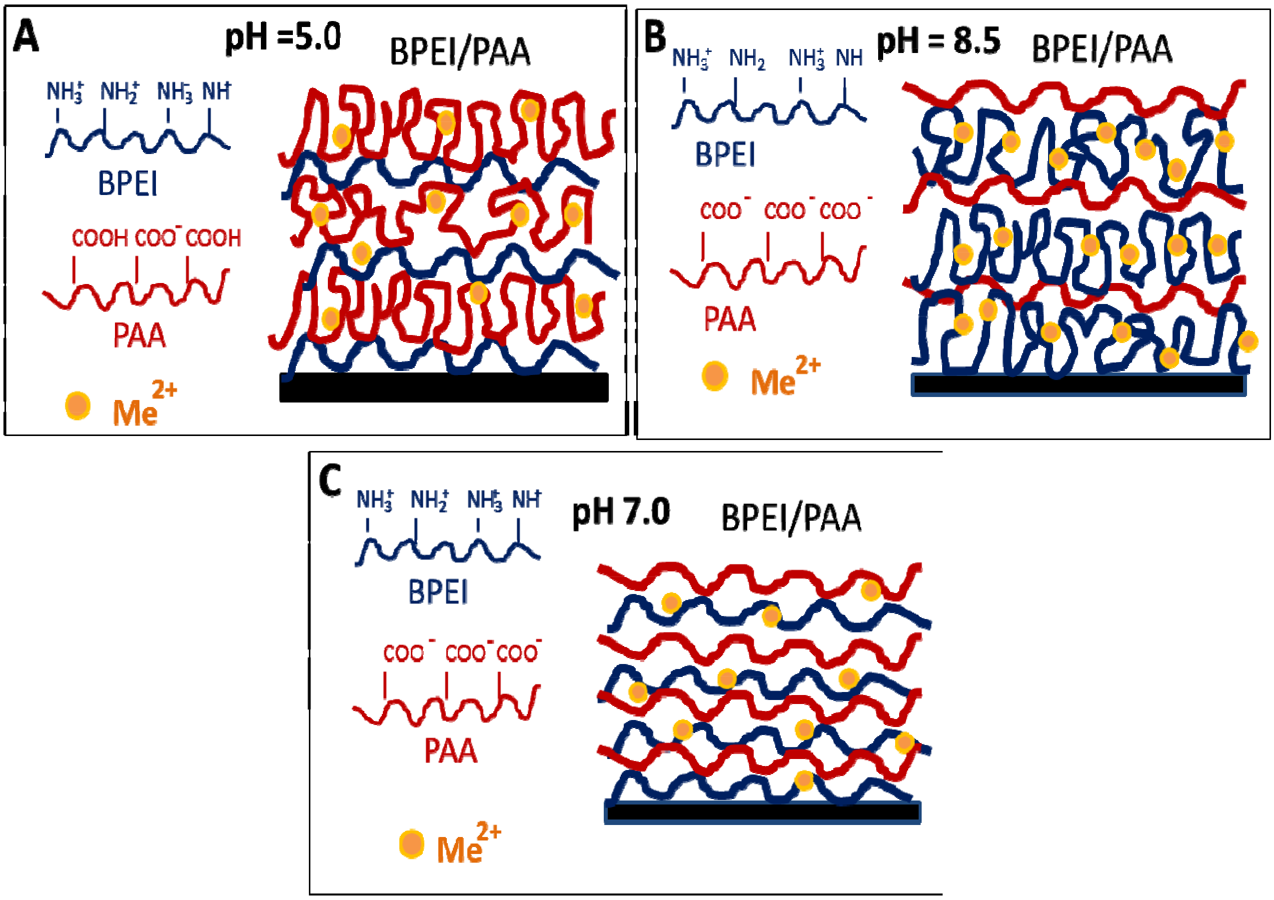

Fig. 6. Schematic representation of internal structure of BPEI/PAA and QX/PAA films deposited at different conditions and binding of metal ions within PEM films.

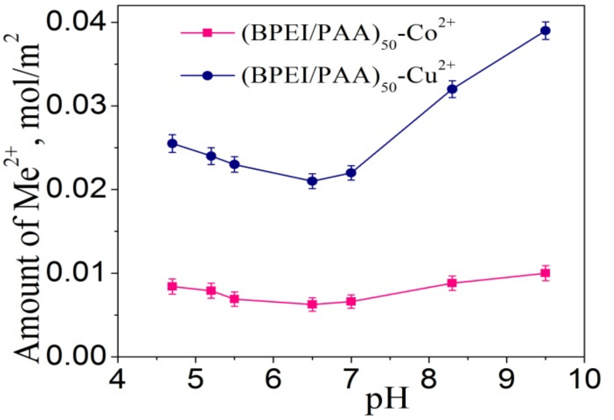

Fig. 7. Amount of Co^{2+} and Cu^{2+} ions absorbed within $(BPEI/PAA)_{50}$ deposited at various pH values, as determined by ICP. All metal cations were loaded within BPEI/PAA films from aqueous salt solutions at pH 5.0. The amounts were quantified from ICP OES analysis.

