Monolayers of cationic polyelectrolytes on mica – Electrokinetic studies

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ABSTRACT

Physicochemical properties of cationic polyelectrolytes: poly(allylamine hydrochloride) (PAH), poly(ethylene imine) (PEI), and poly(dimethyldiallylammonium chloride) (PDDA), having molar mass of 70,000, 75,000, and 120,000, respectively, were examined and compared. The bulk characteristics comprised the diffusion coefficient and electrophoretic mobility determined as a function of pH (3.5–9) and ionic strengths (10^{-4} M to 0.15 M NaCl). These measurements allowed one to determine the amount of electrokinetic charge of the polyelectrolyte molecules and their isoelectric points. On the other hand, formation of polyelectrolyte monolayers on mica and their properties were investigated using the *in situ* streaming potential method. Additionally, using this method, the stability of monolayers, evaluated via desorption kinetic measurements, was determined. The investigations showed that PAH molecules form the most stable monolayers, which can be used as supporting layers for particle deposition and multilayer formation.

1. Introduction

Polyelectrolytes (PEs) are charged molecules consisting of ionizable groups, which release counterions when desolating in polar solvents such as water. In the recent years, polyelectrolytes have been extensively studied due to a number of potential applications in many industrial processes, such as filtration, water treatment, papermaking, food manufacturing, and mineral extraction. [1–5]. In those processes, they are widely used as thickeners, emulsifiers, flocculants, and conditioners [6]. Moreover, the adsorption of polymers and biomolecules at solid/liquid interface is of great significance to many practical and natural processes such as formation of nanocoatings on textiles [7], nano-encapsulation for controlled drug delivery and release [8–10], cell adhesion [11], or protein and enzyme immobilization and separation [12,13].

Due to the growing applications of polyelectrolytes, especially in medicine, many techniques have been exploited to manufacture the monolayer and multilayer films of desired coverage and structure. Thin polyelectrolyte films have been fabricated using various techniques such as Langmuir–Blodgett or self-assembly.

One of the most promising techniques of surface modification using polyelectrolytes was the layer-by-layer (LBL) assembly technique, developed by Decher and co-workers in the early 1990s. This technique has become a powerful tool for fabricating thin materials (nano- and microcapsules) with precise control of film composition and structure [11–17].

Thin organic films such as monolayer and multilayer polyelectrolyte films are widely used for the development of immunosensing [18], in electronics, optoelectronics, or in anticorrosion coatings and ultrahydrophobic surfaces [19–22].

Despite of a vital significance of these processes, there are few experimental results concerning polyelectrolyte adsorption and monolayer formation under wet conditions obtained by *in situ* experimental techniques. Therefore, the aim of this work is deriving such thorough characteristics of cationic polyelectrolyte monolayers on mica using the reliable streaming potential method. The measurements are quantitatively interpreted in terms of the three-dimensional (3D) electrokinetic model [23,24], which was successfully used for analyzing monolayer formation of latex particles [25], nanoparticles [26,27], and protein adsorption and desorption on solid substrates [28,29]. Using this theoretical model, one can determine, *inter alia,* the isoelectric points of polyelectrolyte molecules and estimate the stability of the monolayers obtained in the self-assembly process. This enables one to gain clues on polyelectrolyte adsorption mechanisms driven

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by electrostatic interactions, which has significance to basic science.

2. Experimental

2.1. Materials

In our experimental studies, the following polyelectrolytes were used: (1) poly(allylamine hydrochloride) hereafter referred to as PAH, the cationic polyelectrolyte having a molar mass of 70 kDa, purchased from Polysciences, (2) poly(ethylene imine) hereafter referred to as PEI, the cationic polyelectrolyte having a molar mass of 75 kDa, was purchased from Sigma–Aldrich, and (3) poly(diallyl-dimethylammonium chloride) hereafter referred to as PDDA, the cationic polyelectrolyte having a molar mass of 100–200 kDa was also purchased from Sigma–Aldrich.

As a solid substrate for polyelectrolyte adsorption, the natural ruby mica sheets obtained from Continental Trade were used. The solid pieces of mica were freshly cleaved into thin fragments of desired area and used in each experiment without any pretreatment. Ultrapure water, used throughout the investigation, was obtained using the Milli-Q Elix & Simplicity 185 purification system from Millipore SA Molsheim, France.

2.2. Methods

The diffusion coefficients and the electrophoretic mobility of PE molecules were measured by dynamic light scattering (DLS) and microelectrophoresis, respectively, using the Zetasizer Nano ZS Malvern instrument.