Instead, BPEI is relatively weakly charged at basic pH values (pK_b = 8.8) and deposit within the film as thick layers with loopy conformation, bringing in large amounts of free amino groups which are available for coordination with metal cations. At neutral pH both polymers form thin highly ionically crosslinked layers with the smallestabsorption capacity for Me^{2+} ions. $(BPEI/PAA)_{50}$ films deposited at pH 9.5 and pH 5.0 absorb almost the same amount of Co^{2+}, consistent with the binding strength and stoichiometry of Co^{2+}-BPEI and Co^{2+}-PAA complexes in Table 1. At the same time, films assembled at basic pHs contain twice the amount of more Cu^{2+} absorbed within films constructed at pH 5.0. This shows the higher affinity of BPEI to cupper. With BPEI/PAA multilayers, the amount of Cu^{2+} absorbed by the film was ~ 4 times that found with Co^{2+} for the same films.

SiO_2 particles were coated by $(BPEI/PAA)_8$ PEMs as well. As shown in Fig. 8 the particles were covered uniform and smooth by BPEI/PAA multilayers.

We then studied the catalytic activity of Co^{2+} and Cu^{2+} ions loaded within $(BPEI/PAA)_{30}$ films deposited at pH 5.0 and pH 8.5, for oxidation of toluene by molecular oxygen oxidation at atmospheric pressure and moderate temperature of 75°C. Preliminary investigation showed that the PEMs with copper and cobalt ions catalytic activity.

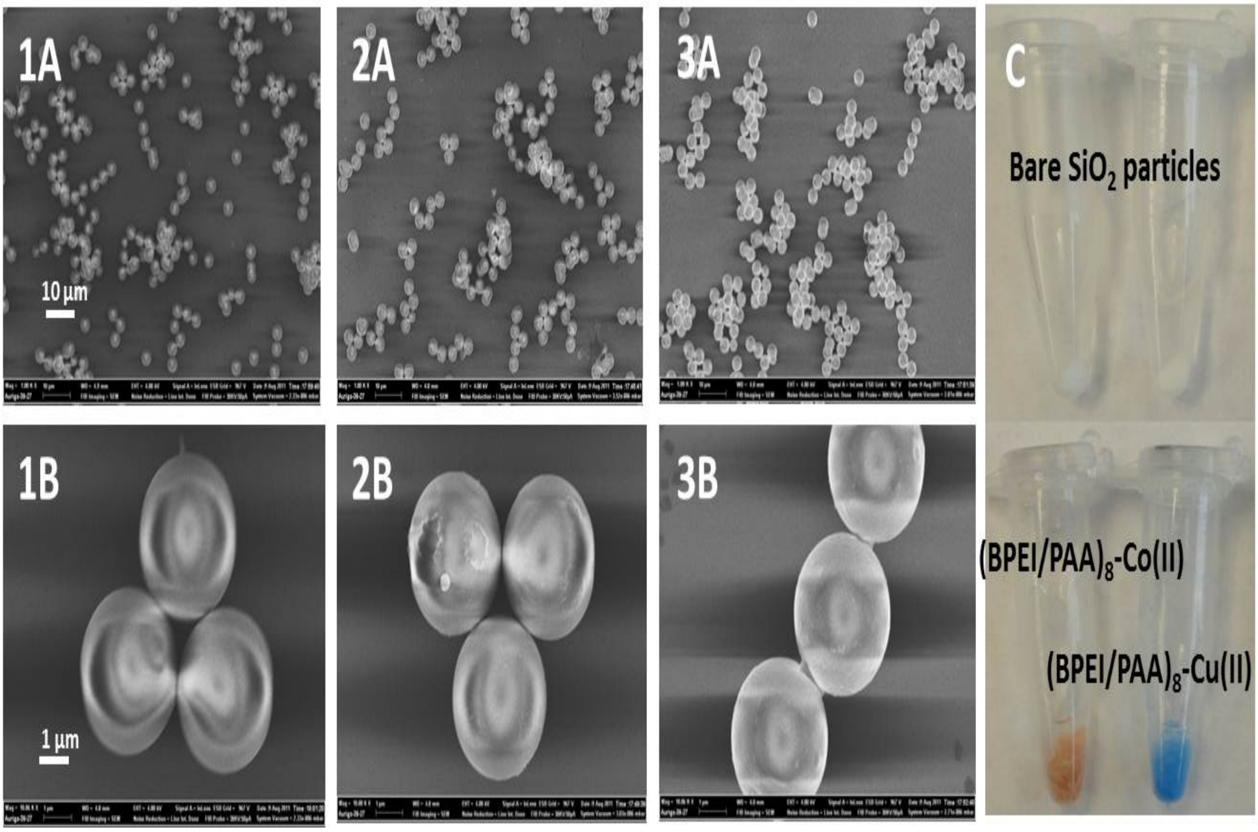

Fig. 8. SEM images (a, b) and optical images (c) of bare silica particles (with diameter 4±0.2 microns), as well as the particles with deposited $(BPEI/PAA)_8$ and loaded Co^{2+} and Cu^{2+} ions.

Conclusions

In this study themodynamic characteristics as stability constant, free Gibbs energy, enthalpy and entropy of complex forming processes of BPEI and PAA with Co(II) and Cu(II) cations in water solution were calculated at different temperature and ionic strength. It was determined by potentiometric titration that the ratio of Me:L is 1:4 in the investigating systems Cu^{2+}:BPEI and Co^{2+}:BPEI and in the systems Co^{2+}:PAA - 1:2. It was found that the thickness of PEMs films as well as amount of impregnated metal ions are dependent not only on the nature of metal ion, but is also strongly determined by the type of assembled polyelectrolytes and conditions of film assembly. Preliminary investigation have shown that metal containing PEMs has catalytic activity for oxidation of toluene with molecular in mild condition. It was demonstrated that immobilization of transition metal ions within LbL matrices provides a new method for constructing recyclable catalysts useful for conversion of organic compounds.

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