Zeta potential of bare and PE-covered mica was determined via streaming potential measurements using a homemade cell described in detail in our previous works [30,31]. The main part of the cell was a parallel-plate channel with dimensions of $2b_c \times 2c_c \times L = 0.027 \times 0.29 \times 6.2$ cm, formed by mica sheets separated by a perfluoroethylene spacer. The streaming potential E_s was measured using a pair of Ag/AgCl electrodes as a function of the hydrostatic pressure difference ΔP, which was driving the electrolyte flow through the channel. The overall cell electric conductivity K_e was determined using a pair of Pt electrodes. Knowing the slope of the E_s vs. ΔP dependence, the apparent zeta potential of substrate surface (ζ_i) was calculated from the Smoluchowski relationship:

$$\zeta_i = \frac{\eta L}{4\varepsilon b_c c_c R_e}\left(\frac{\Delta E_s}{\Delta P}\right) = \frac{\eta K_e}{\varepsilon}\left(\frac{\Delta E_s}{\Delta P}\right) \tag{1}$$

where η is the dynamic viscosity of the solution, ε is the dielectric permittivity, and R_e is the net electric resistance of the cell being the sum of the bulk and surface resistances. The correction for the surface contribution was introduced in an standard way, previously described [24,30–33]. The correction was ca. 10% for ionic strength of 10^{-4} M and practically negligible for higher ionic strength.

3. Results and discussion

3.1. PAH, PEI and PDDA bulk characteristics

The size of polyelectrolyte molecules (hydrodynamic diameter) was obtained via diffusion coefficient measurements by dynamic light scattering (DLS) technique, using the Zetasizer Nano ZS Malvern instrument. The Nano ZS instrument incorporates noninvasive backscatter (NIBS) optics and this technique is based on measurements of the time dependent fluctuations in the intensity of scattered light (measurement range of 0.6 nm to 6 μm). Knowing the diffusion coefficient, D, one can determine the

hydrodynamic diameter of molecules using the Stokes–Einstein relationship:

$$d_H = \frac{kT}{3\pi\eta D} \tag{2}$$

where d_H is the hydrodynamic diameter, k is the Boltzmann constant, T is the absolute temperature, and η is the dynamic viscosity of solvent. The hydrodynamic diameters and diffusion coefficients for all three polyelectrolytes studied in this work are collected in Table 1. The electrophoretic mobility of polyelectrolyte molecules μ_e was determined by microelectrophoresis. This quantity is of essential significance for characterizing particle stability and interactions with surfaces leading to particle deposition. In Fig. 1, the dependence of μ_e on pH for various ionic strengths and for the three polyelectrolytes is shown. Knowing the electrophoretic mobility and the hydrodynamic diameter, one can determine the effective (uncompensated) charge per polyelectrolyte molecule q from the Lorentz–Stokes relationship [28,29]:

$$q = \frac{kT}{D}\mu_e = 3\pi\eta d_H \mu_e \tag{3}$$

where $\mu_e = \langle U \rangle / E$, and $\langle U \rangle$ is the averaged migration velocity of polyelectrolyte molecules in the uniform electric field E.

Eq. (3) can be directly used for calculations of the average number of elementary charges per molecule considering that $e = 1.602 \times 10^{-19}$ C, thus:

$$N_c = \frac{30\pi\eta}{1.602}d_H \mu_e \tag{4}$$

where N_c is expressed as the number of elementary charge e per molecule, η is the solution dynamic viscosity expressed in $g\,(cm\,s)^{-1}$, d_H is molecule hydrodynamic diameter expressed in nm, and μ_e is molecule electrophoretic mobility expressed in $\mu m\,cm\,(V\,s)^{-1}$.

The number of uncompensated (electrokinetic) charges for each polyelectrolyte and ionic strength ranging from 10^{-4} M to 0.15 M NaCl, and its variations with pH are collected in Table 2.

As can be seen, the mobility of all three polyelectrolytes is highly positive for the low pH range, attaining the value of

Table 1
Physicochemical properties of polyelectrolytes.

Quantity (unit)	Value		
	PAH	PEI	PDDA
Specific density (g/cm³)	1.15 Ref. [34]	1.12 Ref. [33]	1.04 Sigma–Aldrich
Geometrical cross-sectional area (nm²)	155 Ref. [34]	88.32 Ref. [33]	–
$I = 10^{-4}$ M			
Diffusion coefficient (cm²/s)	1.41×10^{-7}	4.4×10^{-7}	2×10^{-7}
Hydrodynamic diameter (nm)	34.7	11.2	24.7
$I = 10^{-3}$ M			
Diffusion coefficient (cm²/s)	1.5×10^{-7}	4.14×10^{-7}	1.91×10^{-7}
Hydrodynamic diameter (nm)	32.7	11.9	25.6
$I = 10^{-2}$ M			
Diffusion coefficient (cm²/s)	1.51×10^{-7}	4.73×10^{-7}	1.95×10^{-7}
Hydrodynamic diameter (nm)	32.5	10.4	25.2
$I = 0.15$ M			
Diffusion coefficient (cm²/s)	1.57×10^{-7}	3.15×10^{-7}	2.5×10^{-7}
Hydrodynamic diameter (nm)	31.2	15.6	19.6

Footnotes: Polyelectrolyte bulk concentration $c_p = 1000$ mg L^{-1}, pH = 5.5, $T = 298$ K, standard deviation for hydrodynamic diameter of PAH was ±4 nm, for PEI ±2 nm and for PDDA ±3 nm.